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QUALITY ASSURANCE PROJECT PLAN FOR OU2 SUPPLEMENTAL REMEDIAL INVESTIGATION (including Baseline Ecological Risk Assessment)

VOLUME II – APPENDIX E

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APPENDIX E

LABORATORY SOPS AND FIELD SCREENING PROCEDURES

Accutest Laboratories
Standard Operating Procedure

Lab Manager

QA Manager

Effective Date 9-11-09

TEST NAME: METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

METHOD REFERENCE: SW846 8260B (Revision 2, December 1996)

Revised Section: 2.8

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of volatile organic compounds by gas chromatographic/mass spectrometric (GC/MS) following purge and trap utilizing the intemal standard technique. The compounds in Table 1 may be detennined by this method. An option has been included for the analysis of 1,4-Dioxane by selected ion monitoring GC/MS (GC/SIM-SIM).

1.2 This analytical method is designed for nearly all types of samples, regardless of water content, Including ground water, aqueous sludges, liquors, waste solvents, oily wastes, tars, filter cakes, sediments and soils.

1.3 The applicable concentration range of this method is compound, matrix, and instrument dependent. Volatile water-soluble compounds can be included in this analytical technique. However, for some low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, quantitation limits are approximately ten times higher because of poor purging efficiency. Determination of some structural Isomers (i.e. xylenes) may also be hampered by coelution.

2.0 SUMMARY OF METHOD

2.1 Volatile compounds are introduced inlo the gas chromatograph by purge-and-trap (Method 5030/5035). Method 5030 may be used directly on ground water samples. Method 5035 is used for iow-concentration and medium-concentration soils, sediments, and wastes. Medium concentration samples are preserved and stored in methanol prior to purge-and-trap analysis.

2.2 An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column.

2.3 The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound Is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a database of approximately 75,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

2.7 Water soluble volatile organic and other poor purging compounds maybe analyzed using this methodology, however this method is not the method of choice for these compounds and the laboratory's ability to achieve all calibration and quality control criteria for this method cannot be guaranteed. These compounds are noted as (pp) in Table 7.

2.8 The method includes an analytical option for the analysis of 1,4-Dioxane by GC/MS-SIM. The selected ions that are characteristic of the analytes of interest are analyzed using lower concentrations of calibration standards under the same MS conditions. SIM analysis is performed upon client request and is documented in the report.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve and may vary depending on matrix interferences, sample volume or weight and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. See Table 10.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank, Instrument Blank, Storage Blank, Cleanup Blank and Sulfur Blank.

4-BROMOFLUOROBENZENE (BFB) - the compound chosen to establish mass spectral instrument performance for volatile (VOA) analyses.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with **99%** confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at **105**°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below **105** °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph: a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

INSTRUMENT BLANK – a system evaluation sample containing lab reagent grade water with internal standards and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The

analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

6.4 Contamination by carry-over can occur whenever high level and low-level samples are sequentially analyzed.

6.4.1 Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of an instrument blank to check for cross contamination. Refer to Table 11 for compounds that may cause carryover for this method.

6.4.2 It may be necessary to wash the purging device with methanol, rinse it with organic-free water, and then dry the purging device in an oven at 105^0 C. Follow the instrument manual for instructions on cleaning. Document the occurrence in the maintenance log and notify the manager/supervisor.

6.4.2.1 Clean and bake purging tube.

6.4.2.2 Clean or replace purge needle.

6.4.2.3 Clean and bake sample filter or sparge filter.

6.4.2.4 Clean and bake sample loop.

6.4.2.5 Replace trap if necessary.

6.4.2.6 Replace water management module if necessary.

6.4.2.7 Rinse transfer line with methanol. Caution: disconnect the trap before rinsing.

6.4.3 In extreme situations, the entire purge-and trap device may require dismantling and cleaning. Follow the instrument's manual for instructions on disassembly. Document the occurrence in the maintenance log and notify the manager/supervisor. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples.

6.4.4 If the contamination has been transferred to gas chromatograph, any of the following approaches may be used to cleanup the instrument.

6.4.4.1 Baking out the column between analyses.

6.4.4.2 Change the injector liner to reduce the potential for cross-contamination.

6.4.4.3 Remove a portion of the analytical column in the case of extreme contamination.

6.4.5 The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are stripped from the chromatographic column.

6.4 Special precautions must be taken during the analysis to avoid contamination from methylene chloride and other common laboratory solvents.

6.5.1 The sample storage and analytical area should be isolated from all atmospheric sources of methylene chloride or other common solvents.

6.5.2 Laboratory clothing worn by the analyst should be clean and used in designated areas only. Clothing previously exposed to solvent vapors in the organics sample preparation laboratory can contribute to sample contamination.

7.0 SAMPLE HANDLING AND PRESERVATION AND HOLDING TIME

7.1 HANDLING and PRESERVATION

7.1.1 Water samples

7.1.1.1 Container - 40 ml glass screw-cap VOA vial with Teflon-faced silicone septum. The 40-ml glass VOA vials are pre-cleaned and certified.

7.1.1.2 Collect all samples in duplicate. Test all samples for residual chlorine using test paper for free and total chlorine. If samples contain residual chlorine, three milligrams of sodium thiosulfate should be added for each 40 ml of water sample.

7.1.1.3 Fill sample bottles to overflowing, but do not flush out the dechlorinating agent. Sample should be taken with care so as to prevent any air or bubbles entering vials creating headspace.

7.1.1.4 Adjust the pH of all samples to ≤ 2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 ml of sample. Seal the sample bottles, Teflon face down, and mix for one minute.

Note: Do not mix the sodium thiosulfate with the HCl in the sample bottle prior to sampling.

7.1.1.5 The samples must be protected from light and refrigerated at 2 - 6 °C from the time of receipt until analysis.

7.1.2 Soil Samples

7.1.2.1 Refer to the SOP for SW846 Method 5035 for preservation requirement of non-aqueous solids. ForOhio VAP freezing is not allowed; samples must be preserved with sodium bisulfate.

7.2 HOLDING TIME

7.2.1 Water Samples.

7.2.1.1 All samples are to be analyzed within 14 days of sampling (HCl preserved for aqueous sample) unless otherwise specified by the contract. If aqueous

samples are received unpreserved, the client is notified of the deficiency and the samples must be analyzed within 7 days. The sample preservation deficiency is noted on the chain of custody.

7.2.2 Soil Samples

7.2.2.1 Refer to the SOP for SW846 Method 5035 for holding time requirement of non-aqueous solids.

7.2.2.2 All samples are analyzed within 14 days of sampling unless otherwise specified.

8.0 APPARATUS AND MATERIALS

8.1 SYRINGE

8.1.1 10, 25, 50, 100, 500 and 5000 µl graduated syringes, manually held (Hamilton/equiv.).

8.1.2 5 ml and 50 ml glass gas tight syringes with Lueriok end, if appropriate for the purging device.

8.2 BALANCE

8.2.1 Analytical balance capable of weighing 0.0001 gram.

8.2.2 Top loading balance capable of weighing 0.1 gram.

8.3 PURGE AND TRAP DEVICES

8.3.1 The autosampler models are used for purging, trapping and desorbing the sample into GC column.

- O.I. Model 4560 sample concentrator with 4551 vial multi-sampler
- O.I. Model 4560 sample concentrator with 4552 Water/Soil multi-sampler

8.3.2 The sample purge vial must be designed to accept 5 ml samples with a water column at least 3 cm deep.

8.3.3 The auto-sampler is equipped with a heater capable of maintaining the purge chamber at 40 °C to improve purging efficiency. The heater is to be used for low level soil/sediment analysis, but not for water or medium level soil/sediment analysis.

8.3.4 The OI #10 trap is 42 cm with an inside diameter of 0.105 inches. The trap must be packed to contain the following absorbents (3-ring) and should be conditioned at 180 °C for 30 minutes by backflushing with a Helium gas flow at least 20 ml/min before initial use.

- Tenax (2,6-Diphenylene oxide polymer).
- Silica gel.
- Carbon Molecule Sieve (CMS).

8.3.5 The desorber should be capable of rapidly heating the trap to 190^0 C for desorption. Do not exceed 210 ^{0}C during bake-out mode. Alternatively, follow manufacturer's instructions.

8.3.6 The response of chloromethane and bromonethane can be tracked for thermal decomposition products formed. If levels over the calibration requirement, the trap must be replaced and the system re-calibrated after the manager/supervisor been notified.

8.4 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.4.1 Gas Chromatograph.

8.4.1.1 An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

8.4.1.2 The injection port should be suitable for split or splitless with appropriate interface.

8.4.1.3 The narrow bore capillary column is directly coupled to the source for HP-6890 model.

8.4.1.4 The wide bore capillary column is interfaced through a jet separator to the source for HP-5890 model.

8.4.2 Column.

- 75 m x 0.53mm ID x 3 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.
- 105 m x 0.53mm ID x 3 μm film thickness capillary column coated with HP-VOA, or equivalent. Condition as per manufactures directions.
- 60 m x 0.25mm ID x 1.4 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.
- 60 m x 0.45mm ID x 1.7 μm film thickness capillary column coated with DB-VRX (J&W Scientific), or equivalent. Condition as per manufactures directions.

8.4.3 Mass Spectrometer.

8.4.3.1 HP5973 or HP5970 is capable of scanning from 35 to 300 amu every 2 seconds or less, utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.

8.4.3.2 The mass spectrometer must be capable of producing a mass spectrum which meets all the criteria in Table 3 when injecting or purging 50 ng of the GC/MS tuning standard - Bromofluorobenzene (BFB).

8.4.3.3 SIM Mode – Capable of selective ion grouping at specified retention times for increased compound sensitivity (Table 2a).

8.5 DATA SYSTEM

8.5.1 Data Acquisition and Instrument Control (HP Chemstation) - A computer system is interfaced to the mass spectrometer, which allows the continuous acquisition and storage on a machine-readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.5.2 Data Processing (HP Enviroquant) - The software accommodates searching of GC/MS data file for target analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The data system includes the recent version of the EPA/NBS or NIST98 mass spectral library for qualitative searches of non-target compounds present in the chromatogram. The data system flags all data files that have been edited manually by laboratory personnel.

8.5.3 Off line Magnetic Tape Storage Device (Lagato Networker) - The magnetic tape storage device copies data for long-term, off-line storage.

9.0 REAGENTS AND STANDARDS

9.1 Solvent

9.1.1 Methanol: purge-and-trap grade quality or equivalent. Store separately, away from the other solvents.

9.2 Reagent Water

9.2.1 Reagent water is defined as water in which an interferant is not observed at the method detection limit of the parameters of interest.

9.2.2 Reagent water is generated by either passing tap water through a bed of approximately one pound of activated carbon or by using the water purification system at Accutest that is a series of deionizers and carbon cartridges.

9.3 Stock Standard Solutions

9.3.1 Commercially prepared standards used.

9.3.1.1 EPA Method 524.2 Volatiles (78 components): Absolute (or equivalent) at 200 µg/ml or 2,000 µg/ml concentration.

9.3.1.2 Custom Volatiles Mix A: Restek (or equivalent) at 2,000 µg/ml concentration.

9.3.1.3 Custom Volatiles Mix B: Restek (or equivalent) at 2,000 - 100,000 µg/ml concentration.

9.3.1.4 VOC Gas Mixture: Ultra (or equivalent) contains 200 µg/ml or 2,000 µg/ml of the following compounds in methanol.

- Bromomethane
- Chloroethane
- Chloromethane
- Dichlorodifluoromethane
- Trichlorofluoromethane
- Vinyl Chloride

9.3.1.5 Multiple neat compounds.

9.3.1.6 Surrogate standard mixture: Ultra (or equivalent) at a concentration of 2,500 µg/ml each surrogate compound.

- 1,2-Dichloroethane-d_4
- Dibromofluoromethane
- Toluene-d_8
- 4-Bromofluorobenzene

9.3.1.7 Internal standard mixture: Ultra (or equivalent) at a concentration of 2,000 µg/ml for all the compounds except Tert Butyl Alcohol-d_9, which is from Absolute (or equivalent) at a concentration of 50,000 µg/ml. The following five internal standards are used that exhibit similar analytical behavior to the compounds of interest.

- 1,4-Dichlorobenzene-d_4
- 1,4-Difluorobenzene
- Chlorobenzene-d_8
- Pentafluorobenzene
- Tert Butyl Alcohol-d_9

9.3.1.8 1,4-Dioxane Solution for SIMS : Ultra (or equivalent) at 100 µg/ml in methanol .

9.3.2 Unopened stock standard (ampoules) must be stored according to manufacturer's documented holding time and storage temperature recommendations (usually placed on the ampoule).

9.3.3 After opened, stock standards, internal standards, and surrogate solutions must be replaced after 6 months (one month for purgeable gases standard) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.3.4 Store all stock standards in vials with minimal headspace and Teflon lid liners after open, protect from light, and refrigerate to –10°C or colder or as recommended by the standard manufacturer.

9.3.5 Return the standards to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

9.4 Internal Standard and Surrogate Solution

9.4.1 Five internal standard and surrogate spiking solutions are prepared in methanol per Table 8.A.

9.4.1.1 25 µg /ml internal standard and surrogate mixture.

9.4.1.2 250 µg /ml internal standard and surrogate mixture.

9.4.1.3 100 µg/ml surrogate mixture.

9.4.1.4 25 µg /ml internal standard mixture.

9.4.1.5 250 µg /ml internal standard mixture.

9.4.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.4.3 Each 5 ml sample, QC sample, and blank undergoing analysis should be spiked with any one of the above spiking solutions (depending upon the type of standards addition modules used), resulting in a concentration of 50 µg/l of each compound.

9.4.4 Prepare fresh internal standard and surrogate spiking solutions every six months, or sooner, if manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.5 Secondary Dilution Standards

9.5.1 Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together.

9.5.1.1 100 µg /ml V8260 mixture: prepared from 2,000 µg /ml stock solution. (see Table 8-C)

9.5.1.2 100 µg /ml V8260 custom mixture: prepared from 2,000 µg /ml stock solution. (see Table 8-C)

9.5.1.3 100 µg /ml Gas mixture: prepared from 2,000 µg /ml stock solution. (see Table 8-C)

9.5.2 Replace after one month for non-gas mixtures (one week for gas mixtures) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.5.3 Store all secondary dilution standards in vials with no headspace and Teflon lid liners, protect from light, and refrigerate to – 10°C or colder or according to manufacturer's storage temperature recommendation.

9.5.4 Return the standards to the freezer as soon as preparation is finished to prevent the evaporation of volatile compounds.

9.6 Aqueous Calibration Standard Solutions

9.6.1 Initial Calibration Standards

9.6.1.1 Prepare a minimum of five aqueous calibration standard solutions containing the surrogate compounds as Table 8-D.1 or 8-D.2.

9.6.1.2 To prepare a calibration standard, add a measured volume of secondary dilution standard solutions and the surrogate spiking solution to an aliquot of reagent water in the flask. Use a micro-syringe and rapidly inject the methanol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask.

9.6.1.2.1 1,4-Dioxane for SIMS analysis is prepared from primary stock standard (100ppm).

9.6.2 Continuing Calibration Standard

9.6.2.1 A continuing calibration standard at a concentration of 50 µg/l is prepared as the scheme ouflined in Table 8-E.

9.6.3 Aqueous standards are not stable and may be stored up to 24 hours if held in Teflon sealed screw-cap vials with zero headspace at 4^0C (± 2^0C). Protect the standards from light. If not so stored, they must be discarded after use, unless they are set up to be purged by an autosampler.

9.6.4 When using an autosampler, standards may be retained up to 12 hours if they are in purge tubes connected via the autosampler to the purge and trap device.

9.7 Second Source Calibration Check Standard (ICV)

9.7.1 Prepare the second source calibration check standards from separate sources of stock standards from the calibration curve following the procedures in Section 9.6. At a minimum, an ICV should be analyzed with every initial calibration.

9.7.2 For 1,4-Dioxane via SIMS: Prepare the second source calibration check standard using 2.5 pl of a 1000ppm (Absolute or equivalent) to 50 mL of reagent water which yields a 50 ppb standard.

9.8 4-Bromofluorobenzene (BFB) Standard

9.8.1 Two BFB solutions are prepared in methanol per Table 8-B.

9.8.1.1 25 µg /ml solution for direct injection.

9.8.1.2 250 µg /ml solution for purging.

9.8.2 The solution must be replaced after 6 months or sooner if mass spectrum indicates degradation or if manufacture expiration date comes first.

10.0 CALIBRATION

10.1 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

Purge and Trap Device:

Clean & bake purge tube
Bake trap and transfer lines
Check or refill internal/surrogate spike solufion on SIM/SAM vials
Clean/replace syringe (if necessary)
Change and refill rinse bottle
Empty and rinse waste bottle

GC Oven: (if necessary)

Change septum
Change liner
Clip column, indicated by carbon build-up

10.2 Initial Calibration

10.2.1 The calibration range covered for routine analysis under RCRA, and SIM, employs standards of 1(specified compounds only), (2)*, 5, 10, 20, 50, 100, 200,(300 or 400)* µg/l. (*instrument dependent). A minimum of five standards must be run sequentially. The low calibration standard defines the reporting limit. Lower concentration standards (1.0 or 2.0 µg/l) may be needed to meet the reporting limit requirements of state specific regulatory programs. Refer to Table 8-D-1 and 8-D-2 for calibration standard preparafion.

10.2.2 A calibrafion range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.2.2.1 For most samples and spikes both the internal standard and the surrogate are added automafically. When doing an inifial calibrafion surrogates are added manually. In order to compensate for the difference between the automatic and manual surrogate additions a correction factor must be applied to the amount of surrogate added in Table 8-D. To determine the correction factor divide the surrogate concentration from an automatic injection by the surrogate concentration from a manual injection for each of the surrogates. Average the result for each of the surrogates to determine the correction factor. Finally multiply the correction factor by the appropriate amount of surrogate from Table 8-D and add this amount to the standard.

10.2.3 For water and medium-level soil calibration: Transfer and till up (no air space) each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4 For low-level soil calibration: Transfer 5 ml of each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial otherwise do not add sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Cap the vial with Teflon septum and place it into O.I sample tray.

10.2.5 The linear range covered by this calibration is the highest concentration standard.

10.2.6 Program the autosampler to add internal standard mixture to each standard. This results in a concentration of 50 µg/l for each internal standard.

10.2.6.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard solution (Section 9.4.1.4) to each standard.

10.2.6.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard solution (Section 9.4.1.5) to each standard.

10.2.7 Analyze the standard solutions using the conditions established in Section 11.0. Whenever the highest concentration standard is analyzed, it is usually followed by the analyses of two reagent water blanks. Further analysis may not proceed until the blank analysis is demonstrated to be free of interferences.

10.2.8 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 7.

10.2.9 The Response Factor (RF) is detined in Section 13.1. Calculate the mean RF for each target analyte using minimum of tive RF values calculated from the initial calibration curve.

10.2.10 For the initial calibration to be valid, the following criteria must be met.

10.2.10.1 Five compounds (System Performance Check Compounds, SPCCs) are checked for a minimum average response factor. The minimum mean response factors are listed in Table 6. If the initial calibration criteria for SPCCs are not achieved, perform corrective action before completing the calibration

10.2.10.2 The % RSD for each individual Calibration Check Compound (CCC) must be less than 30 %. This check is used to identify gross instrument operating problems. If the initial calibration criteria for CCCs are not achieved, perform corrective action before completing the calibration.

10.2.10.3 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than 15 %.

10.2.10.4 If the average response factor criteria cannot be achieved, and if the problem is associated with one or more of the standards, reanalyze the standards and recalculate the RSD. The instrument logbook should have clear documentation as to what the suspected problem was.

10.2.10.4.1 A calibration standard is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. Notify the team leader/manager. Document this occurrence in the instrument log.

10.2.10.5 Alternately, if the average response factor criteria cannot be achieved, the calibration range can be narrowed by dropping the low or high point of the curve.

10.2.10.5.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end.

10.2.10.6 If the average response factor criteria still cannot be achieved, employ an alternative calibration linearity model. Specitically, linear regression using a least squares approach may be employed.

10.2.10.6.1 If Linear regression is employed select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.2.10.6.2 The correlation coefficient (r value) must be ≥0.99 for each compound to be acceptable.

10.2.10.6.3 Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.2.10.7 The initial calibration criteria for this method applies to all additional compounds of concern specitied by the client.

10.2.10.8 The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

10.3 Initial Calibration Veritication (ICV) - Second Source Calibration Check Standard

10.3.1 The calibration is veritied with a calibration check standard at 50 µg/l from an external source (Section 9.7). It must be analyzed immediately following the initial calibration.

10.3.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 20% for all the target compounds.

10.3.2.1 If % D is greater than 20%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.3.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that matches each other and repeat the initial calibration.

10.4 Continuing Calibration Veritication Standard(CCV)

10.4.1 A continuing calibration veritication standard at a concentration near mid-level of the initial calibration range (50 µg/l) must be acquired every 12 hrs or at the beginning of each analytical batch.

10.4.1.1 For water and medium level soil analysis: Transfer and till up (no air space) the calibration veritication standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.1.1 Vary the concentration of the continuing calibration veritication standard on altemate veritications (i.e. every other calibration veritication) using an alternative concentration standard. The standard selected must be lower than the midpoint calibration standard.

10.4.1.2 For low-level soil analysis: Transfer 5 ml of the calibration veritication standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.2.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the calibration veritication standard into vial, otherwise do not use sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Analyze as per Section 11.7.

10.4.1.3 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be veritied, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.4.2 For the continuing calibration to be valid, all of the following specitied criteria must be met.

10.4.2.1 The minimum RF for SPCC compound is shown on Table 6. Each SPCC compound in the calibration veritication standard must meet its minimum response factor.

10.4.2.2 The percent difference (% D, see Section 13.3) for CCC must be less than 20%.

10.4.2.2.1 If the CCCs and SPCCs are not required analytes, such as the shortlist analysis for BTEX only, then all required project analytes must meet the 20 %D.

10.4.3 If the tirst continuing calibration veritication does not meet criteria, a second standard may be injected after notify the team leader/manager and checking the system for defects.

10.4.3.1 A continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the tirst check fails to meet the criteria, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.4.3.2 If the calibration veritication is being performed using an auto sampler for night batch, two (2) vials of standard solution are placed in the device for analysis. The second standard must meet continuing calibration criteria and is used for calibration veritication. The second check may be discarded because of a purge failure or incorrect spike concentration provided the tirst calibration standard meets the requirement. In this case, the tirst calibration standard is used as calibration veritication following team leader/manager approval. Document this occurrence on instrument log.

10.4.4 If the veritication criteria cannot be achieved, a new initial calibration must be performed.

10.4.5 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.4.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.4.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

10.5 Corrective Action Maintenance For Failed Tuning and Calibration Procedures

10.5.1 Inability to achieve criteria for instrument tuning or calibration may indicate the need for instrument maintenance. Maintenance may include routine system cleaning and replacement of worn expendables or the need for outside service if the scope of the repair exceeds the capability of the staff.

10.5.2 If maintenance is performed on an instrument, return to control must be demonstrated before analysis can continue. Return to control is demonstrated as follows:

10.5.2.1 Successful instrument tune using PFTBA.

10.5.2.2 Successful tune veritication by the analysis of 4-bromofluorobenzene.

10.5.2.3 Successful initial calibration or continuing calibration.

11.0 PROCEDURE

11.1 Instrument conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Moditications of parameters specitied with an asterisk are allowed as long as criteria of calibration are met. Any moditication should be approved by team leader/manger.

11.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, use the same GC conditions for the analysis of all standards, blanks, samples, and QC samples.

11.2 Purge and Trap Device conditions.

11.2.1 See Table 2.

11.2.2 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

Purge and Trap Device:

- Clean & bake purge tube.
- Bake trap and transfer lines.
- Check or retill internal/surrogate spike solution on SIM/SAM vials.
- Clean/replace syringe (if necessary).
- Change and retill rinse bottle.
- Empty and rinse waste bottle.

11.3 Step 1: Daily GC/MS performance check.

11.3.1 Every 12 hours, either

- Inject 2 µl (50 ng) of BFB solution directly on column or
- Purge 10 µg/l of 5ml (50ng) to GC column.

11.3.2 The GC/MS system must be checked to verify acceptable performance criteria are achieved (see Table 3).

11.3.3 This performance test must be passed before any samples, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.3.3.1 Select the scans at the peak apex and one to each side of the apex.

11.3.3.2 Calculate an average of the mass abundances from the three scans.

11.3.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peaks and no

more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.3.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.3.4.5 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of tive averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.3.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.3.6 Until performance check is acceptable, then calibration check (step 2) can be analyzed.

11.4 Step 2 : Daily calibration check

11.4.1 Initial calibration

11.4.1.1 Refer to Section 10.2.

11.4.1.2 An initial calibration must be established (or reestablished) on each instrument:

- Prior to any sample analyses;
- Whenever a new column is installed;
- Whenever instrument adjustments that affect sensitivity are made; and
- Whenever a continuing calibration standard fails to meet the specitied acceptance criteria, on the second trial.

11.4.2 Initial Calibration Veritication - Second Source Calibration Check Standard

11.4.2.1 This standard is only analyzed when initial calibration provided. Refer to Section 10.3.

11.4.3 Continuing Calibration veritication standard

11.4.3.1 Refer to Section 10.4.

11.4.4 The method blank (step 3) cannot be analyzed until the continuing calibration veritication meets the criteria.

11.5 Step 3 : Method blank

11.5.1 The acceptable method blank must be analyzed for every 12-hour time period or sooner.

11.5.1.1 Water and medium-level soil samples - Place a 40 ml vial, tilled with DI water onto the autosampler.

11.5.1.2 Low-level soil samples without sodium bisulfate - Transfer 5 ml of DI water to a 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.5.1.2.1 Low-level soil samples with sodium bisulfate (Method 5035) - Add 1g of sodium bisulfate to a 40 ml vial before aliquot 5 ml of DI water into the vial and cap with Teflon septum, then place the vial onto the autosampler.

11.5.2 Program the autosampler to add internal standard and surrogate solution to the method blank for a concentration of 50 µg/l for each internal standard and surrogate.

11.5.2.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard and surrogate solution (Section 9.4.1.1) to the method blank.

11.5.2.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard and surrogate solution (Section 9.4.1.2) to the method blank.

11.5.3 No compound can be present above the laboratory's MDL. If common laboratory solvents (i.e. methylene chloride, acetone) are present in the sample between the MDL and RL, the analyst must determine if the contamination will negatively impact data quality. If the contamination impacts data quality, all affected samples must be re-analyzed.

11.5.4 Surrogates must meet recovery criteria specitied in house limits.

11.5.5 If the method blank does not meet surrogate criteria or contains target analytes above the MDL, then

11.5.5.1 All samples analyzed following an out of control method blank must be reanalyzed.

11.5.5.2 Check for the potential of contamination interference from the following areas. Make sure all items are free contamination.

- the analytical system,
- dust and vapor in the air,
- glassware and
- Reagents.

11.5.5.3 Re-analyze the method blank following the system evaluation. In this situation, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second blank to pass.

11.5.5.4 If re-analyzed method blank remains out of control, notify team leader or manager.

11.5.6 If two consecutive method blanks are analyzed during unattended operations, the second analysis must meet criteria for the subsequent sample analysis to be valid. Always report the second method blank. The second analysis can only be discarded because of a purge failure provided that the tirst blank meets the

requirement. In this case, the tirst blank is reported following team leader/manager approval. Document this occurrence on the instrument log.

11.5.7 The blank spike (BS) (step 4) cannot be analyzed until the method blank meets criteria.

11.6 Step 4: Blank spike (BS)

11.6.1 An acceptable blank spike must be analyzed with every analytical batch. The maximum number of samples per analytical batch is twenty.

11.6.2 Spike 50 ml of reagent water with appropriate amount of the standards to prepare a blank spike containing 50 µg/L of each analyte. In situations where lower detection limits are required, a blank spike at 20 µg/L may be prepared. The stock solution for the BS must be from a different source than the initial calibration solution. Refer to Table 8-F for the preparations of the blank spikes.

11.6.2.1 Water and medium-level soil samples - Place a 40 ml vial, tilled with DI water onto the autosampler.

11.6.2.2 Low-level soil samples without sodium bisulfate - Aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.2.2.1 Low-level soil samples with sodium bisulfate for Method 5035 - Add 1g of sodium bisulfate to labeled 40 ml vial before aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.3 Initiate auto addition of internal standard and surrogate into the syringe per 11.5.2.

11.6.4 Compare the percent recoveries (% R) (see Section 13.5) to the in house limits acceptance criteria. If a blank spike is out of control, all the associated samples must be reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required.

11.6.5 Do not analyze samples and MS/MSD (step 5) unless the BS meets acceptance criteria.

11.7 Step 5: Samples /MS/MSD analysis

11.7.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11.7.2 Select the sample dilution factor to assure the highest concentration analyte is above the calibration range midpoint, but below the upper limit of the range depend on project requirements. See Table 9 for dilution guideline.

- Utilize FID screen data.
- Utilize acquired sample data.
- Utilize the history program.
- Sample characteristics (appearance, odor).

11.7.3 Water samples.

11.7.3.1 Using O.I.Model 4560 sample concentrator with 4551 or 4552 vial multisampler,

- Place the 40 ml vial in the tray, or
- Load 5ml sample into purge tube if sample volume limited.

11.7.4 Sediment/ soil sample

11.7.4.1 Low-level soil method

11.7.4.1.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 low - level soil samples.

11.7.4.1.2 Weigh out 5 g of each sample into a labeled vial. Add 5 ml of reagent water and cap the vial quickly. Transfer the 40ml vial to the autosampler tray. Stir and heat the sample at the time of analysis.

11.7.4.2 Medium-level soil method

11.7.4.2.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 medium - level soil samples.

11.7.4.2.2 Select a methanol aliquot of appropriate volume (see Table 9) determined via screening and transfer to 40 ml of reagent water.

11.7.5 Program the autosampler to inject the internal standard and surrogate solution into the robotic syringe used to withdraw sample from the 40 ml vial. This addition to 5 ml of sample is equivalent to a concentration of 50 µg/L of each internal standard and surrogate.

11.7.5.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard and surrogate solution (Section 9.4.1.1) to each sample.

11.7.5.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard and surrogate solution (Section 9.4.1.2) to each sample.

11.7.6 Purge the sample for 11 minutes with Helium.

11.7.6.1 Low-level soil sample must be performed at 40 °C while the sample is being agitated with the magnetic stirring bar or other mechanical means.

11.7.6.2 To improve the purging efficiency of water-soluble compounds, aqueous samples may also be purged at 40 °C as long as all calibration standards, samples and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

11.7.7 One sample is randomly selected from each analytical batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results. A matrix spike and matrix spike duplicate are performed by spiking the sample for a concentration of 50 µg/l or 50 µg/kg based on 5 g dry weight. In situations where lower detection limits are required, a blank spike at lower concentration may be prepared.

11.7.8 Desorb the sample for 4 minutes by rapidly heating the trap to 190 °C while backflushing with Helium. Desorb time may require performance optimum between 2.0 and 4.0 minutes as dictated by trap manufacturers specitications or instrument characteristics.

11.7.9 Program the purge and trap system to automatically rinse purge tube at least twice with heated organic-free water (reagent water) between analyses to avoid carryover of target compounds. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol solution between analyses, rinse it with distilled water.

11.7.10 Bake the trap at least 10 minutes at 210 °C to remove any residual purgeable compounds.

11.7.11 If the initial analysis of the sample or a dilution of the sample has a response for any ion of interest that exceeds the working range of the GC/MS system, the sample must be reanalyzed at a higher dilution.

11.7.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

11.8 Sample dilutions

11.8.1 Using Screening Data to Determine Dilution Factors

11.8.1.1 Dilution for High Concentration Analytes Exceeding The Calibration Range

11.8.1.1.1 The highest concentration target compound detected in the screen data is compared to the highest concentration calibration standard used for determinative volatile organics analysis.

11.8.1.1.1.1 Divide the calibration concentration of the highest concentration calibration standard by the screen concentration.

11.8.1.1.1.2 If the result is >1, sample dilution is considered.

11.8.1.1.2 The result from step 11.8.1.1.1 determines the dilution factor. The dilution factor is targeted to assure that the highest concentration diluted analyte is at the mid-range concentration of the calibration curve for the determinative analysis.

11.8.1.1.3 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.1.2 Dilution for High Concentration Matrix Interferences

11.8.1.2.1 The peak height of the background is compared to the peak height of the later eluting calibration standards from the screening analysis.

11.8.1.2.1.1 A rough estimate of background concentration is calculated by dividing the background peak height by the peak height of the selected screening standard and multiplying by its concentration.

11.8.1.2.2 If the result is >1, sample dilution is considered.

11.8.1.2.3 The result from step 11.8.1.2.1 determines the dilution factor. The dilution factor is targeted to avoid Carry-over contamination between samples and facilitate qualitative and quantitative analysis of target compounds present in the sample.

11.8.1.2.4 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.2 If the concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and re-analyzed. Until the diluted sample is in a sealed sample vial, all steps in the dilution procedure must be performed without delay.

11.8.3 Water Samples.

11.8.3.1 Prepare all dilutions of water samples in volumetric flasks (10 ml to 100 ml). Intermediate dilutions may be necessary for extremely large dilutions.

11.8.3.2 Calculate the approximate volume of reagent water, which will be added to the volumetric flask, and add slightiy less than this quantity to the flask. Refer to Table 9 for dilution guideline.

11.8.3.3 Inject the proper sample aliquot from a syringe into the volumetric flask. Dilute the flask to the volume mark with reagent water. Cap the flask and invert the flask three times.

11.8.3.4 Fill a 40 ml sample vial and seal with a Teflon baked silicon septa, load the diluted sample into the autosampler and analyze according to Section 11.7.

11.8.3 Low-level Soil Samples.

11.8.3.1 The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low-level soil method or the medium-level soil method.

11.8.3.2 If any target compound exceeds the initial calibration range from the analysis of 5 g sample, a smaller sample size must be analyzed. However, the smallest sample size permitted is 0.5 g. If smaller than 0.5 g sample size is needed to prevent any target compounds from exceeding the initial calibration range, the medium level method must be used.

11.9 Data interpretation

11.9.1 Qualitative identificafion.

11.9.1.1 The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.2 The characteristic ions for target compounds that can be determined are listed in Table 7. Table 4 and Table 5 list the characteristic ions for internal standards and surrogate compounds respectively.

11.9.1.3 The criteria required for a positive identificafion are listed below.

11.9.1.3.1 The sample component must elute at the same relafive retenfion fime (RRT) as the daily standard. Criteria are the RRT of sample component must be within ± **0.06** RRT units of the standard component.

11.9.1.3.2 The relafive intensities of these ions must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.)

11.9.1.3.2.1 Compounds can have secondary ions outside criteria from co-eluting compounds and/or matrix effect that can contribute to ion abundances. The interference on ion ratios can't always be subtracted out by software programs resulting in qualified compound identification.

11.9.1.3.2.2 Quantitation reports display compounds that have secondary ions outside the ratio criteria with a "#" flag.

11.9.1.3.2.3 Any quant reports with compounds that are deemed to be reportable despite the "#" flag, will be initialed in the "#" column by the analyst. Further review to the reporting of qualified compounds will be done by a supervisor or team leader and inifialed on the quantitation.

11.9.1.3.3 Stmctural isomers that produce very similar mass specrtra should be identified as individual isomers if they have sufficientiy different GC retenfion fimes. Sufficient GC resolufion is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Othenwise, structural isomers are identified as isomeric pairs.

11.9.2 Quantitative analysis

11.9.2.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 7). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.2.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate (see Table 7). This is characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

11.10 Library search for tentatively identified compounds.

11.10.1 If a library search is requested, the analyst should perform a forward library search of NBS or NIST98 mass spectral library to tentatively identify 15 non-reported compounds.

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

11.10.2.5 The relative intensities of the major ions should agree within ± 20 %. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.2.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.2.9 The resulting concentration should be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.11 An instrument blank is a system evaluation sample containing lab reagent grade water with internal standards and surrogates. An instrument blank is used to remove and or evaluate residual carryover from high level standards, spike samples and field samples. Since target compound lists have expanded to overlap some volatile and semi-volatile compounds, instrument blanks are necessary to remove carryover contamination.

11.11.1 The compounds that may exhibit carryover for this method are listed in Table 11.

11.11.2 If instrument blanks following a standard or spike sample exhibits carrry-over effect, then any samples that show the same carryover profile, after a comparable concentrafion must be considered suspect and rerun for confirmation. For example, if an instrument blank has 1ppb detected after a 200ppb standard, then any sample following a sample containing 200ppb or above of the same compound must be confirmed for possible carryover.

11.11.3 If an Instrument Blank(s) was run following suspect high concentrafion samples and it exhibits the same carryover profile after a comparable concentration must be considered suspect and rerun for confirmafion.

11.11.4 In some cases, several instrument blanks may have to be run to eliminate contaminafion from over loaded samples.

11.11.5 The analytical system is considered free of carryover, when no target analytes can be detected above the MDL.

11.12 Selected Ion Monitoring (SIM) Option Selected Ion Monitoring (SIM) Option

11.12.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention fimes, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a.) Select a mass dwell time of 50 milliseconds for all compounds.

11.12.2 Calibrafion: Calibrate the mass spectrometer in the selected ion monitoring mode using **6** calibrafion standards of 5, 10, 20, 50, 100, 200 ug/l. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs.

11.12.3 Initial Calibrafion Verification. Verify the initial calibration after its completion using a 50 ug/l calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria of Section 10.2.

11.12.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 50 ug/l calibration. The continuing calibration verification must meet the criteria of Section 10.4.

11.12.5 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary

BFB	Beginning of the analytical shift and every 12 hours
Second Source Calibration Check Standard	Following initial calibration
Calibration Verification Standard	Every 12 hours
Method Blank	Every 12 hours

Blank Spike	One per analytical batch*
Matrix Spike	One per analytical batch*
Matrix Spike Duplicate	One per analytical batch*
Surrogate	Every sample and standard
Internal Standard	Every sample and standard

*The maximum number of samples per analytical batch is twenty.

12.2 Daily GC/MS Performance Check - BFB

12.2.1 Refer to Section 11.3.

12.3 Second Source Calibration Check Standard

12.3.1 Refer to Section 10.3.

12.3.2 Calibration Verificafion Standard

12.3.3 Refer to Section 10.4.

12.5 Method Blank

12.5.1 Refer to Section 11.5.

12.6 Blank Spike

12.6.1 Refer to Section 11.6.

12.7 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

12.7.1 One sample is selected at random from each analytical batch of similar matrix types and spiked in duplicate to check precision and accuracy.

12.7.2 Assess the matrix spike recoveries (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the control limits..

12.7.3 If the matrix spike recoveries do not meet the criteria, check the blank spike recovery to verify that the method is in control. If the blank spike did not meet criteria, the method is out of control for the parameter in question and should be reanalyzed or qualified with an estimate of potential bias. Otherwise, matrix interference is assumed and the data is reportable. No further corrective action is required.

12.8 Surrogates

12.8.1 All standards, blanks, samples, and matrix spikes contain surrogate compounds, which are used to monitor method performance. If the recovery of any surrogate compound does not meet the control limits, the result must be flagged and:

12.8.1.1 The calculation must be checked.

12.8.1.2 The sample must be reanalyzed if the recovery of any one surrogate is out of control limit.

12.8.2 If the sample exhibits matrix interference, defined as excessive signal levels from target or non-target interfering peaks. In this case, reanalysis may not be required following team leader/manager approval.

12.8.3 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data must be submitted with the reanalysis reported.

12.8.4 If surrogates are still outside control limits upon reanalysis, then both sets of data should be submitted with the first analysis reported.

12.9 Internal Standard

12.9.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 µg/l standard of initial calibration.

12.9.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (12 hr. time period).

12.9.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.9.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

12.9.5 If areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

13.0 CALCULATION

13.1 Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where:
As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/l).
Cis = Concentration of the specific internal standard (ug/l).

13.2 Percent Relative Standard Deviation (% RSD)

$$\%RSD = \frac{SD}{RFav} \times 100$$

where:
SD = Standard Deviation
RFav = Average response factor from initial calibration.

13.3 Percent Difference (%D)

$$\%D = \frac{(RFav - RFcv)}{RFav} \times 100$$

where:
RFcv = Response factor from Calibration Veritication standard.
RFav = Average response factor from initial calibration.

13.4 Concentration (Cone.)

For water:

$$\text{Cone. } (\mu g/l) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

For soil/sediment low level (on a dry weight basis):

$$\text{Cone. } (\mu g/kg) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Ws \times M}$$

For soil/ sediment medium level (on a drv weight basis)

$$\text{Cone. } (\mu g/kg) = \frac{Ac \times Cis \times Vo \times Vt}{Ais \times RF \times Vme \times Ws \times M}$$

Where:
Ac = Area of characteristic ion for compound being measured.
Ais = Area of characteristic ion for internal standard.
Cis = Concentration of internal standard
RF = Response factor of compound being measured(from initial calibration)
Vi = Initial volume of water purged (ml)
Vp = 5 ml (Total Purge Volume)
Vme = Volume of Methanol aliquot
Vt = Ml Solvent + ((100-% solid)/100 x Ws)
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100 or % solids / 100

13.5 Percent Recovery (% R)

$$\%R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD)

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

Where:
MSC = Matrix Spike Concentration

MSDC = Matrix Spike Duplicate Concentration

13.7 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{A} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.8 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the Comments secfion.

14.2 Standards Preparation Logbook must be completed for all standard preparations. All information must be completed; the page must be signed and dated by the appropriate person.

14.2.1 The Accutest lot number must be cross-referenced on the standard vial.

14.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any correcfions to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properiy. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

Table 1. TARGET COMPOUNDS		
Acetone	1,3-Dichlorobenzene	Methyl Methacrylate
Acetonitrile	1,4-Dichlorobenzene	4-Methyl-2-pentanone (MIBK)
Acrolein	Dichlorodifluoromethane	Methylene Bromide
Acrylonitrile	1,1-Dichloroethane	Methylene Chloride
Allyl Chloride	1,2-Dichloroethane	1-Methylnaphthalene (1)
Benzene	1,1-Dichloroethene	2-Methylnaphthalene (1)
Benzyl chloride	cis-1,2-Dichloroethene	Naphthalene
Bromobenzene	trans-1,2-Dichloroethene	2-Nitropropane (1)
Bromochloromethane	1,2-Dichloropropane	Pentachloroethane
Bromodichloromethane	1,3-Dichloropropane	Propionitrile
Bromoform	2,2-Dichloropropane	Propyl Acetate (1)
Bromomethane	1,1-Dichloropropene	n-Propylbenzene
2-Butanone (MEK)	cis-1,3-Dichloropropene	Styrene
Butyl Acetate (1)	trans-1,3-Dichloropropene	Tert Butyl Alcohol
n-Butyl Alcohol (1)	1,4-Dioxane	tert-Amyl Methyl Ether
n-Butylbenzene	Epichlorohydrin (1)	tert-Butyl Ethyl Ether
sec-Butylbenzene	Ethyl Acetate	1,1,1,2-Tetrachloroethane
tert-Butylbenzene	Ethyl Ether	1,1,2,2-Tetrachloroethane
Carbon Disulfide	Ethyl Methacrylate	Tetrachloroethene
Carbon Tetrachloride	Ethylbenzene	Tetrahydrofuran
Chlorobenzene	p-Ethyltoluene (1)	Toluene
Chlorodifluoromethane (1)	Freon 113	trans-1,4-Dichloro-2-Butene
Chloroethane	Heptane (1)	1,2,3-Trichlorobenzene
2-Chloroethyl Vinyl Ether	Hexachlorobutadine	1,2,4-Trichlorobenzene
Chloroform	Hexachloroethane	1,1,1-Trichloroethane
Chloromethane	Hexane (1)	1,1,2-Trichloroethane
Chloroprene (2-chloro-1,3-butadiene)	2-Hexanone	Trichloroethene
o-Chlorotoluene	Iodomethane (Methy iodide)	Trichlorofluoromethane
p-Chlorotoluene	IsoAmyl Alcohol (1)	1,2,3-Trichloropropane
Cyclohexane (1)	Isobutyl Alcohol	1,2,4-Trimethlylbenzene
Cyclohexanone	Isopropyl Acetate (1)	1,3,5-Trimethylbenzene
di-Isobutylene (1)	Isopropylbenzene	Vinyl Acetate
di-Isopropyl Ether	p-Isopropyltoluene	Vinyl Chloride
1,2-Dibromo-3-Chloropropane	Methacrylonitriie	Vinyltoluene (1)
Dibromochloromethane	Methyl Acetate (1)	m,p-Xylene
1,2-Dibromoethane	3 Methyl-1-Butanol (1)	o-Xylene
Dibromomethane (1)	Methyl Tert Butyl Ether	Ethanol
1,2-Dichlorobenzene	Methylcyclohexane (1)	Methyl Acrylate

(1) NELAC Accreditation is not offered for this compound. Results may not be useable for regulatory purposes in States where this accreditation option is not offered.

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/ Mass Spectrometer	
Carrier Gas (linear velocity)	Helium at *30 cm/sec
Mass range	35 – 300 amu
Electron Energy	70 volts (nominal)
Scan time	not to exceed 2 sec. per scan
Injection port temperature	200 - 225 °C
Source temperature	200 - 250 °C
Transfer line temperature	220 - 280 °C
Analyzer temperature	220 - 250 °C
Gas Chromatograph temperature program*	
Initial temperature	*40 °C
Time 1	*3 minutes
Column temperature rate	*8 degrees/min.
Final temperature	*220 °C.- 240 °C
Total run time	*25 – 50 mins
Purge and Trap Device	
Purge time	9 min. (at 40 °C for low-level soil) SIM – 6 min @ 50 °C
Desorb**	4 min. at 190 °C
Bake	>10 min. at 210 °C
Transfer line	100 - 130 °C
Valve temperature	approx. transfer line temperature

* Parameter modification allowed for performance optimization provided operational and QC criteria is achieved.(must be approved by team leader/manager)

** Desorb time may require performance optimum between 2.0 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics

Table 2a – SIM Group Parameters		
Group No.	Retention Time (minutes)	Ions
1	0 – 10.8	58, 65, 66, 88
2	10.8 – 16.0	95, 174, 176, 98, 100, 70

Table 3. BFB KEY IONS AND ION ABUNDANCE CRITERIA	
Mass	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 4. INTERNAL STANDARD QUANTITION IONS	
Internal Standard	Primary/Secondary Ions
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119
Pentafluorobenzene	168
1,4-Dichlorobenzene-d4	152 / 115, 150
Tert Butyl Alcohol-d9	65/66
Internal Standard (SIM)	
Tert Butyl Alcohol-d9	65/66

Table 5. SURROGATE QUANTITION IONS	
Surrogate Compound	Primary/Secondary Ions
1,2 Dichloroethane – d_4	102
Dibromofluoromethane	113
Toluene-d8	98
4-Bromofluorobenzene	95 / 174, 176

Table 6. CRITERIA FOR CCC AND SPCC		
Initial Calibration	Maximum % RSD for CCC is 30 %	
Continuing Calibration	Maximum % D for CCC is 20 %	
Calibration check compounds (CCC)	Volatile Compound	
	Vinyl chloride 1,1-Dichloroethene Chloroform 1,2-Dichloropropane Toluene Ethylbenzene	
System Performance Check Compounds (SPCC)	Compound Name	Minimum RF
	Chloromethane	0.1
	1,1-Dichloroethane	0.1
	Bromoform	0.1
	1,1,2,2-Tetrachloroethane	0.3
	Chlorobenzene	0.3

Table 7. Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9			Dibromomethane	93	95, 174
Tert Butyl alcohol	59	57	Di-isobutylene	57	
Ethanol	45	46	Epichlorohydrin (pp)	57	57, 49, 62, 51
Pentafluorobenzene			Ethyl methacrylate	69	69, 41, 99, 86, 114
1,1,1-Trichloroethane	97	99, 61	Heptane	57	
1,1-Dichlorethane	63	65, 63	Hexane	56	
1,1-Dichloroethene	96	61, 63	Isopropyl acetate	43	
2,2-Dichloropropane	77	97	Methyl cyclohexane	83	
2-Butanone (pp)	72	43, 72	Methyl methacrylate	69	69, 41, 100, 39
Acetone (pp)	58	43	n-Butanol (pp)	56	41
Acetonitrile (pp)	41	41, 40, 39	Propyl Acetate	43	
Acrolein (pp)	56	55,58	tert Amyl Methyl Ether	73	
Acrylonitrile (pp)	53	52, 51	Toluene	92	91
Allyl Chloride	41		Toluene-d_8	98	
Bromochloromethane	128	49, 130	trans-1,3-Dichloropropene	75	77, 39
Bromomethane	94	96	Trichloroethene	95	97, 130, 132
Carbon disulfide	76	78			
Chlorodifluouromethane	51	86	Chlorobenzene-d5	117	82,119
Chloroethane	64	66	1,1,1,2-Tetrachloroethane	131	133, 119
Chloroform	83	85	1,2-Dibromoethane	107	109, 188
Chloromethane	50	52	1,3-Dichloropropane	76	78
Chloroprene	53	53, 88, 90, 51	Bromoform	173	175, 254
cis-1,2-Dichloroethene	96	61, 98	Butyl Acetate	56	
Cyclohexane	84		Chlorobenzene	112	77, 114
Dibromofluoromethane	113		Dibromochloromethane	129	127
Dichlorodifluoromethane	85	87	Ethylbenzene	91	106
Dichloroethane-d_4	102	65	m-Xylene	106	91
Diethyl ether	74	45, 59	o-Xylene	106	91
Diisopropyl ether	45	102	p-Xylene	106	91
Ethyl acetate (pp)	88	43, 45, 61	Styrene	104	78
Ethyl tert Butyl Ether	59		Tetrachloroethene	164	129,131,166
Freon 113	151				
Iodomethane	142	127, 141	1,4 Dichlorobenzene-d4	152	115,150
Isobutyl alcohol (pp)	43	43, 41, 42, 74	1,1,2,2-Tetrachloroethane	83	131, 85
Methacrylonilriie (pp)	41	41, 67, 39, 52, 66	1,2,3-Trichlorobenzene	180	182, 145
Methyl Acetate	43	74	1,2,3-Trichloropropane	75	77
Methylene chloride	84	86, 49	1,2,4-Trichlorobenzene	180	182, 145
Methyl-t-butyl ether	73	57	1,2,4-Trimethylbenzene	105	120
Propionitrile (ethyl cyanide)(pp)	54	54, 52, 55, 40	1,2-Dibromo-3-chloropropane(pp)	75	155, 157
Tetrahydrofuran	42		1,2-Dichlorobenzene	146	111,148
trans-1,2-Dichloroethene	96	61, 98	1,3,5-Trimethylbenzene	105	120
Trichlorofluoromethane	151	101, 153	1,3-Dichlorobenzene	146	111, 148
Vinyl acetate	43	86	1,4-Dichlorobenzene	146	111, 148
Vinyl chloride	62	64	2-Chlorotoluene	91	126
Methyl Acrylate	55	85	4-Bromofluorobenzene	95	174, 176
1,4 Difluorobenzene	114	63, 88	4-Chlorotoluene	91	126
1,1,2-Trichloroethane	83	97, 85	Benzyl chloride	91	91, 126, 65, 128
1,1-Dichloropropene	75	110, 77	Bromobenzene	156	77, 158
1,2 Dichloroethane	62	98	Cyclohexanone	55	
1,2 Dichloropropane	63	112	Hexachlorobutadiene	225	223, 227
1,4-Dioxane (pp)	88	88, 58, 43, 57	Hexachloroethane (pp)	201	166, 199, 203
2-Chloroethyl-vinylether (pp)	63	65, 106	Isopropylbenzene	105	120

Table 7. Volatile Internal Standards with Corresponding Ahalytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Sccondary Characteristir Ion (s)
2 – Hexanone	43	58,57,100	Naphthalene	128	-
2-Hexanone (pp)	43	58, 57, 100	n-Butylbenzene	91	92, 134
2-Nitropropane	46	-	n-Propylbenzene	91	120
3 Methyl –1 butanol	55		Pentachloroethane (pp)	167	167,130,132,165,169
4-Methyl-2-pentanone (pp)	100	43, 58, 85	p-isopropyltoluene	119	134,91
Benzene	78	-	sec-Butylbenzene	105	134
Bromodichloromethane	83	85, 127	tert-Buytlbenzene	119	91, 134
Carbon tetrachloride	117	119	trans-1,4-Dichloro-2-butene (pp)	53	88, 75
cis-1,3-Dichloropropene	75	77, 39			
			(pp) = Poor Purging Efficiency		

Table 7-1 SIM - Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9		
1,4-Dioxane	88	58
Toluene –d8	98	100
4-BFB	95	174, 176

Table 8. STANDARDS PREPARATION

A) Internal standard and Surrogate mixtures:

	a) 25/250 µg/ml	b) 250/2,500 µg/ml
Internal Standard Mixture (2,000 µg/ml)	1.25 ml	1 .25 ml
Tert Butyl Alcohol-d_9 (50,000 µg/ml)	0.5 ml	0.5 ml
Surrogate Mixture (2,500 µg/ml)	1 ml	1 ml
Methanol	97.25 ml	7.25 ml
Total	100 ml	10 ml

- 25/250 µg /ml internal standard and surrogate mixture: The mixture is prepared by measuring 1.25ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), 1 ml of 2,500 µg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 100 ml with methanol.

- 250/2,500 µg /ml internal standard and surrogate mixture: The mixture is prepared by measuring 1.25 ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), 1 ml of 2,500 µg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 10 ml with methanol.

- 100 µg/ml surrogate mixture: The solution is prepared at 100 µg/ml by measuring 0.4 ml of 2,500 µg/ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 10 ml with methanol.

- 25/250 µg /ml internal standard mixture: The solution is prepared by measuring 1.25 ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), and bringing to 100 ml with methanol.

- 250/2,500 µg /ml internal standard mixture: The solution is prepared by measuring 1.25 ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), and bringing to 10 ml with methanol.

B) Bromofluorobenzene (BFB):

	a) 25 µg/ml	b)) 250 µg/ml
BFB (25,000 µg/ml)	0.1 ml	0.1 ml
Methanol	99.9 ml	9.9 ml
Total	100 ml	10 ml

- 25 µg /ml solution for direct injection: The BFB is prepared at 25 µg /ml by measuring 0.1 ml of 25,000 µg /ml (Absolute Stock or equivalent) and diluting to 100 ml with methanol.

- 250 µg /ml solution for purging: The BFB is prepared at 250 µg /ml by measuring 0.1 ml of 25,000 µg /ml (Absolute Stock or equivalent) and diluting to 10 ml with methanol.

Table 8. STANDARD PREPARATION (Continued)

C) Secondary dilution standards:

2nd Dilution Standards	Stock Solution	Concentration (ug/ml)	Volume Added (µl)	Final Volume in Methanol (ml)	Final Concentration (µg/ml)
V8260 Mixture	EPA Method 524.2 Volatiles	2,000	2,500	50	100
	Acrolein	Neat (90%)	66.2		1,000
	Acrylonitrile*	Neat	25		500+
	Propionitrile**	Neat	58.9		1,000++
	Di-iso Butylene	Neat	7.1		100
	Cyclohexane	Neat	6.5		100
	Cyclohexanone	Neat	52.9		1,000
V8260 Custom Mixture	Custom Volatiles Mix A	2,000	2,500	50	100
	Custom Volatiles Mix B	2,000 -100,000	2,500		100 - 5,000
	Epichlorohydrin	Neat	21.4		500
	Iso-Amyl alcohol	Neat	125		2,000
	2-Chloroethyl vinyl ether	Neat	20.1		500
	Ethyl tert-butyl ether	Neat	6.8		100
	Tert-Amyl methyl ether	Neat	6.56		100
	Benzyl chloride	Neat	4.6		100
Gas Mixture	VOC Gas Mixture	2,000	1,000	20	100

- 100 µg /ml V8260 mixture: The mixture is prepared at 100 µg /ml by measuring 2 ml of 2,000 µg /ml EPA Method 524.2 Volatiles stock standard, appropriate amount of some neat compounds, and bringing to 50 ml with methanol.
  * Acrylonitrile = 400 µg /ml (Neat) + 100 µg /ml (EPA Method 524.2 Volatiles)
  ** Propionitrile = 900 µg /ml (Neat) + 100 µg /ml (EPA Method 524.2 Volatiles)

- 100 µg /ml V8260 custom mixture: The mixture is prepared at 100 - 5,000 µg /ml by measuring 2.5ml of 2,000 µg /ml Custom Volatiles Mix A, 2.5 ml of 2,000 - 100,000 µg/ml Custom Volatiles Mix B, appropriate amount of some neat compounds, and bringing to 50 ml with methanol.

- 100 µg /ml gas mixture ***: The mixture is prepared at 100 µg /ml by measuring 1 ml of 2,000 µg /ml stock standard and bring to 20 ml with methanol.
  *** Gas mixture should be prepared weekly.

Table 8. STANDARD PREPARATION (Continued)

D).1 Initial Calibration Standards: using DI water bring to 50 ml final volume: all mixtures used should be secondary dilution standards at 100 ppm.

Standard and Surrognte Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)	Surrogate Mix (100ppm)
1 ppb	0.5 µl	0.5 µl	0.5 µl	0.5 µi#
2 ppb *	1.0 µl	1.0 µl	1.0 µl	1.0 µi#
5 ppb	2.5 µl	2.5 µl	2.5 µl	2.5 µi#
10 ppb *	5 µl	5 µl	5 µl	5 µi#
20 ppb	10 µl	10 µl	10 µl	10 µi#
50 ppb	25 µl	25 µl	25 µl	25 µi#
100 ppb	50 µl	50 µl	50 µl	50 µi#
200 ppb	100 µl	100 µl	100 µl	100 µi#
300 ppb *	150 µl	150 µl	150 µl	150 µi#
400 ppb *	200 µl	200 µl	200 µl	200 µi#

* depending upon the instrument.
\# See Section 10.2.2.1 for correction factor.

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

D).2 Initial Calibration Standards for 1,4-Dioxane using SIMS

Standard and Surrogate Concentration (ppb)	1,4-Dioxano Solution (100ppm)	Surrogate Mix (100ppm)	DI Water – Final Volume (ml)
2	2 µl	1 µl	100
5	5 µl	2 µl	100
25	25 µl	5 µl	100
50	25 µl	2.5 µl	50
100	50 µl	5 µl	50
200	100 µl	10 µl	50
400	200 µl	20 µl	50

Table 8. STANDARD PREPARATION (Continued)

E) **Continuing Calibration Standard: using DI water bring to 50 ml final volume:** All mixtures used are secondary dilution standards at 100 ppm.

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 µl	25 µl	25 µl

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the confinuing calibration standard into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

F) **Blank Spike (BS): using DI water bring to 50 ml final volume:** All mixtures used are 100 ppm secondary dilution standards.

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 ul	25 ul	25 ul

For lower detection level required (test code: V8260LL)

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
20 ppb	10 ul	10 ul	10 ul

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the blank spike into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

Table 9. **GUIDELINE FOR DILUTION PREPARATION**

Water Sample

Dilution	Sample amount taken	Final volume A (volumetric)	Take from final volume A	Final volume B (volumetric)
1:2	25 ml	50 ml		
1:5	10 ml	50 ml		
1:10	5 ml	50 ml		
1:20	2.5 ml	50 ml		
1: 25	2 ml	50 ml		
1:50	1 ml	50 ml		
1:100	0.5 ml	50 ml		
1:200	250 µl	50 ml		
1:250	200 µl	50 ml		
1:500	100 µl	50 ml		
1:1000	50 µl	50 ml		
1:2000	25 µl	50 ml		
1:2500	20 µl	50 ml		
1:5000	10 µl	50 ml		
1:10000	0.5 ml	50 ml	0.5 ml	50 ml
1:20000	0.5 ml	50 ml	250 µl	50 ml
1:25000	0.5 ml	50 ml	200 µl	50 ml
1:50000	0.5 ml	50 ml	100 µl	50 ml
1:100000	0.5 ml	50 ml	50 µl	50 ml

Soil-Low level (Non-Encore sample)

Dilution	Sample amount taken	Final volume
1:2	2.5 gram	5 ml
1:5	1 gram	5 ml
1:10	0.5 gram	5 ml

Soil-medium level

Additional Dilution	Sample in Methanol amount taken	Final volume (volumetric)
1:1	1 ml	50 ml
1:2	0.5 ml	50 ml
1:5	200 µl	50 ml
1:10	100 µl	50 ml
1:20	50 µl	50 ml
1: 25	40 µl	50 ml
1:50	20 µl	50 ml
1:100	10 µl	50 ml
1:200	5 µl	50 ml
1:250	4 µl	50 ml
1:500	2 µl	50 ml

Table 10. **REPORTING LIMITS**

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Chlorodifluoromethane	5	5	Chloroform	5	5
Dichlorodifluoromethane	5	5	Freon 113	5	5
Chloromethane	5	5	Methacrylonitrile	10	10
Vinyl chloride	5	5	Butyl Acetate	5	5
Bromomethane	5	5	1,1,1-Trichloroethane	5	5
Chloroethane	5	5	Heptane	5	5
Trichlorofluoromethane	5	5	n-Propyl acetate	5	5
Ethyl ether	5	5	2-Nitropropane	10	10
Acrolein	50	50	Tetrahydrofuran	10	10
1,1-Dichloroethene	2	2	2-Chloroethyl Vinyl Ether	20	20
Tertiary butyl alcohol	50	50	n-Butyl alcohol	250	250
Acetone	5	5	Cyclohexane	5	5
Methyl acetate	5	5	Carbon Tetrachloride	1	1
Allyl chloride	5	5	1,1-Dichloropropene	5	5
Acetonitrile	100	100	Isopropyl Acetate	5	5
Iodomethane	25	25	Benzene	1	1
Iso-butyl alcohol	50	50	1,2-Dichloroethane	2	2
Carbon disulfide	5	5	Trichloroethene	1	1
Methylene chloride	2	2	Methyl methacrylate	10	10
Methyl tert butyl ether	1	1	1,2 Dichloropropane	1	1
Trans-1,2-Dichloroethene	5	5	Di-isobutylene	5	5
Di-isopropyl ether	5	5	Dibromomethane	5	5
2-Butanone	5	5	1,4 Dioxane	125	125
1,1-Dichloroethane	2	2	Bromodichloromethane	1	1
Hexane	5	5	cis-1,3-Dichloropropene	1	1
Chloroprene	5	5	4-Methyl-2-pentanone	5	5
Acrylonitrile	5	5	Toluene	1	1
Vinyl acetate	10	10	trans-1,3-Dichloropropene	1	1
Ethyl acetate	5	5	Ethyl methacrylate	10	10
2,2-Dichloropropane	5	5	1,1,2-Trichloroethane	3	3
Cis-1,2-Dichloroethene	5	5	2-Hexanone	5	5
Bromochloromethane	5	5	Cyclohexanone	5	5

Table 10. **REPORTING LIMITS (Continued)**

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Tetrachloroethene	1	1	4-Chlorotoluene	5	5
1,3-Dichloropropane	5	5	1,3,5-Trimethylbenzene	5	5
Dibromchloromethane	5	5	tert-Butylbenzene	5	5
1,2-Dibromoethane	2	2	1,2,4 Trimethylbenzene	5	5
Chlorobenzene	2	2	sec-Butylbenzene	5	5
1,1,1,2-Tetrachloroethane	5	5	1,3-Dichlorobenzene	5	5
Ethylbenzene	1	1	p-Isopropyltoluene	5	5
M,p-Xylene	1	1	1,4-Dichlorobenzene	5	5
o-Xylene	1	1	1,2-Dichlorobenzene	5	5
Styrene	5	5	n-Butylbenzene	5	5
Bromoform	4	4	1,2-Dibromo-3-choropropane	10	10
Isopropylbenzene	2	2	1,2,4-Trichlorobenzene	5	5
Bromobenzene	5	5	Hexachlorobutadiene	5	5
1,1,2,2-Tetrachloroethane	2	2	Naphthalene	5	5
Trans-1,4-Dichloro-2-butene	5	5	1,2,3-Trichlorobenzene	5	5
1,2,3-Trichloropropane	5	5	Epichlorohydrin	100	100
n-Proplybenzene	5	5	3-Methyl-1-butanol	5	5
2-Chlorotoluene	5	5	Hexachloroethane	5	5
Ethanol	50	--	Methyl Acrylate	5	--
Benzyl Chloride	1	--			

Table 11. **COMPOUNDS THAT MAY EXHIBIT CARRYOVER**

Compound
1,2,4-Trichlorobenzene
Hexachlorobutadiene
Naphthalene
1,2,3-Trichlorobenzene

Lab Manager_____

QA Manager_____

Effective Date:_____

TEST NAME: METHOD 8270D, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

REFERENCE: SW846 8270D (Revision 4, February 2007)

Revised Sections: 2.1, 9.5.1, 10.1.1, 11.11.2, 12.6.2, 12.6.3, 12.8.3, Tables 7C, 9, 10
Added Section 12.11

SCOPE AND APPLICATION

1.1 The following method describes the analytical procedure that is utilized by Accutest to analyze semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and water samples. Options are incorporated for the analysis of sixteen (16) polyaromatic hydrocarbons (PAH) and other compounds listed in table 8A by selected ion monitoring GC/MS (GC/MS-SIM).

1.2 Table 1 lists the neutral, acidic, and basic organic compounds that can be determined by this method. The applicable concentration range of this method is compound and instrument dependent. Some compounds may require special treatment due to the limitations caused by sample preparation and/or chromatographic problems.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with the following extraction methodologies in SW846: 3510, 3520, 3545, 3550 and 3580.

2.2 The resultant methylene chloride extract is injected into a tuned and calibrated GC/MS system equipped with a fused silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.4 Once identified, the compound is quantitated by internal standard techniques with an average response factor generated from the calibration curve.

2.5 Additional unknown peaks with a response greater than 10 % of the closest internal standard may be processed through a library search with comparison to a NIST98 database. An estimated concentration is quantitated by assuming a response factor of 1.

2.6 This method includes analytical opfions for PAHs and other selected compounds by GC/MS-SIM. The extract is fortified with an additional SIM specific internal standard mix and analyzed using selected ions that are characteristic of the compounds of interest following the analysis of lower concentration

calibration standards analyzed under the same MS scan conditions. Qualitative and quantitative identification is conducted using the procedures employed for full scan analysis.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at either method detection limit or the lowest concentration standard in the calibration curve, depending on the requirements of different regulatory programs. Detected concentrations below this concentration cannot be reported without qualification. See table 9.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BATCH - a group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BLANK - an analytical sample designed to assess specific sources of laboratory contamination.

CONTINUING CALIBRATION - a mid-range calibration check standard run every 12 hours to verify the initial calibration of the system.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations which cover the working range of the instrument; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds and must be analytes that are not sample components.

MATRIX - the predominant material of which the sample to be analyzed is composed.

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards, is carried throughout the entire preparatory and analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentrafion is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequentiy analyzed parameters.

PERCENT DIFFERENCE (%D) - As used to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which no interferant is observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RESOLUTION - also termed separation or percent resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by **100**.

INITIAL CALIBRATUION VERIFICATION (SECOND SOURCE CALIBRATION STANDARD) - a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run whenever an initial calibration is performed.

SURROGATES - pure analytes added to every blank, sample, matrix spike, matrix spike duplicate, and standard in known amounts before extraction or other processing; used to evaluate analytical efficiency

by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and 4,4'-DDT. Prepare primary standards of these toxic compounds in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.4 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

7.0 SAMPLE COLLECTION, PRESERVATION, & HOLDING TIMES

7.1 Water samples may be collected in 1-liter glass bottles with Teflon insert in caps. Soil samples may be collected in 250-ml wide-mouth amber glass bottles.

7.1.1 Sample should be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus avoiding possible phthalate contamination.

7.2 Test all aqueous samples for residual chlorine using test paper for free and total chlorine. If the sample tests positive for residual chlorine, add 80 mg of sodium thiosulfate to each liter of sample.

7.3 The samples must be protected from light and refrigerated at $\leq$6° C from the time of receipt until extraction and analysis.

7.4 Store the sample extracts at -10 °C in amber vials (protected from light), in sealed vials equipped with unpierced PTFE-lined septa.

7.5 HOLDING TIME

7.5.1 Aqueous samples must be extracted within 7 days of sampling.

7.5.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

7.5.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS & MATERIALS

8.1 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.1.1 Gas Chromatograph. HP-5890, HP-6890, or Agilent 6890-N which includes an analytical system that is complete with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases.

8.1.1.1 The injection port is designed for splitiess injection with capillary columns.

8.1.1.2 The capillary column is directly coupled to the source.

8.1.2 Column.

8.1.2.1 30 m x 0.25 mm fused silica (0.25 μm tilm thickness) DB-5MS or equivalent capillary column. Condition the column as per manufacture's directions.

8.1.3 Mass Spectrometer (HP-5972, HP-5973 or Agilent 5975).

8.1.3.1 Full Scan Mode -Capable of scanning from 35-500 amu every 1 second or less utilizing 70 volt (nominal) electron energy in the electron impact ionization mode.

8.1.3.2 SIM Mode- Capable of selective ion grouping at specitied retention times for increased compound sensitivity (table 2a).

8.1.3.3 Capable of producing a mass spectrum which meets all the EPA performance criteria in Table 3 when injecting 50 ng of Decafluorotriphenyl phosphine (DFTPP).

8.2 DATA SYSTEM

8.2.1 Acquisition and Instrument Control: HP Chemstation. A computer system is interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable

media (disc) of all mass spectra obtained throughout the durafion of the chromatographic program.

8.2.2 Data Processing: HP Enviroquant. The software accommodates searching of GC/MS data files for analytes which display specific fragmentafion patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The data system includes the NIST98 spectra library for qualitative searches of non-target compounds present in the chromatogram. It flags all data files that have been edited manually by laboratory personnel.

8.2.3 Offline Magnetic Tape Storage Device (Lagato Networker) - the magnetic tape storage device copies data for long term, offline storage.

8.3 SYRINGE

8.3.1 10 µl graduated, auto sampler (Hamilton or equiv.).

8.3.2 Micro liter syringes, various sizes

9.0 REAGENTS AND STANDARDS

9.1 Solvents - Ultra pure, chromatography grade methylene chloride and acetone.

9.2 Stock Standard Solutions.

9.2.1 Certified, commercially prepared standards, from two separate sources are used.

9.2.1.1 Base Neutrals.

- Base/Neutrals Mix #1 (Absolute: Semivolatile Organics Standard Mix # 1).
- Base/Neutrals Mix #2 (Absolute: Semivolatile Organics Standard Mix # 2).
- PAH Mix (Absolute: Semivolatile Organics Standard Mix # 7).
- PAH Mixture #2 (Ultra).
- PAH Selected Ion Monitoring Mixture
- Benzidines Mix (Absolute: Semivolatile Organics Standard Mix # 6).
- Toxic Substances #2 (Absolute: Semivolatile Organics Standard Mix # 5).
- Pyridines Mixture (Ultra).
- Additonal requested compound(s) mix (Absolute).
- Base Neutral Mixture (2nd Source).

Acids.

- Phenols Mix (Absolute: Semivolatile Organics Standard Mix # 8).
- Toxic Substances #1(Absolute: Semivolatile Organics Standard Mix # 4).
- Acid Mixture (2nd Source).Internal Standard Mixtures.

9.2.2 Internal Standard Mixtures

9.2.2.1 Ultra (or equivalent) at a concentration of 4,000 µg/ml for each of the following compounds.

Full Scan

- 1,4-Dichlorobenzene-d4
- Naphthalene-d8
- Acenaphthene-d10
- Phenanthrene-d10
- Chrysene-d12
- Perylene-d12

SIM

- 1,2-Dichlorobenzene-d4
- 1-Methylnaphthalene-d10
- Fluorene-d10
- Fluoranthene-d10
- Benzo(a)pyrene-d12

9.2.2.2 The internal standards should permit most of the components of interest in a chromatogram to have retention times of 0.8 - 1.20 relative to one of the internal standards.

9.2.2.3 Each 1 ml sample extract, and standard undergoing analysis should be spiked with 10 µl of the internal standard mixtures, resulting in a concentration of 40 µg/ml of each internal standard for full scan analysis and 4 ug/ml for SIM analysis.

9.2.3 Surrogate Standard Mixture.

9.2.3.1 B/N Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 5,000 µg/ml each surrogate compound.

- Nitrobenzene-d5.
- 2-Fluorobiphenyl.
- p-Terphenyl-d14.

9.2.3.2 Acid Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 7,500 µg/ml each surrogate compound.

- Phenol-d5.
- 2-Fluorophenol.
- 2,4,6-Tribromophenol.

9.2.4 DFTPP Tune Stock.

9.2.4.1 Protocol (or equivalent) at a concentration of 2,500 µg/ml for the following compounds.

- Decafluorotriphenylphosphine.
- 4,4'-DDT.

- Benzidine.
- Pentachlorophenol.

9.2.5 Store at -10 °C or less when not in use or according to the manufacturer's documented holding time and storage temperature recommendations. Stock standard solutions must be replaced after 1 year or sooner if manufacture's expiration date comes first or comparison with quality control check samples indicates degradation.

9.3 Surrogate Spiking Solutions.

9.3.1 Two surrogate spiking solutions, base/neutral surrogate solution and acid surrogate solution, at a concentration of 100 µg/ml are prepared in Extraction. Spike each sample, and blank with 0.5 ml of each solution, prior to extraction, for a final concentration of 50 µg/l of each surrogate compound in the extract.

9.3.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.3.3 Store at -10 °C or less or according to the manufacturer's documented storage temperature recommendations. Prepare fresh surrogate spiking solutions every year, or sooner, if the manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.4 Intermediate Calibration Standard Solution.

9.4.1 The calibration stock solution is prepared by adding an appropriate amount of each stock and surrogate compounds into a 10 ml volumetric flask. Dilute the solufion to the volume with methylene chloride and mix thoroughly. Refer to Table 7A for details.

9.5 Calibrafion Standards.

9.5.1 Initial Calibration Standards.

9.5.1.1 Calibration standards containing the surrogate compounds should be made by quantitative dilutions of the above intermediate solution. The calibration standards are prepared at a minimum of five concentrations to cover the range of 1 - 100 µg/ml for full scan and 0.02 – 5ug/ml for SIM, depending upon project specific requirements. Suggested levels and preparafions are shown in Table 7A and 7B.

9.5.2 Continuing Calibration Verification.

9.5.2.1 The concentration of the mid range standard used for continuing calibrafion verification is altemated between 25 and 50 µg/ml for full scan and 2.5 and 1.0 for SIM.

9.5.3 Store the calibration standards in a refrigerator at $\leq$ 6 °C and prepare every 6 months or before the manufacturer's expiration date, whichever is sooner. Standards must be replaced immediately if the analysis of check standards indicates degradation.

9.6 Initial Calibration verification (ICV) -Second source calibration check standard.

9.6.1 The ICV standard is prepared per Table 7E, using the intermediate solutions prepared in Extraction.

9.6.2 The ICV is analyzed after each initial calibration.

9.7 Daily GC/MS Performance Checks.

9.7.1 The solution is prepared at 50 µg/ml by making a 1:50 dilution of DFTPP stock solution (Section 9.2.4) in methylene chloride.

9.8 Matrix Spike Solutions.

9.8.1 The matrix spike solutions for both Base/Neutral and Acid are prepared in Acetone at a concentration of 100 µg/ml for each compound. Prepare the matrix spike, matrix spike duplicate and blank spike by spiking the selected sample and the blank with 0.5 ml of these solutions for a final concentration of 50 µg/l of each compound.

9.9 All organic new standard solutions are analyzed prior to use to verify the accuracy of the prepared concentration.

9.9.1 The prepared standard solution is analyzed using the determinative (instmmental) technique for the method.

9.9.2 The solution is analyzed following the completion of instrument calibration or a calibration check.

9.9.3 The concentration of the standard solution is determined using the software routines used in determining the acceptability of calibrafion verification.

9.9.4 The data is evaluated and the percent difference determined. The standard solution is approved for use if all designated compounds are present in the solution and the percent difference is less than the established criteria (±20%).

10.0 CALIBRATION

10.1 Initial Calibration.

10.1.1 The calibration range covered for routine analysis under RCRA employs standards of 1, 2, 5, 10, 25, 50, 80, 100 µg/ml for full scan and 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml for SIM. A minimum of five standards must be run sequenfially. The reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of surrogate spiking solutions to the calibration solution to define a range similar to the target compounds.

10.1.3 Aliquot 1 ml of each calibration standard into a 2 ml crimp top vial.

10.1.4 Prior to analysis, add 10 µl of the applicable (Full scan and/or SIM) internal standard solution (Section 9.2.2) to each standard. This results in a concentration of 40 µg/ml (Full scan) and 4ug/ml (SIM) for each internal standard.

10.1.5 Analyze the standard solutions using the conditions established in Section 11.0. Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 6.

10.1.6 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte, using minimum of five RF values calculated from the initial calibration curve.

10.1.7 For the initial calibration to be valid, the following criteria must be met.

10.1.7.1 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than or equal to 20%.

10.1.7.2 If the %RSD of any individual compound is ≥20%, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.1.7.2.1 If a linear regression is employed, select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.1.7.2.2 The correlation coefficient (r value) must be ≥0.99 for each compound to be acceptable.

10.1.7.2.2.1 When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve.

10.1.7.2.2.2 The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration.

10.1.7.2.3 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient for the linear calibration option, then the chromatographic system is considered too reactive for the analysis to begin. Perform

corrective action and recalibrate if the calibration criteria cannot be achieved.

10.1.7.3 It is recommended that the minimum response factor for the most common target analytes in the following table should be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected.

Minimum Response Factor Table

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis (2-chloroethyl) ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxyl)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrobenzene	0.200

Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fiuoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

10.1.7.3.1 Due to the large number of compounds, some compounds will fail to meet the minimum response factor criteria. They may be used as qualified data or estimated values for screening purposes. Non-detects may be reported if adequate sensitivity has been demonstrated at the applicable lower quantitation limit.

10.1.7.4 The initial calibration criteria for this method applies to all additional compounds of concern specified by the client.

10.1.7.5 The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

10.2 Initial Calibration Verificafion (ICV) - Source Calibration Check Standard.

10.2.1 The calibration is verified with a calibration check standard at 50 µg/ml (Full scan) or 1ug/ml (SIM) from an external source (Section 9.6). It must be analyzed immediately following the initial calibration.

10.2.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 30% for all the target compounds.

10.2.2.1 If % D is greater than 30%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification Standard - CCV

10.3.1 A calibration verificafion standard at close mid-level concentration of the initial calibration range at alternating 25 and 50ug/ml for full scan and 2.5ug/ml and 1ug/ml for SIM must be acquired every 12 hrs.

10.3.1.1 The calibration verification standard selected must be near concentration of the midpoint calibration standard or near the action level for the project specified.

10.3.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.3.2.1 Each of the most common target analytes in the calibration verificafion standard should meet the minimum response factors as noted in the Minimum Response Factor Table in section 10.1.7.3.

10.3.2.2 All target compounds of interest must be evaluated using a 20% D criteria. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibrafion for that compound is assumed to be valid.

10.3.2.3 Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the 20% D criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples.

10.3.2.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to the compound at the applicable quantitation limits. For situation when the failed compound is present, the concentrations must be reported as estimated.

10.3.3 If the first continuing calibration verification does not meet criteria, a second standard may be injected after notifying the team leader/manager and checking the system for defects.

10.3.3.1 A continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed or refer to section 10.3.2.4. In situations where the first check fails to meet the criteria, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.4 If the verificafion criteria cannot be achieved, a new initial calibration must be performed or refer to section 10.3.2.4.

10.3.5 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retenfion time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.3.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.3.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

11.0 PROCEDURE

11.1 Instrument Conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modificafion should be approved by team leader/manger.

11.2 Daily GC/MS Performance Checks.

11.2.1 Mass Spectrometer Tuning. Every 12-hour, inject 1 µl of 50 ng/µl or 2 µl of 25 ng/µl DFTPP solution directiy on to the column.

11.2.2 The GC/MS system must be checked to verify that acceptable performance criteria are achieved (see Table 3).

11.2.3 This performance test must be passed before any sample extracts, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.2.3.1 Select the scans at the peak apex and one to each side of the apex.

11.2.3.2 Calculate an average of the mass abundances from the three scans.

11.2.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and acquired within no more than 20 scans to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.2.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.2.4.1 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of

five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.2.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.2.6 In order to assess GC column performance and injection port inertness, the DFTPP tune standard also contains appropriate amount of 4,4'-DDT, benzidine and pentachlorophenol.

11.2.6.1 Injection Port Inertness Check.

11.2.6.1.1 The injection port inertness of the GC portion of the GC/MS is evaluated by the percent breakdown of 4,4'-DDT. DDT is easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated by high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a GC/MS tune standard containing 4,4'-DDT every 12 hour, regardless of whether DDT is a target analyte. The degradation of DDT to DDE and DDD should not exceed 20%, in order to proceed with calibration procedures. Refer to Section 13.7 for calculation. Print the check and keep it on file.

11.2.6.2 Column Performance Check.

11.2.6.2.1 The condifion of the GC column is evaluated by the tailing of benzidine and pentachlorophenol every 12 hour. Benzidine and pentachlorophenol should be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factors. The tailing factor criteria for benzidine (base-neutral fraction) must be ≤ 2 and for pentachlorophenol (acid fraction) must be ≤ 2. Print the check daily and keep on file:

11.2.6.3 If degradafion is excessive and/or poor chromatography is observed, the injector port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

11.3 Initial Calibration

11.3.1 Refer to Section 10.1.

11.4 Initial calibration Verificafion (ICV) - Second Source Calibration Check

11.4.1 This standard must at least be analyzed when initial calibration provided. Refer to Section 10.2.

11.5 Continuing Calibration Checks

11.5.1 Refer to Section 10.3.

11.6 Sample Analysis.

11.6.1 Allow the sample extract to warm to room temperature. Spike 10 µl of the appropriate internal standard mix (4,000 µg/ml for full scan and 400ug/ml for SIM) into 1 ml sample extract, just prior to analysis. This is equivalent to a concentration of 40 µg/ml (full scan) and 4ug/ml (SIM) of each internal standard.

11.6.2 Inject 1 µl aliquot of the sample extract into the GC/MS system. A splitless injection technology is used.

11.6.3 If the response for any ion of interest exceeds the working range of the GC/MS system, dilute a stored extract if available and reanalyze.

11.6.4 When the extracts are not being used for the analyses, store them at -10°C, protected from light, in sealed vials equipped with unpierced PTFE-lined septa.

11.7 Sample Dilution

11.7.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

11.7.2 If no lower dilution has been reported, the dilution factor chosen should keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

11.7.3 Preparing Dilutions.

11.7.3.1 Prepare sample dilutions quantitatively. Dilute the sample extract with methylene chloride using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc. Large dilutions may require serial dilutions or the use of a Class A 10 ml volumetric flask.

11.7.3.2 Syringe dilutions. – Calibrated syringes are used to prepare dilutions. Add the appropriate amount of methylene chloride to a clean autosampler vial. Add the proper amount of sample using a calibrated syringe of the appropriate volume for the dilution. Add sufficient internal standard to maintain a concentration of 40ug/ml. Cap the vial and gently shake to disperse the sample through the solvent.

11.7.3.3 Volumetric Flask Dilufions – Large dilutions may require the use of a 10 ml Class A Volumetric flask.

11.8 Establishing Search Criteria for target compounds. Search criteria for each compound listed in the method must be entered into the method quantitation/Identification file in the Enviroquant software package. This activity must be performed before attempting qualitative and quantitative analysis on any acquired data file. The search criteria are based on compound retention time and the characteristic ions from the reference mass spectrum. Characteristic ions are defined as the three

ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The number of secondary ions displayed for each compound search varies between compounds.

11.8.1 Select the primary ion for the target compound from the characterisfic ions in Table 6. If multiple characteristic ions are listed, the first ion is the major (primary) ion. Enter this ion as the search ion. Enter the relative abundance of this ion (100% for base peak ions) and set the relative abundance window at ± 30%.

11.8.1.2 Alternate primary ions may be selected when interferences exist from ion abundance contribution from close eluting compounds.

11.8.2 Enter the remaining ions as secondary ions. Secondary ions are not be used to locate peaks within the search window, but are be used to support the qualitative identification of selected peaks. The number of secondary ions displayed for each compound search varies between compounds depending on the number of ions in the spectra >30% relative abundance.

11.8.3 Set the relative abundance windows for the secondary ions at ± 30%.

11.8.4 Establish the relative retention window for each compound. Because it is a relative retention window the same width window applies to all compounds on the quantitation list. The window must be established at a minimum of 0.06 relative retention time units.

11.9 Data Interpretation.

11.9.1 Executing Qualitative Searches. The target compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.1 The search procedure will identify peaks within the search window using the primary ion only. Secondary ions and the relative retention are used to determine "the best match". If the best match contains secondary ions outside the relafive abundance window, they will be flagged with a # sign.

11.9.2 Qualitative Identificafion. The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Compounds are identified when the following criteria are met.

11.9.2.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.9.2.2 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criterion is the RRT of sample component must be within ± 0.06 RRT units of the standard.

11.9.2.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an

abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

11.9.2.3.1 If a chromatographic peak exhibits a spectrum containing an ion with relative abundance outside the relative abundance window is selected for reporting, the analyst must annotate the spectra that the compound qualified based on his/her best judgement. This circumstance will most often occur from coeluting compounds with similar ions or background matrix interferences.

11.9.3 Quantitative Analysis.

11.9.3.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 6). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.3.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. The secondary ion must be used to generate a new response factor.

11.10 Library Search for Tentafively Identified Compounds.

11.10.1 If a library search is requested, the analyst should perform a forward library search of the NIST98 mass spectral library to tentatively identify 10 to 15 non-reported compounds (15 for base, 10 for acid, 25 for base/acid fracfion).

11.10.2 Guidelines for making tentative identificafion are listed below.

11.10.2.1 These compounds should have a response greater than 10% of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

11.10.2.5 The relative intensities of the major ions should agree within ± 20 %. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.3 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.4 The resulting concentration should be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.10.5 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched and reported but not counted towards the total TIC count.

11.10.6 Any peak naming as "System artifact" (from the column bleedings) or "Internal Standard" (added by lab for other test, like SIM analysis) shall be searched and reported but not counted towards the total TIC count.

11.11 Selected Ion Monitoring (SIM) Option

NOTE: The use of SIM is not allowed by the SCDHEC for samples from South Carolina.

11.11.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a, Table 8a) Select a mass dwell time of 50 milliseconds for all compounds.

11.11.2 Calibrafion: Calibrate the mass spectrometer in the selected ion monitoring mode using 7 calibration standards of 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs using the procedures and criteria described in Section 10.1.6, 10.1.7.3 and 10.1.7.4.

11.11.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 1.0 ug/ml calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria of Section 10.2.2.

11.11.4 Continuing Calibration Verification. Verify the inifial calibration every 12 hours using a 1.0 or 2.5 ug/ml calibration. The continuing calibration verification must meet the criteria of Section 10.3.

11.11.5 Sample Extract Analysis: Each extract has been previously spike with the SIM internal standard at 4 ug/ml. Analyze the sample extracts for the compounds of interest using the SIM scan parameters employed for the calibrafion standards.

11.11.6 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis at 50 ug/ml.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary.

Daily GC/MS Performance Checks	Beginning of the analytical shift and every 12 hours
Initial Calibration	Whenever needed.
Second Source Calibrafion Check	Following initial calibration
Continuing Calibration Verification	Every 12 hours.
Method Blank	One per extraction batch*.
Blank Spike	One per extraction batch*.
Matrix Spike	One per extraction batch*.
Matrix Spike Duplicate	One per extraction batch*.
Surrogate	Every sample extract and standard.
Internal Standard	Every sample extract and standard.

*The maximum number of samples per batch is twenty or per project specificafion.

12.2 Daily GC/MS Performance Checks.

12.2.1 Refer to Section 11.2.

12.3 Initial Calibration.

12.3.1 Refer to Section 10.1.

12.4 Initial Calibration Verification (ICV) - Source Calibration Check.

12.4.1 Refer to Section 10.2.

12.5 Confinuing Calibration Verification.

12.5.1 Refer to section 10.3.

12.6 Method blank.

12.6.1 The method blank is either reagent water or anhydrous sodium sulfate (depending on the sample matrix) which must be extracted with each set of 20 or less samples. For a running

batch, a new method blank is required for each different extraction day. The method blank is then extracted and carried through all stages of the sample preparation and measurement.

12.6.2 If the method blank contains a target analyte above its MDL , the entire batch must be re-extracted and re-analyzed.

12.6.3 Surrogate compounds are added to the method blank prior to extraction. If the surrogate accuracy in the method blank does not meet in house criteria , it must be reanalyzed. If the reanalysis confirms the original data, the entire batch should be re-extracted.

12.7 Blank Spike

12.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same volume. It is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

12.7.2 The blank spike recoveries should be assessed using laboratory in house limits.

12.7.3 If a blank spike is out of control, the following corrective actions must be taken and all the associated samples must be re-extracted and reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required.

12.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

12.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

12.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

12.8 Matrix Spike(MS) / Matrix Spike Duplicate(MSD)

12.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, and determinative procedures.

12.8.2 Matrix spikes are prepared by spiking an actual sample at a concentration of 50 µg/l for both base/neutral and acids.

12.8.3 Assess the matrix spike recoveries (% R) (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the in house control limits.

12.8.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. In such case, matrix interference is assumed and the data is reported with footnote (e.g., spike recovery indicates possible matrix interference). No further corrective action is required.

12.9 Surrogates

12.9.1 All standards, blanks, sample extracts, and matrix spikes contain surrogate compounds which are used to monitor the performance of the extraction and analytical system.

12.9.2 The recoveries (Section 13.5) of the surrogates must be evaluated to determine whether or not they fall within surrogate control limits developed by the laboratory annually.

12.9.3 If the recovery of any surrogate compound does not meet the control limits, the calculation must be checked for possible error. The surrogate solution should be checked for degradation. Contamination and instrument performance should also be reviewed.

12.9.3.1 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

12.9.3.2 If the data from the reanalysis is also out of control, re-extract and reanalyze the sample.

12.9.3.3 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

12.9.3.4 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

12.9.4 If the sample exhibits matrix interference, defined as excessive signal where target or non-target responses are greater than the response of the internal standards. In this case, reanalysis may not be required following team leader/manager approval; the surrogates will be qualified as outside the limits due to matrix interference. Alternatively, sample may be reanalyzed on dilution, if the reanalysis is again not within the limit, the sample should be reported with a footnote indicating that there were possible matrix interference.

12.10 Internal Standards.

12.10.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 µg/ml standard of initial calibration.

12.10.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area of the latest calibration standard (12 hr. time period).

12.10.3 If the area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.10.4 If the areas are acceptable upon reanalysis, the reanalysis data is reported.

12.10.5 If the areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

12.11 Refer to Project Specific Bench Notes(MS8270) for additional program or client specific QC requirements

13.0 CALCULATION

13.1 Response Factor (RF).

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Area of the characterisfic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_s = Concentrafion of the compound being measured (µg/ml).
C_{is} = Concentration of the specific internal standard (µg/ml).

13.2 Percent Relative Standard Deviation (%RSD).

$$\%RSD = \frac{SD}{RF_{av}} \times 100$$

where:

SD = Standard Deviation.
RF_{av} = Average response factor from initial calibration.

13.3 Percent Difference (%D).

$$\% D = \frac{|RF_{av} - RF_{cv}|}{RF_{av}} \times 100$$

where: RF_{cv} = Response factor from Calibration Verification Standard.

13.4 Concentration (Conc.).

13.4.1 <u>for water:</u>

$$\text{Cone. } (\mu g/l) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times V_i}$$

13.4.2 for soil/sediment (on a dry weight basis):

$$\text{Conc. } (\mu g/kg) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times W_s \times S}$$

where:

V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100.

13.5 Percent Recovery (%R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD).

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

where:

MSC = Matrix Spike Concentration.
MSDC = Matrix Spike Duplicate Concentration.

13.7 Percent Breakdown.

$$\% \text{ Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where:

Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD.

13.8 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{a} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard

b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.9 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

14.2.1 The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instmment Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Unused blocks of any form must be X'ed and Z'ed by the analyst before submitting the data for review.

14.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properiy. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 DATA REVIEW AND REPORTING

15.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

15.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

15.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

15.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

15.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

15.3.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

15.3.2 Manual integration of chromatographic peaks must be identified by the analysts. Upon review, the supervisor will initial and date the changes made to the report.

15.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

15.4.1 Compare the printed values to the original values to verify transfer accuracy.

15.4.2 If transfer errors occurred, the errors must be corrected before the data is re-submitted.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes
16.2.3 Chlorinated organic solvents
16.2.4 Non-chlorinated organic solvents
16.2.5 Hazardous solid wastes
16.2.6 Non-hazardous solid wastes

Table 1 – Target Compounds by SW846 8270C			
Benzenethiol (1)	4-Bromophenyl phenyl ether	Di-n-octyl phthalate	5-Nitro-o-toluidine (1)
Benzoic Acid	Butyl benzyl phthalate	Diethyl phthalate	Naphthalene
2-Chlorophenol	Benzyl Alcohol	Dimethyl phthalate	Nitrobenzene
4-Chloro-3-methyl phenol	1,1'-Biphenyl (1)	2,3-Dichloroaniline (1)	n-Nitrosodimethylamine
2,4-Dichlorophenol	Butyl Stearate (1)	Decane	4-Nitroquinoline 1-Oxide (1)
2,4-Dimethylphenol	2-Chloronaphthalene	Octadecane (1)	N-Nitroso-di-n-propylamine
2,4-Dinitrophenol	4-Chloroaniline	bis(2-Ethylhexyl)phthalate	N-Nitrosodi-n-butylamine
2,6-Dichlorophenol	Carbazole	Ethyl methanesulfonate	N-Nitrosodiethylamine
4,6-Dinitro-2-methylphenol	Caprolactam (1)	Famphur	N-Nitrosodiphenylamine
Dinoseb	Chiorobenzilate	Fluoranthene	N-Nitrosomethylethylamine
2-Methylphenol	Chrysene	Fluorene	N-Nitrosomorpholine
3&4-Methylphenol	Cumene (1)	Hexachlorobenzene	N-Nitrosopiperidine
2-Nitrophenol	bis(2-Chloroethoxy)methane	Hexachlorobutadiene	N-Nitrosopyrrolidine
4-Nitrophenol	bis(2-Chloroethyl)ether	Hexachlorocyclopentadiene	O,O,O-Triethyl phosphorothioat
Pentachlorophenol	bis(2-Chloroisopropyl)ether	Hexachloroethane	2-Picoline
Phenol	4-Chlorophenyl phenyl ether	Hexachlorophene	Parathion
2,3,4,6-Tetrachlorophenol	1,2-Dichlorobenzene	Hexachloropropene	Pentachloroethane (1)
2,4,5-Trichlorophenol	1,2-Diphenylhydrazine	Indene (1)	Pentachlorobenzene
2,4,6-Trichlorophenol	1,3-Dichlorobenzene	Indeno(1,2,3-cd)pyrene	Pentachloronitrobenzene
2-Acetylaminofluorene	1,4-Dichlorobenzene	Isodrin	Phenacetin
4-Aminobiphenyl	2,4-Dinitrotoluene	Isophorone	Phenanthrene
Acenaphthene	2,6-Dinitrotoluene	Isosafrole	Phorate
Acenaphthylene	3,3'-Dichlorobenzidine	Kepone	Pronamide
Acetophenone	3,3'-Dimethylbenzidine	1-Methylnaphthalene	Pyrene
Aniline	1,4-Dioxane (1)	2-Methylnaphthalene	Pyridine
Anthracene	7,12-Dimethylbenz(a)anthracene	3-Methylcholanthrene	p-Phenylenediamine
Aramite	Dimethylnaphthalenes (total) (1)	4,4'-Methylenebis(2-chloroaniline)	Quinoline (1)
Atrazine (1)	Diallate	Methapyrilene	Safrole
alpha-Terpineol	Dibenz(a,h)acridine	Methyl methanesulfonate	1,2,4,5-Tetrachlorobenzene
A,A-Dimethylphenethylamine	Dibenzo(a,h)anthracene	Methyl parathion (1)	1,2,4-Trichlorobenzene
Benzidine	Dibenzofuran	6-Methyl Chrysene (1)	1,2,3-Trichlorobenzene (1)
Benzaldehyde (1)	Dimethoate	1,4-Naphthoquinone	1,3,5-Trichlorobenzene (1)
Benzo(a)anthracene	Diphenylamine	1-Naphthylamine	Thionazin (1)

Benzo(a)pyrene	Disulfoton	2-Naphthylamine	o-Toluidine
Benzo(b)fluoranthene	m-Dinitrobenzene	2-Nitroaniline	sym-Trinitrobenzene (1)
Benzo(g,h,i)perylene	p-(Dimethylamine) azobenzene (1)	3-Nitroanlline	Tetraethyl dithiopyrophosphate (1)
Benzo(k)fluoranthene	Di-n-butyl phthalate	4-Nitroaniline	

(1) NELAC Accreditation is not offered for this compound.

Table 2 – RECOMMENDED OPERATING CONDITIONS: Gas Chromatograph/ Mass Spectrometer	
Injection Type	Splitless
Carrier Gas (linear velocity)	Helium at 30 cm/sec*
Mass range	35-500 AMU
Electron Energy	70 volts (nominal)
Scan time	not to exceed 1 sec. per scan
Injection port temperature	200-300 °C
Source temperature	220-270 °C
Transfer line temperature	250-300 °C
Analyzer temperature	220-250 °C
Gas Chromatograph Temperature Program*	
Initial temperature	40-50 °C*
Time 1	2-4 minutes*
Column temperature rate	8-25 degrees/min*
Final temperature	290-320 °C according to column type*
Total run time	*20-40 minutes*

* Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 2a – SIM Group Parameters		
Group No.	Retention Time (minutes)	Ions
1	0 – 7.8	150, 64, 93, 82, 152, 99, 63, 128, 112, 42, 95
2	7.8 – 11	150, 128, 225, 142, 172, 152, 129, 223, 141, 171, 122, 127, 227, 115, 170
3	11 – 13.8	172, 152, 166, 182, 334, 266, 176, 153, 165, 330, 284, 264, 174, 154, 77, 332, 286, 268
4	13.8 – 18	266, 179, 202, 122, 268, 212, 203, 284, 178, 213, 244, 286
5	18 – 22	244, 229, 167, 122, 226, 202, 228, 149, 203
6	22 – 34.7	264, 149, 253, 278, 263, 150, 250, 139, 265, 252, 276, 138

Table 3 - DFTPP KEY IONS AND ION ABUNDANCE CRITERIA	
Mnss	Ion Abundance Criteria
51	30-60 of mass 198
68	<2 % of mass 69
70	<2 % of mass 69
127	40-60 % of mass 198
197	<1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	>1 % of mass 198
441	Present but less than mass 443
442	>40 % of mass 198
443	17-23 % of mass 442

Table 4 – INTERNAL STANDARDS	
Internal Standard (Full Scan)	Prim/Sec. Ions
1,4-Dichlorobenzene-d4	152 / 150, 115
Naphthalene-d8	136 / 68
Acenaphthene-d10	164 / 162, 160
Phenanthrene-d10	188 / 94, 80
Chrysene-d12	240 / 120, 236
Perylene-d12	264 / 260, 265
Internal Standard (SIM)	Prim/Sec. ions
1,2-Dichlorobenzene-d4	152/ 150
1-Methylnaphthalene-d10	150/ 152, 122
Fluorene-d10	174/ 176
Fluoranthene-d10	212/ 213
Benzo(a)pyrene- d12	264/ 263, 265

Table 6 – Full Scan Semivolatile Internal Standards with Corresponding Analytcs Assigned for Quantitation			
1,4-Dichlorobenzene-d4	Ions	Acenaphthene-d10	Ions
Aniline	(93/66,65)	Acenaphthene	(154/153,152)
Benzaldehyde	(105)	Acenaphthylene	(152/151,153)
Benzenethiol	(110)	1-Chloronaphthalene	(162/127,164)
Benzyl alcohol	(108/79,77)	2-Chloronaphthalene	(162/127,164)
Bis(2-chloroethyl)ether	(93/63,95)	4-Chlorophenylphenyl ether	(204/206,141)
Bis (2-chloroisopropyl)ether	121	Dibenzofuran	(168/139)
2-Chlorophenol	(128/64,130)	Diethyl phthalate	(149/177,150)
Cumene	(105,120)	Dimethyl phthalate	(163/149,164)
Decane	(43)	m-Dinitrobenzene	(168)
1,3-Dichlorobenzene	(146/148,111)	2,4-Dinitrophenol	(184/63,154)
1,4-Dichlorobenzene	(146/148,111)	2,4-Dinitrotoluene	(165/63,89)
1,2-Dichlorobenzene	(146/148,111)	2,6-Dinitrotoluene	(165/63,89)
1,4 Dioxane	(88)	Fluorene	(166/165,167)
Ethyl methanesulfonate	(79/109,97)	Hexachlorocyclopentadiene	(295/237,142)
2-Fluorophenol (SURR.)	(112)	1,4 – Naphthoquinone	(158)
Hexachloroethane	(117/201,199)	1- Naphthylamine	(143/115,116)
Indene	(116)	2- Naphthylamine	(143/115,116)
Methyl methanesulfonate	(80/79,64)	2-Nitroaniline	(65/92,138)
2-Methylphenol	(108/107,79)	3-Nitroaniline	(138/108,92)
4-Methylphenol	(108/107,79)	4-Nitroaniline	(138/108,92)
N-Nitrosodiethylamine	(102)	4-Nitrophenol	(139/109,65)
N-Nitrosodimethylamine	(74/42)	5 Nitro-o-toluidine	(152)
N-Nitroso-di-n-propylamine	(70/101,130)	Pentachlorobenzene	(250/252,248)
N-Nitrosomethyethylamine	(42)	Pentachloronitrobenzene	(237/235,272)
N-Nitrosomorpholine	(56)	Phenacetin	(108/109,179)
N-Nitrosoptrolidine	(41)	Phorate	(75)
O-Toluidine	(106)	Pronamide	(173/175,145)
Petachloroethane	(167)	1,2,4,5-Tetrachlorobenzene	(216/214 218)
Phenol	(94)	2,3,4,6-Tetrachlorphenol	(232/230,131)
Phenol-d5 (SURR.)	(99)	Tetraethyldithiopyrophosphate	(322)
2-Picoline	(93/66,92)	Thioazin	(143)
Pyridine	(79)	2,4,6-Trichlorophenol	(196/198,200)
		2,4,5-Trichlorophenol	(196/198,200)

Table 6 (cont'd) – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
Naphthalene-d8	Ions	Phenanthrene-d10	Ions
A,A-Dimethylphenethylamine	(58)	4-Aminobiphenyl	(169/168,170)
Acetophenone	(105/77,51)	Anthracene	(178/176,179)
Benzoic acid	(184/92,185)	Atrazine	(58)
Bis(2-chloroethoxy)methane	(93/95,123)	4-Bromophenyl phenyl ether	(248/250,141)
Caprolactam	(55)	Carbazole	(167)
4-Chloroaniline	(127)	Diallate	(86)
4-Chloro-methylphenol	(107/144)	Dimethoate	(87)
2,3 Dichloroaniline	(161)	Di-n-Butyl phthalate	(149/150)
2,4-Dichlorophenol	(162/164,98)	4,6-Dinitro-2-methylphenol	(198/51,105)
2,6-Dichlorophenol	(162/164,98)	Dinoseb	(211)
Dimethylnaphthalene	(156)	Diphenylamine	(169/168,167)
2,4-Dimethylphenol	(122/107)	1,2-Diphenylhydrazine	(77/105)
a,a-Dimethyl-phenethylamine	(58/91,42)	Disulfoton	(88)
Hexachlorobutadiene	(225/223,227)	Fluoranthene	(202/101,203)
Hexachloroprene	(213)	2-Fluorobiphenyl (SURR)	(172)
Isophorone	(82/95,138)	Hexachlorobenzene	(284/142,249)
Isosafrole	(127)	Isodrin	(193)
1-Methylnaphthalene	(142)	Methapyriline	(58)
2-Methylnaphthalene	(142/141)	Methyl Parathion	(125)
Naphthalene	(128/129,127)	N-Nitrosodiphenylamine	(169/168,167)
Nitrobenzene	(77/123,65)	4-Nitroquinoline 1-oxide	(190)
Nitrobenzene-d5 (SURR.)	(82)	Octadecane	(57)
N-Nitroso-di-n-butylamine	(84/57/41)	Parathion	(109)
2-Nitrophenol	(139/109,65)	Pentachlorophenol	(266/264,268)
Quinoline	(129)	Phenanthrene	(178/179,176)
N-Nitrosopiperidine	(42/114,55)	Pronamide	(173)
p-Phenylenediamine	(108)	sym- Trinitrobenzene	(213)
O,O,O-Triethylphosphorthioat	(198)	2,4,6 Tribromophenol (SURR)	(330)
Safrole	(162)		
alpha –Terpineol	(128)	Perylene-d12	Ions
1,2,3-Trichlorobenzene	(180/182,145)	Benzo(b)fluoranthene	(252/125)
1,2,4-Trichlorobenzene	(180/182,145)	Benzo(k)fluoranthene	(252/125)
1,3,5-Trichlorobenzene	(180/182,145)	Benzo(g.h.i)perylene	(276/138,277)
		Benzo(a)pyrene	(252/253,125)
Chrysene-d12	Ions	Dibenz(a,j)acridine	(279/280)
2 –Acetylaminofluorene	(181)	Dibenz(a,h)anthracene	(278/139,279)
Aramite	(194)	7,12-Dimethylbenz(a)anthracene	(256/241,257)
Benzidine	(184)	Di-n-Octyl Phthalate	(149)
Benzo(a)anthracene	(228/229/226)	Hexachlorophene	(196)
Bis(2-ethylhexyl)phthalate	(149/167,279)	Indeno(1,2,3-d)pyrene	(276)
Butylbenzyl phthalate	(149/91)	3-Methylchloanthrene	(268/253)
Chlorobenzilate	(251)		
Chrysene	(228/226,229)		
3,3'-Dichlorobenzidine	(252/254,126)		
p-Dimethylaminoazobenzene	(120/225,77)		
3,3 Dimethylbenzidine	(212)		
Famphur	(218)		
Kepone	(272)		
Methyl Chrysene	(242)		

Pyrene	(202/200,203)		
Terphenyl-d14 (SURR.)	(244)		
Table 6a – SIM Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
1,4-Dichlorobenzene-d4	Ions	Fluoranthene-d10	Ions
2-Fluorophenol (Surr)	(112)	Fluoranthene	202, 101, 203
Phenol-d5 (Surr)	(99)	Pyrene	202, 203
Bis-(2-chloro-ethyl)ether	93, 63, 95	Terphenyl-d14 (Surr)	(244)
Nitrobenzene-d5 (Surr)	(82)	Benzo(a)anthracene	228, 229, 226
		Chrysene	228, 226, 229
1-Methylnaphthalene-d10	Ions	Bis(2-ethylhexylphthalate	149, 167, 279
Naphthalene	128, 129, 127		
Hexachlorobutadiene	225, 223, 227	Benzo(a) pyrene-d12	Ions
2-Methyl Naphthalene	142, 141, 115	Di-n-octyl phthalate	149, 150, 43
2-Fluorobiphenyl (Surr)	(172)	Benzo(b)fluoranthene	252, 253
		Benzo(k)fluoranthene	252, 125
Fluorene-d10	Ions	Benzo(a)pyrene	252, 253, 125
Acenaphthylene	152, 151, 153	Indeno(1,2,3-cd)pyrene	276, 277, 138
Acenaphthene	153, 152, 154	Dibenzo(a,h)anthracene	278, 139, 279
Fluorene	166, 165, 167	Benzo(g,h,i)perylene	276, 138, 277
1,2-Diphenylhydrazine	77, 105, 182		
2,4,6-Tribromophenol (Surr)	(330)		
Hexachlorobenzene	284, 286		
Pentachlorophenol	266, 264		
Phenanthrene	178, 179, 176		
Anthracene	178, 176, 179		

Table 7. STANDARD PREPARATION

Table 7A – Intermediate Calibration Standard Solution				
Stock Solution	Stock Conc., µg/ml	Volume Added, µl	Final Vol. In $MeCl_2$, ml	Final Conc. µg/ml
Semivolatile Standard Mix # 1	2,000	500	10	100
Semivolatile Standard Mix # 2	2,000	500	10	100
Semivolatile Standard Mix # 4	2,000	500	10	100
Semivolatile Standard Mix # 5	2,000	500	10	100
Semivolatile Standard Mix # 6	2,000	500	10	100
Semivolatile Standard Mix # 7	2,000	500	10	100
PAH Mixture #2	2,000	500	10	100
Semivolatile Standard Mix # 8	2,000	500	10	100
Additional Requested Compound(s) Mix	2,000	500	10	100
Pyridines Mixture	2,000	500	10	100
1,2,3-Trichlorobenzene	1,000	1,000	10	100
1,3,5-Trichlorobenzene	1,000	1,000	10	100
Butyl Stearate	10,000	200	10	200
Pentachlorophenol	1,000	1,000	10	100
B/N Surrogate Standard Mix	5,000	200	10	100
Acid Surrogate Standard Mix	7,500	134	10	100.5

Table 7B – Intermediate Calibration Standard Solution -SIM				
Stock Solution	Stock Conc., µg/ml	Volume Added, µl	Final Vol. in $MeCl_2$, ml	Final Cone. ng/ml
Semivolatile Standard Mix # 1	2,000	50	10	10
Semivolatile Standard Mix # 2	2,000	50	10	10
Toxic #2	2,000	50	10	10
PAH Mixture #2	2,000	50	10	10
Semivolatile Standard Mix # 8 (Acids)	2,000	250	10	50
1-Methynaphthalene	1,000	100	10	10
B/N Surrogate Standard Mix	5,000	100	10	50
Acid Surrogate Standard Mix (Full Scan)	7500	67	10	50

Table 7C – Initial Calibration Standards Prep Scheme

Standard Solution	Intermediate Conc., µg/ml	Intermediate added, µl Full Scan	Final Volume in $MeCl_2$, ml	Final Conc., µg/ml – Full Scan
STD 1	100	1,000	1	100
STD 2	100	800	1	80
STD 3	100	500	1	50
STD 4	100	250	1	25
STD 5	100/10 (SIM)	100	1	10
STD 6	100	50	1	5
STD 7	100	20	1	2
STD8	100	10	1	1

Table 7D Initial Preparation Standards Prep Scheme - SIM				
Standard Solution	Intermediate Conc., µg/ml	Intermediate added, µl SIM	Final Volume in $MeCl_2$, ml	Final Conc., µg/ml – SIM Scan
STD 1	10/50	500	1	5 BN / 25 Acids
STD 2	10/50	250	1	2.5 BN / 12.5 Ac
STD 3	10/50	100	1	1 BN / 5 Acids
STD 4	1	200	1	0.2 BN / 1 Acids
STD 5	1	100	1	0.1 BN / 0.5 Acids
STD7	0.1	500	1	0.05 BN / 0.25 AC
STD 6	0.1	200	1	0.02 BN / 0.1 AC

Table 7E– ICV -Second Source Calibration Check Standard				
Intermediate	Intermediate Conc., µg/ml	Volume Used, µl (Full/SIM)	Final Volume in Acetone, ml	Final Conc., µg/ml (Full/SIM)
Base Neutrals Mixture	100	500/ 50	1	50/ 5
Acid Mixture	100	500/ 50	1	50/ 5

Table 8a –Selected Ion Monitoring: Masses and Dwell Times		
Compound	Mass Ion (m/z)	Dwell Time (ms)
Acenaphthene	153, 152, 154	50
Acenaphthylene	152, 151, 153	50
Anthracene	178, 176, 179	50
Benzo(a)anthracene	228, 229, 226	50
Benzo(a)pyrene	252, 253, 125	50
Benzo(b)fluoranthene	252, 253	50
Benzo(g,h,i)perylene	276, 138, 277	50
Benzo(k)fluoranthene	252, 125	50
Chrysene	228, 226, 229	50
Dibenzo(a,h)anthracene	278, 139, 279	50
Fluoranthene	202, 101, 203	50
Fluorene	166, 165, 167	50
Indeno(1,2,3-cd)pyrene	276, 277, 138	50
Naphthalene	128, 129, 127	50
Phenanthrene	178, 179, 176	50
Pyrene	202, 203	50
2-Methyl Naphthalene	142, 141, 115	50
Bis-(2-chloro-ethyl)ether	93, 63, 95	50
Pentachlorophenol	266, 264	50
Hexachlorobutadiene	225, 223, 227	50
1,2-Diphenylhydrazine	77, 105, 182	50
Bis(2-ethylhexylphthalate	149, 167, 279	50
Di-n-octyl phthalate	149, 150, 43	50
Hexachlorobenzene	284, 286	50
2-Fluorophenol	112, 64, 63	50
Phenol-d5	99, 42	50
Nitrobenzene-d5	82, 128	50
2-Fluorobiphenyl	172, 171, 170	50
2,4,6-Tribromophenol	330, 332, 334	50
Terphenyl-d14	244, 122	50

Table 9. REPORTING LIMITS

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Benzoic Acid	20	667	Chlorobenzilate	5	167
2-Chlorophenol	5	167	Chrysene	1	33
4-Chloro-3-methylphenol	5	167	bis(2-Chloroethoxy)methane	2	67
2,4-Dichlorophenol	5	167	bis(2-Chloroethyl)ether	2	67
2,4-Dimethlyphenol	5	167	Bis(2-Chloroisopropyl)ether	2	67
2,4-Dinitrophenol	20	667	4-Chlorophenyl phenyl ether	2	67
4,6-Dinitro-o-cresol	20	667	1,2-Dichlorobenzene	2	67
Dinoseb	5	167	1,3-Dichlorobenzene	2	67
2-Methylphenol	2	67	1,4-Dichlorobenzene	2	67
4-Methylphenol	2	67	2,4-Dinitrotoluene	2	67
2-Nitrophenol	5	167	2,6-Dinitrotoluene	2	67
4-Nitrophenol	10	333	3,3'-Dichlorobenzidine	5	167
Pentachlorophenol	10	333	3,3'-Dimethylbenzidine	5	167
Phenol	2	67	7,12-Dimethylbenz(a)anthracene	5	167
2,3,4,6-Tetrachlorophenol	5	167	Diallate	5	167
2,4,5-Trichlorophenol	5	167	Dibenzo(a,h)anthracene	1	33
2,4,6-Trichlorophenol	5	167	Dibenzofuran	2	67
2-Acetylaminofluorene	5	167	Dimethoate	5	167
4-Aminobiphenyl	5	167	Diphenylamine	5	167
Acenaphthene	1	33	Disulfuton	5	167
Acenaphthylene	1	33	m-Dinitrobenzene	5	167
Acetophenone	5	167	p-(Dimethylamine)azobenzene	5	167
Aniline	2	67	Di-n-butyl phthalate	2	67
Anthracene	1	33	Di-n-octyl phthalate	2	67
Aramite	5	167	Diethyl phthalate	2	67
A,A-Dimethylphenethylamine	5	167	Dimethyl phthalate	2	67
Benzo(a)anthracene	1	33	bis(2-Ethylhexyl)phthalate	2	67
Benzo(a)pyrene	1	33	Ethyl methansulfonate	5	167
Benzo(b)fluoranthene	1	33	Famphur	30	1000
Benzo(g,h,i)perylene	1	33	Fluoranthene	1	33
Benzo (k)fluoranthene	1	33	Fluorene	1	33
4-Bromophenyl phenyl ether	2	67	Hexachlorobenzene	2	67
Butyl benzyl phthalate	2	67	Hexachlorobutadiene	1	33
Benzyl Alcohol	2	67	Hexachlorocyclopentadiene	20	667
2-Chloronaphthalene	2	67	Hexachloroethane	5	167
4-Chloroaniline	5	167	Hexachlorophene	50	1700
Carbazole	1	67	Hexachloropropene	5	167

Table 9 (Cont'd)

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Indeno(1,2,3-cd)pyrene	1	33	N-Nitrosomethylethylamine	5	167
Isodrin	5	167	N-Nitrosomorpholine	5	167
Isophorone	2	67	N-Nitrosopiperidine	5	167
Isosafrole	5	167	N-Nitrosopyrrolidine	5	167
Kepone	30	1000	O,O,O Triethylphosphorothioat	5	167
2-Methylnaphthalene	2	667	2-Picoline	5	167
3-Methylcholanthene	5	167	Parathion	5	167
Methapyrilene	5	167	Pentachlorobenzene	5	167
Methyl Methanesulfonate	5	167	Pentachloroethane	5	167
Methyl Parathion	5	167	Pentachloronitrobenzene	5	167
1,4 Naphthoquinone	5	167	Phenacetin	5	167
1-Naphthylamine	5	167	Phenanthrene	1	33
2-Naphthylamine	5	167	Phorate	5	167
2-Nitroaniline	5	167	Pronamide	5	167
3-Nitroaniline	5	167	Pyrene	1	33
4-Nitroaniline	5	167	Pyridine	2	67
5-Nitro-o-toluidine	5	167	p-Phenylenediamine	5	167
Naphthalene	1	33	Safrole	5	167
Nitrobenzene	2	67	1,2,4,5 Tetrachlorobenzene	5	167
n-Nitrosodimethylamine	2	67	1,2,4-Trichlorobenzene	2	67
4-Nitroquinoline-1-Oxide	10	333	Thionazin	5	167
N-Nitroso-di-n-propylamine	2	67	o-Toluidine	5	167
N-Nitrosodi-n-butylamine	5	167	sym-Trinitrobenzene	5	167
N-Nitrosodiethylamine	5	167	Tetraethyl dithiopyrophosphate	5	167
N-Nitrosodiphenylamine	5	167			

Table 10. Selected Ion Monitoring Reporting Limits

Compound	Water	Soil	Compound	Water	Soil
	µg/i	µg/kg		µg/l	µg/kg
Pentachlorophenol	0.3	17	Fluoranthene	0.1	3.3
Acenaphthene	0.1	3.3	Fluorene	0.1	3.3
Acenaphthylene	0.1	3.3	Hexachlorobenzene	0.02	3.3
Anthracene	0.1	3.3	Hexachlorobutadiene	0.1	3.3
Benzo(a)anthracene	0.1	3.3	Indeno(1,2,3-cd)pyrene	0.1	3.3
Benzo(a)pyrene	0.1	3.3	2-Methylnaphthalene	0.1	3.3
Benzo(b)fluoranthene	0.1	3.3	Naphthalene	0.1	3.3
Benzo(g,h,i)perylene	0.1	3.3	Phenanthrene	0.1	3.3
Benzo (k)fluoranthene	0.1	3.3	Pyrene	0.1	3.3
Chrysene	0.1	3.3	bis(2-Chloroethyl)ether	0.2	6.6
Dibenzo(a,h)anthracene	0.1	3.3	Bis (2-ethylhexyl) phthalate	0.2	6.6
1,2-Diphenylhydrazine	0.2	6.6	Di-n-octyl phthalate	0.2	6.6

Lab. Manager:

QA Manager:

Effective Date: 12/15/2010

Title: EXTRACTION OF SEMIVOLATILE ORGANICS FROM SOLIDS BY SONICATION
(Base, Neutral, Acid Organics; Pesticides, Polychlorinated Biphenyls, Diesel Range Organics)

METHOD REFERENCE: SW-846, Method 3550C (Rev 3. Febmary 2007)

Applicable Matrices: Soils, Sediments, Wipes and Sludges

Revised Sections: *1.1.1,*
Added Sections 10.8.6, 10.8.7, 10.8.8, 10.8.9, 12.4

1.0 Scope and Application.

1.1 This method describes the extraction procedure of semi-volatile organic compounds (Base, Neutral, Acid Organics; Pesticides, Polychlorinated Biphenyls) in soil, sludge, wipes and other solid matrices for analysis by gas chromatograph/mass spectrometer (GC/MS), gas chromatography/ electron capture detector (GC/ECD), gas chromatography/ flame ionization detector (GC/FID), or high performance liquid chromatography (HPLC).

1.1.1 This method is used primarily for Method 8270 , Base Neutral and Acid extractables, 8100, and 8310, PAH's. Pesticides, PCB's and other soil extracts are generally prepared using Accelerated Solvent Extraction, EOP040A. The procedures for all methods are included in this SOP Herbickle extraction for soils is described in EGC8151.

2.0 Summary

2.1 A 30-gram aliquot of sample is mixed with anhydrous sodium sulfate. Wipe samples are extracted in their entirety, without weighing. The mixture is extracted with methylene chloride/acetone 3 times using ultrasonic extraction. The extract is decanted and concentrated for analysis using instrumental techniques using SW-846 Methods 8081B, 8082A, 8100, 8270D, 8015B and 8310. Where necessary, solvent exchange from methylene chloride to hexane is performed prior to analysis to accommodate instmment detectors. Alternatively, a 2-gram sample is extracted once with 10ml of with methylene chloride/acetone. The extract is filtered and adjusted to the desired volume for analysis using instrumental techniques using SW-846 Methods 8081B, 8082A, 8100, 8270D 8015B and 8310.

3.0 Reporting Limit and Method Detection Limit

3.1 See determinative method.

4.0 Definitions

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank, Instrument Blank, Storage Blank, and Sulfur Blank.

CLASS A GLASSWARE – Volumetric laboratory glass that has been manufactured, calibrated and certified to established ASTM volume standards. Class A glassware does not require volume calibration or verification.

KUDERNA DANISH – A three-stage glass solvent concentration device consisting of a large volume receiving flask (250 or 500ml), a small volume concentrator tube and a three-ball air cooled condenser. Use this device to evaporate large volumes of solvent used for organic extractions to increase the concentration of the analyte in the solvent.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantifies of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, Internal standards, and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

PERCENT DIFFERENCE (%D) - As used in this SOW and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit bf the parameters of interest.

SEPARATORY FUNNEL – A large volume (500, 1000 or 2000ml) closed funnel used for separating immiscible liquids from each other. The device is used for shaking samples with solvent to extract organic constituents. One of the phases of the mixture is removed through the stopcock opening in the base to effect the separation.

TURBOVAP CONCENTRATOR – An automated device for the concentration of organic solvent extracts concentration. The apparatus is capable of accepting whole volume extracts and automatically evaporating and concentrating solvent extracts to a pre-designated volume using a water bath heated to a specified temperature combined with a nitrogen blow-down system.

ULTRASONIC – High frequency sound waves that increase molecular vibration of molecules absorbed to surfaces of solid materials. The process can readily mobilize adsorbed organics from solids into organic solvents.

WIPE – An inert fabric of known area used to swab the surface of a contaminated area for the purpose of removing the contamination from the surface for chemical analysis.

5.0 Health and Safety

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is available to all personnel involved in these analyses.

5.3 Primary standards of toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of toxic compounds.

6.0 Interferences

6.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. Blanks must be analyzed to demonstrate that these materials are free from interferences under the conditions of the analysis.

6.2 Interferences co-extracted from the samples will vary considerably from source to source. If interferences prevent the analysis of an extracted sample, further cleanup of the sample extract may be employed if necessary. Refer to SW-846 Method 3600 for cleanup procedures.

6.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Avoid plastics in particular because they contain phthalates, used as plasticizers, which can leach from these materials. Practice sound, consistent materials control to avoid phthalate contamination, which may occur at any time. Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This occurs in glassware that is difficult to rinse (e.g., 500-mL K-D flask). Carefully hand-rinse these items to avoid this problem.

7.0 Collection, Preservation and Holding Times

7.1 Collect samples in 250-mL widemouth glass amber bottles.

7.2 Collect wipe samples in 150-mL widemouth glass amber bottles.

7.3 Cool samples to $\leq 6^{\circ}C$ and store at $\leq 6^{\circ}C$ until extraction.

7.4 Thirty (30) grams of solid samples are required for an extraction. Additional sample volume may be necessary for any samples used for matrix duplicates and matrix spikes.

7.5 Extract samples within 14 days of sampling and analyze the extract within 40 days of the extraction.

7.6 Store the base, neutral, & acid sample extracts at –10°C in amber vials (protected from light) sealed with PTFE-lined septa. Store pesticide & PCB extracts at 4°C in the same type vial.

8.0 Apparatus and Materials

8.1 Beakers - 250 ml or 250 ml Erlenmyer flasks.

8.2 Sonicator/sonic disrupter, 300 watt output minimum, with soundproof casing.

8.2.1 The sonicator must be tuned to manufacturer's specifications prior to each use. Document tuning activities in the tuning logbook.

8.2.2 A ¾-horn for the low concentration method procedure and a 1/8-inch tapered microtip attached to a ½-inch horn for the medium/high concentration procedure.

8.3 Drying column – glass funnel containing pre-washed filter paper and sodium sulfate.

8.4 Kuderna-Danish (K-D) Evaporator

8.4.1 500 & 250 ml receiving flasks
8.4.2 three ball Snyder column
8.4.3 10ml graduated concentrator tubes
8.4.4 Class A volumetric vessels: 1ml, 5ml and 10ml

8.5 TurboVap concentrator Apparatus(Zymark or equivalent)

8.6 TurboVap concentrator tubes – 200ml

8.7 1ml volumetric pipettes or pre-calibrated 1ml syringe

8.8 2ml crimp vials

8.9 Glass Wool

8.10 Porous Boiling Chips or Glass beads, solvent extracted

8.11 Evaporating steam baths capable of temperatures from 55 - 90°C.

8.11.1 Record the operating temperature daily with use.

8.12 Nitrogen blow down apparatus with waterbath, capable of maintaining a temperature of 35°C+/-3°C.

8.12.1 Record the operating temperature daily with use.

8.13 Top Loading balance, capable of weighing to 0.01g.

8.14 Cotton fabric cloth wipe 5cm^2, pre washed with hexane.

8.15 Class A volumetric flasks: 1ml, 5ml, 10ml.

8.16 Disposable wood spatulas

9.0 Reagents

9.1 Hexane – reagent grade for pesticide residue analysis.

9.2 Acetone – reagent grade for trace organic analysis.

9.3 Methylene Chloride– reagent grade for trace organic analysis.

9.4 Methylene Chloride/Acetoμe. 1:1 - reagent grade for trace organic analysis – mix equal parts of each solvent.

9.5 Sodium sulfate - granular anhydrous, prepared by baking at 400°C for a minimum of 4 hours.

9.6 Nitrogen Gas – High Purity Grade.

9.7 Whatman 41 filter paper (or equivalent)

9.8 Surrogate and Matrix Spiking Solufions. See SOP for target compound specifications.

Method	Surrogate Cone.	Vol Spike ml	Target CMPD Spike Conc.	Vol Spike ml	SOP
SW 846-8081B	400 ng/ml	1.0	250 ng/ml	1.0	EGC8081B
SW 846-8081B Tox	400 ng/ml	1.0	5 μg/ml	1.0	EGC8081B
SW 846-80818 Chl	400 ng/ml	1.0	4 μg/ml	1.0	EGC8081B
SW 846-8082A	400 ng/ml	1.0	2 ug/ml	1.0	EGC8082A
SW 846-8100	100 ug/ml	1.0	10 ug/ml	1.0	EGC8100
SW 846-8270D BN	100 ug/ml	0.5	100 ug/ml	0.5	EMS8270D
SW 846-8270D Ac	100 ug/ml	0.5	100 ug/ml	0.5	EMS8270D
SW 846-8015B	50 μg/ml	1.0	1000 μg/ml	1.0	EGC8015B
SW 846-8310	10 μg/ml	1.0	10 μg/ml	1.0	EGC8310

9.8.1 Pesticide Surrogate: SW 846-8081B.

9.8.1.1 Prepare surrogate from a 200 ug/ml solution of decachlorobiphenyl / Tetrachloro-m-Xylene obtained from commercial sources.

9.8.1.2 Dilute the commercial stock 1:500 in acetone. The final solution concentrafion is 400 ng/ml.

9.8.2 Pesticide Target Compound: SW 846-8081B.

9.8.2.1 Prepare target compound spike from a 10 ug/ml stock solution of the target organochiorine pesticides obtained from commercial sources.

9.8.2.2 Dilute the commercial slock 1:40 in acetone. The final solution concentration is 250 ng/ml.

9.8.2.3 Prepare a Toxaphene spike if required from a 100 µg/ml stock solution obtained from commercial sources. Dilute the commercial stock 1:20 in acetone. The final solution concentration is 5 µg/ml.

9.8. 2.4 Prepare a Chlordane spike if required from a 100 µg/ml stock solution obtained from commercial sources. Dilute the commercial stock 1:25 in acetone. The final solufion concentration is 4 µg/ml.

9.8.3 PCB Surrogate: SW 846-8082A. See 9.8.1

9.8.4 PCB Target Compound: SW 846-8082A.

9.8.4.1 Prepare target compound spike from a 1000 ug/mi solution of Aroclor 1016 and Aroclor 1260 obtained from cbmmercial sources.

9.8.4.2 Dilute the commercial stock 1:500 in acetone. The final solution concentration is 2.0 ug/ml.

9.8.5 PAH Surrogate: SW-846-8100. See 9.8.7.

9.8.6 PAH Target Compound: SW-846-8100

9.8.6.1 Prepare target compound spike from a 2000 ug/ml solution of PAH target compounds obtained from commercial sources.

9.8.6.2 Dilute the commercial stock 1:200 in acetone. The final solution concentration is 10.0 ug/ml.

9.8.7 BN Surrogate: SW-846-8270D

9.8.7.1 Prepare surrogate from a 5000 ug/ml stock solution of base neutral surrogate compounds obtained from commercial sources.

9.8.7.2 Dilute the commercial stock 1:50 in acetone. The final solution concentration is 100 ug/ml.

9.8.8 BN Target Compound: SW-846-8270D

9.8.8.1 Prepare single target compound spike solutions from five (5) base neutral stock solutions obtained from commercial sources. Dilute the stocks in acetone combining the final solution into a 50 ml volumetric flask as follows:

Solution Name	Stock Cone. ug/ml	Volume Used ml/50ml	Dilution Factor	Final Cone. Ug/ml
Semi-Volatile Mix	1000	5.0	10	100
Base Neutral Mix	1000	5.0	10	100
Benzidines	2000	2.5	20	100
Methylnaphthalenes	2000	2.5	20	100
Cumene	5000	1.0	50	

9.8.9 Ac Surrogate: SW-846-8270D

9.8.9.1 Prepare surrogate from a 10,000 ug/ml solution of acid surrogates obtained from commercial sources.

9.8.9.2 Dilute the commercial stock 1:100 in acetone. The final solution concentration is 100 ug/ml.

9.8.10 Ac Target Compound: SW-846-8270D

9.8.10.1 Prepare target compound spikes from a 1000 ug/ml solution of acid target compounds obtained from commercial sources.

9.8.10.2 Dilute the commercial stock 1:10 in acetone. The final solution concentration is 100 ug/ml.

9.8.11 DRO Surrogate SW-846-8015B

9.8.11.1 Prepare Surrogate from a 1000 µg/ml solution of stock surrogate obtained from commercial sources.

9.8.11.2 Dilute the commercial stock 1:20 in acetone. The final solution concentration is 50 µg/ml

9.8.12 DRO Target Compound SW-846-8015B

9.8.12.1 Prepare target compound spike from a 50000 µg/ml solution of DRO spiking solution obtained from commercial sources.

9.8.12.2 Dilute the commercial stock 1:50 in acetone. The final solution Concentration is 1000 µg/ml

9.8.13 PAH Surrogate SW-846-8310

9.8.13.1 Prepare PAH surrogate from a 1000 ug/ml solution of stock surrogates obtained from commercial sources. Each surrogate is in a separate solufion (p-Terphenyl & o-Terphenyl).

9.8.13.2 Dilute each commercial stock 1:100 in acetone. The final solution concentration is 10 µg/ml

9.8.14 PAH Target Compound SW-846-8310

9.8.14.1 Prepare target compound spike from a 500 µg/ml stock PAH mix and 1000 µg/ml stock solutions of 1 & 2 methylnaphthalene obtained from commercial sources.

9.8.14.2 Dilute the PAH mix 1:50 in acetone, and the 1 & 2 methylnaphthalene 1:100 in acetone. The final solution concentration is 10 µg/ml.

9.9 Unopened stock solutions must be stored according to the manufacturers documented holding time and storage temperature recommendations.

9.10 After opened, stock standards must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicated degradation.

9.11 Copper Powder Mesh: Aldrich powder, 150 mesh or equivalent

9.11.1 Add copper to a 50ml volumetric flask.
9.11.2 Add 5% Nitric Acid , slurry for 15-20 seconds
9.11.3 Rinse 3-4 times with deionized water.
9.11.4 Rinse with Acetone
9.11.5 Dry with Nitrogen
9.11.6 The copper should be pink and shiny.
9.11.7 Store in an amber vial covered with hexane.

10.0 Procedure

10.1 Obtain custody for the samples selected for analysis and group them into a sample batch. A batch consists of 20 samples, a method blank and a spiked blank extracted on the same day. A matrix spike (sample) and a matrix spike duplicate (sample) are prepared for every 20 sample extracted. Generate the method blank and spiked blank in the laboratory using 30 grams of sodium sulfate for each sample.

10.2 Sediment/soil samples - Decant and discard any water layer on the sediment. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. See SOP EQA042 for additional sample homogenization detail.

10.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

10.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

10.5 Wipes – Transfer the entire wipe and any remaining solvent into the extraction vessel. Weighing is unnecessary.

10.6 Percent Dry Weight Determination - Dry weight determination is performed by another department and incorporated into the final result calculation after sample extraction has been performed.

10.7 Low level concentration of organics (<= 20 mg/kg) expected:

10.7.1 Weigh out approximately 30 g of wet weight soil into a tarred 250 ml beaker and record the weight to the nearest 0.1 g. Samples that do not have a free flowing texture (sandy) are mixed with approximately 60-g anhydrous sodium sulfate to form a free flowing mixture. A sample should be weighed in triplicate for the batch matrix spike and matrix spike duplicate.

10.7.2 Weigh out 30 grams of anhydrous sodium sulfate into each of two, clean 150ml beakers to be used as the method blank and spiked blank. An empty beaker is used as a method blank and spiked blank and should be treated as a sample starting with 10.9.

10.7.3 Wipe samples are transferred to the extraction beaker. Weighing and drying is not necessary.

10.7.4 Perform the following steps rapidly to avoid loss of the more volatile compounds.

10.7.5 Add the appropriate surrogate standard solution as per table 9.8 to all samples, spiked samples, QC samples, and blanks.

10.7.6 For the quality control samples in each batch selected for spiking (Spiked blanks, matrix spikes), add the appropriate matrix spiking solution as per Table 9.8.

10.8 High level concentration of organics (> 20 mg/kg) expected:

10.8.1 Weigh out approximately 2 g of wet weight soil into a tarred 150-ml beaker and record the weight to the nearest 0.1-g. Samples that do not have a free flowing texture (sandy) are mixed with approximately 4-g anhydrous sodium sulfate to form a free flowing mixture. Select a sample to be weighed in triplicate for the batch matrix spike and matrix spike duplicate.

10.8.2 Weigh out 2 grams of anhydrous sodium sulfate into each of two, clean 150ml beakers to be used as the method blank and spiked blank. An empty beaker is used as a method blank and spiked blank and should be treated as a sample starting with 10.9.

10.8.3 Wipe samples are transferred to the extraction beaker. Weighing and drying is not necessary.

10.8.4 Add the appropriate surrogate standard solution as per table 9.8 to all samples, spiked samples, QC samples, and blanks.

10.8.5 For the sample in each batch selected for spiking, add the appropriate matrix spiking solution as per table 9.8.

10.8.6 Immediately add sufficient volume of methylene chloride/acetone to bring the volume to 10.0 ml considering the volume added of surrogates and spiking solution.

10.8.7 Sonicate with the 1/8 inch microtip ultrasonic probe for 2 min at an output of 5 and 50% duty cycle.

10.8.8 Filter the sample through 2-3 cm of glass wool in a pasteur pipette. If the sample does not require further concentration collect the entire sample and seal the container, or proceed to perform clean up procedures as appropriate.

10.8.9 If the sample requires further concentration, collect a known amount of extract, i.e. 5 ml and concentrate to a final volume of 0.5 ml using the nitrogen blowdown technique in section 10.15.

10.9 Add 100 ml of methylene chloride/acetone to each beaker under the hood.

10.10 The sonicator must be tuned per manufacturer's insfructions prior to each day's use.

10.11 The extractor horns for the low concentration and high concentration protocols are not interchangeable.

10.11.1 For low level place the tip of a ¾-inch disrupter horn about ½-inch below the solvent surface but above the sample. Sonicate each sample for three minutes at 50% duty cycle and an output of 10. Check with your supervisor on how to make adjustments.

10.11.2 For medium/high level place the tip of a 1/8-inch tapered microtip.about ½-inch below the solvent surface but above the sample. Sonicate each sample for two minutes at 50% duty cycle and an output of 5. Check with your supervisor on how to make adjustments.

10.12 Prepare a drying funnel by adding approximately 30-g of baked sodium sulfate into a funnel. Place a prepared Kudema Danish apparatus under the column to collect the sample extract. Take the sample extract contained in the 250-ml beaker and pour it into the top of the drying funnel through a funnel containing filter paper and sodium sulfate. Make sure all apparatus is labeled accordingly.

10.12.1 The K-D apparatus can be set up with a concentrator tube or a Class A volumetric vessel.

10.13 Add a second 100-ml volume of methylene chloride/acetone to beakers and sonicate a second time. Decant the extract into the same drying column and combine the extracts in the K-D flask. Perform a third extraction in the same manner.

10.14 After the final extract has passed through the sodium sulfate column, rinse down the funnel and inside of the column with an excess of 30-ml of solvent. Add a glass boiling bead to the K-D flask and attach a three-ball Snyder column, prime the Snyder column by adding 1 ml of methylene chloride to the top.

10.15 SW8270D & SW8100: Position the K-D concentrator setup on the hot water bath with only the 10-ml concentrator tube submersed in the water. Evaporate the extract to about 1-ml not allowing it to go to dryness. Remove the K-D apparatus from the bath and allow the solvents

condensed in the Snyder column to drip back down into the concentrator tube. Allow the solvent to cool for approximately 10 minutes, then remove the Snyder column and K-D flask while rinsing the connector joints with 1 ml of methylene chloride. Since the volume is now greater than 1 ml, concentrate by directing a gentle stream of nitrogen gas over the extract surface to under 1-ml.

10.16 ALTERNATE CONCENTRATION PROCEDURE. SW8270D & SW8100: TurboVap Solvent Concentration. Place the sodium sulfate column onto the top of a TurboVap concentrator tube. Take the sample extract contained in the 150-ml beaker and pour it into the top of the drying funnel through a funnel containing filter paper and sodium sulfate following steps 10.12 – 10.15. Position the concentrator tube on TurboVap workstation. Immersing the tube nipple into the waterbath. Set the bath temperature for the solvent system in the concentrator tube. Methylene chloride: 40-45°C, methylene chloride/acetone: 55-60°C. Select volume setpoint for 1ml and initiate the volume reducfion procedure. Proceed to step 10.19.

Note: This procedure is not normally used for soils, but may be employed in case of equipment malfunctions, or overload.

10.17 Solvent Exchange – Kuderna Danish (SW8081B, SW8082A & SW 8310)

10.17.1 If a solvent exchange is required (methods 8081B, 8082A require exchange to hexane, method 8310 requires acetonitrile), momentarily remove the Snyder column, add 50 ml of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath. Concentrate the extract, as described in Sec. 10.15, raising the temperature of the water (85 ± 5°C for hexane) bath to maintain proper distillation.

10.17.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 ml of hexane. If sulfur crystals are a problem, proceed to EOP011 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 10.18 or adjusted to 10.0 ml with the solvent last used. Proceed to step 10.24.

10.18 Solvent Exchange – TurboVap Concentrator (SW8081B,SW8082A & SW8310). If a solvent exchange is required (methods 8081, 8082 require exchange to hexane, Method 8310 requires acetonitrile), pour 50 ml of the exchange solvent into the concentrator tube after the initial concentration to 1ml. Concentrate the extract, as described in Sec. 11.16, raising the temperature of the water bath to 60 ± 5°C for hexane. Take TurboVap concentrator tube out after it reaches 1 ml and add 9 ml of Hexane to adjust to the final volume of 10 ml. Proceed to step 10.23 for SW8082A or step 10.24 for SW8081B.

10.19 Employ steps 10.20 through 10.22 for SW8100 and SW8270D.

10.20 Remove the K-D apparatus from the bath and allow the solvent condensed in the Snyder column to drip back down into the concentrator tube. Allow the solvent to cool for approximately 10 minutes, then remove the Snyder column and K-D flask while rinsing each connector joint with 1 ml of methylene chloride or hexane

10.21 Since the volume is now greater than 1 ml, concentrate using an N-Evap nitrogen concentrator. Immerse the concentrator tube into the water bath of the N-Evap, which is maintained at 35°C. Direct a gentle stream of nitrogen gas over the extract surface and evaporate the solvent until the desired volume is reached. Occasionally rinse the side- wails of the concentrator tubes with methylene chloride during the final evaporation step.

10.22 Final Volume Adjustments.

10.22.1 If a K-D apparatus with a Class A collection vessel was used to concentrate the sample, adjust the volume to 1-ml directiy in the vessel with the solvent last used. Transfer the extract to a 2-ml crimp vial using a Pastuer pipette. Label the vial with sample number and batch number. Protect the extracts from light and store them in the extract freezer at –10°C.

10.22.2 If a K-D apparatus with a concentrator tube (not Class A) was used to concentrate the sample, transfer the extract to a 1ml Class A volumetric vessel or flask with a Pastuer pipette. Adjust the volume to 1ml with the solvent last used. Label a 2-ml crimp vial with the sample number and batch number. Transfer the extract lo the 2- ml crimp vial with a new Pastuer pipette. Label the vial with sample number and batch number. Protect the extracts from light and store them in the extract freezer at –10°C.

10.22.3 If the TurboVap apparatus was used, transfer the extract to a 1ml Class A volumetric vessel or flask with a Pastuer pipette. Adjust the volume to 1ml with the solvent last used. Label a 2-ml crimp vial with the sample number and batch number. Transfer the extract to the 2- ml crimp vial with a new Pastuer pipette. Label the vial with sampie number and batch number. Protect the extracts from light and store them in the extract freezer at –10°C.

10.23 Sulfuric Acid Cleanup (Required for PCB analysis using SW8082A)

10.23.1 Transfer 2-ml of the extract to a Teflon screw cap 4-ml vial, which contains 2-ml of pure sulfuric acid. Shake vigorously for 1 minute using a touch mixer. The Method Blank and Spike Blank must also undergo this cleanup

10.23.2 Proceed to 10.24.

10.24 Copper Clean-Up

10.24.1 Transfer the extract to a 2-ml Teflon lined crimp vial that contains activated copper. Shake vigorously for 2 minutes and allow settling for 5 minutes. The copper cleanup is performed to remove sulfur contamination and can be repeated to further cleanup the extract. A black precipitate indicates that sulfur is present in the sample. The Method Blank and Spike Blank must also undergo this cleanup.

10.25 Store the vials by batch in the refrigerator located in the extraction laboratory. Protect the extracts from light and refrigerate them at 4°C.

11.0 Calculations

11.1 Not applicable.

12.0 QC Requirements

12.1 A method blank and blank spike is required on each day of extraction or every 20 samples, whichever is more frequent.

12.2 A matrix spike/ matrix spike duplicate is required per 20 samples.

12.3 A separate BSP and MS/MSD set are needed if the sample requires PCBs, Toxaphene and/or chlordane. Therefore, if a sample is to be extracted for pesticides and PCBs, 2 sets of MS/MSDs and BSP are needed.

12.4 Refer to Project Specific Bench Notes(GC8081, GC8082, MS8270) for additional program or client specific QC requirements.

13.0 Documentation

13.1 All the information required by the extraction logbooks must be completed.

13.2 All standards preparation must be documented in the standards preparation logbook.

13.3 Equipment maintenance logs must be maintained.

13.4 A record of the daily sonicator tune is recorded in the sonicator tuning log.

14.0 Data Review And Reporting

14.1 The sample prep supervisor reviews all extraction log information for completeness and accuracy prior to the release of sample extracts for analysis,

14.2 The supervisor updates the sample status in the LIMS upon completion of the extraction.

15.0 Pollution Prevention & Waste Management

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal pf all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid waste

Accutest Laboratories
Standard Operating Procedure

Lab Manager: _____

QA Manager: _____

Effective Date: 12/15/2010

TEST NAME: PRESSURIZED FLUID EXTRACTION (ASE)

METHOD REFERENCE: SW 846 3545A, Revision 1, February 2007

Revised Sections: 1.1, 1.2, Table 1, Added Section 10.7

1.0 SCOPE AND APPLICATION

1.1 Method 3545A is used for extracting water insoluble or slightly water soluble semivolatile organic compounds from soils, clays, sediments, sludges, waste solids, and biota. It is applicable to the extraction of base, neutral, and acid semivolatile organic compounds, PAH's organophosphorus pesticides, organochiorine pesticides, chlorinated herbicides, and PCBS. The method uses elevated temperature (100^{0}C) and pressure (1500 psi) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time lhan the Soxhlet procedure. Method 3645A is applicable to solid samples only, and is most effective on dry materials wilh small particle sizes.

1.2 This method is primarily used with methods 8015B, 8081, 8082. Methods 8270, 8100, 8310 and 8151 use sonication (EOP003).

2.0 SUMMARY

2.1 Samples are prepared for extraction either by mixing the sample with pelletized diatomaceous earth. The sample is then ground to a 100 - 200 mesh powder (150 um to 75 um) and loaded into the extraction cell. The extraction cell containing the sample is heated to the extraction temperature, pressurized with the appropriate solvent system, and extracted for a fixed fime period. The solvenl systems employed are based on the appropriate solvents used for lhe analytes of interest and the matrix being extracted.

2.2 The solvent is collected from the heated extraction vessel and allowed to cool. The extract is concentrated, if necessary, and prepared for analysis based on the requirements of the determinative analytical finish being employed.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 See determinative method.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

CLASS A GLASSWARE – Volumetric laboratory glassware that has been manufactured, calibrated and certified to established ASTM volume standards. Class A Glassware does not require volume calibration or verification.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards (or SMCs for VOA), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

PERCENT DIFFERENCE (%D) - As used In this SOW and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this mariner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboraiory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyt chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 Solvents, reagents, glassware, stainless steel extraction cell and other sample processing hardware may yield artifacts and/or Interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

6.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method SW 846 3600 for guidance on cleanup procedures.

6.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced. Soap residue (e.g. sodium dodecyt sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes.

7.0 REAGENTS

7.1 Organic free reagent water prepared to the specifications of SW846 Chapter One.

7.2 Drying Agents

7.2.1 Pelletized diatomaceous earth.

7.2.2 Optional: Sodium sulfate (granular anhydrous)

7.2.3 Drying agents must be pre-cleaned or by Soxhlet extraction using the solvent system employed for samples followed by heating at 400°C for 4 hours in a shallow tray.

7.3 Sand, 10% HCl and deionized water washed, fired and or muffted at 600°C prior to use.

7.4 Solvents.

7.4.1 Organochiorine pesticides Analysis: Pesticide Grade, acetone/hexane (1:1, v/v) or acetone/methylene chloride (1: l,v/v)

7.4.2 Semivolatile organics Analysis: Pesticide Grade, acetone/hexane (1:1, v/v) or acetone/methylene chloride (1: l,v/v)

7.4.3 PCBs Analysis: Pesticide Grade, acetone/hexane (1:1, v/v) or acetone/methylene chloride (1: l,v/v)

7.4.4 Organophosphorus pesticides Analysis: Pesticide Grade methylene chloride, or acetone/methylene chloride (1: 1, v/v)

7.4.5 Chlorinated herbicides Analysis: Pesticide Grade acetone/methylene chloride/phosphoric acid solution (250:125:15, v/v/v), or acetone/methylene chloride/trifluoroacetic acid solution (250:125:1, v/v/v),. (if trifluoroacetic acid solution is used, prepare by mixing 1% trifluoroacetic acid in acetonitrile.) Make fresh solutions before each batch of extractions. Phosphoric acid solution Prepare a 1:1 (v/v) solution of 85% phosphoric acid in organic-free reagent water.

7.4.6 CAUTION: For best results with very wet samples (e.g., ≥30% moisture), reduce or eliminate the quantity of hydrophilic solvent used.

7.5 Nitrogen, high-purily.

7.6 Surrogate Standard Solutions

7.6.1 Pesticide / PCB Surrogates: 400ppm solution in Acetone (Tetrachioro-meta-xylene, Decachlorobiphenyl).

7.6.2 BN Surrogates: 100ppm solution in acetone(2-Fluorobiphenyl, Nitrobenzene-d_5, Terphenyl-d_{14}).

7.6.3 Acid Surrogates: 100ppm solution in acetone (Phenol-d_5, 2-Fluorophenol, 2,4,6 Tribromophenol).

7.6.4 DRO Surrogates: 50 ppm solution in acetone (o-Terphenyl, Tetracosane-d50, 5α Androstane)

7.6.5 PAH Surrogates Method 8100: 100ppm solution in acetone(2-Fluorobiphenyl, Nitrobenzene-d_5, Terphenyl-d_{14}).

7.6.6 PAH Surrogates Method 8310:10 ppm solution in acetone (p-Terphenyl and o-Terphenyl)

7.7 Target Compound Spiking Solutions.

7.7.1 Pesticide Target Compounds: 250ppb solution (Priority pollutants & Target compound list). Toxaphene 5 ppm and Chlordane 4 ppm if required

7.7.2 PCBs target Compounds: 2ppm solution in acetone (Aroclors 1016, 1260)

7.7.3 BN Target Compounds: Full list - 100 ppm in acetone (Priority pollutants & Target compound list).

7.7.4 Acid Target Compounds:, Full list - 100 ppm in acetone (Priority pollutants & Target compound list).

7.7.5 DRO Target Compounds 1000 ppm in acetone (DRO Spiking Solutions)

7.7.6 PAH Target Compounds Method 8100: 10 ppm in acetone (PAH Target Compounds)

7.7.7 PAH Target Compounds Method 8310: 10 ppm in acetone (PAH Target Compounds + 1&2 Methylnaphthalene)

8.0 APPARATUS

8.1 Dionex pressurized fluid extraction device (Accelerated Solvent Extractor) with 11ml, 22ml, and 33ml stainless steel extraction cells to accommodate 10-g, 20-g and 30-g samples respectively.

8.1.1 Extraction cells must be cleaned following each use. Dis-assemble the cell and discard the extracted sample in an environmentally conscious manner. Rinse the cell caps with deionized water. Also rinse the cell body with deionized water while removing any residual solids with a tube brush. Rinse the entire apparatus, first with acetone, then with methylene chloride. Thoroughly dry the device prior to loading the sample.

8.2 Mortar and pestle, capable of reducing dried sample particle size to <1mm.

8.3 Analytical balance - capable to weighing to 0.01 g.

8.4 40-mL and 60-mL, pre-cleaned, extract collection vials (IChem) with open top, screw-cap and PTFE-lined silicone septum.

8.5 Whatman glass fiber filter disk - 1.91 cm, (PN-18219356).

8.6 Dionex PEEK seal cell cap disks (PN-49454,49455).

8.7 Sieves, # 10 mesh and #1 mesh.

8.8 Class A volumetric flasks 1ml and 10 ml

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Sediment/soil samples - Decant and discard any water layer on a sedimeni sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample with pre-extracted diatomaceous earth (DE) according to the following proportions:

Sample Weight	Weight DE
10 gram - Dry	2 grams
10 gram - Wet	3 grams
15 gram - Dry	3 grams
15 gram - Wet	4 grams

9.1.2 Mix until a free-flowing powder is obtained. Do not use the sodium sulfate option with polar solvents. Sodium sulfate will dissolve in pressurized, heated, polar solvents and re-crystallize in the transfer lines of the apparatus.

9.1.3 Spike the sample with the appropriate surrogate solutions, and, if necessary, target compound solutions.

9.1.3.1 Pesticide / PCB Surrogates: 1ml of the 400ppb solution.

9.1.3.2 Pesticide Target Compounds: 1ml of the 250ppb solution. 1ml of 5 ppm Toxaphene or 1ml of 4 ppm Chlordane if required

9.1.3.3 PCBs: 1ml of the 2ppm Aroclor solution

9.1.3.4 BN Surrogates: 0.5ml of the 100ppm surrogate solution.

9.1.3.5 Acid Surrogates: 0.5ml of the 100ppm surrogate solution.

9.1.3.6 BN Target Compounds: 0.5ml of the 100ppm solution.

9.1.3.7 Acid Target Compounds: 0.5ml of the 100ppm solution.

9.1.3.8 DRO Surrogates: 1.0 ml of the 50ug/ml surrogate solution.

9.1.3.9 DRO Target Compounds 1.0 ml of the 1000 ppm solution.

9.1.3.10 PAH Method 8100 Surrogates: 1.0 ml of the 100 ppm solution.

9.1.3.11 PAH Method 8100 Target Compounds: 1.0 ml of the 10 ppm solution.

9.1.3.12 PAH Method 8310 Surrogates: 1.0 ml of the 10 ug/ml solution.

9.1.3.13 PAH Method 8310 Target Compounds: 1.0 ml of the 10 ppm solution.

9.1.4 Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole using a mortar and pestie. The grinding apparatus must be decontaminated between each sample with soap and water, followed by acetone and hexane rinses.

9.2 NOTE: The note in Sec. 9. 1.1 also applies to the grinding process.

9.3 Grind a sufficient weight of the dried sample from Sec. 9.1 to yield the sample weight needed for lhe determinative method (usually 10 - 15 g). Grind the sample until it passes through a 10 mesh sieve.

9.4 Transfer the ground sample 1o an extraction cell of the appropriate size for the aliquot. Use an 11-mL cell for 10g aliquots, a 22-mL cell for 20g aliquots, and a 33-mL cell for 30g aliquots. The weight of a specific sample that a cell will contain depends on the bulk density of the sample and the amount of drying agent that must be added to the sample in order to make it suitable for extraction. Analysts should ensure that the sample aliquot extracted is large enough to provide the necessary sensitivity and choose the extraction cell size accordingly.

9.5 Place a Whatman GF/B, 1.91 cm glass fiber filter in the cell outiets. Fill any extraction cell volume voids with clean sand.

9.6 Place the extraction cell into the instrument or auto-sampler carrousel.

9.7 Place a pre-cleaned 60ml lChem collection vial inlo the colleclion vial carousel for each sample extracted. The collection vessel carousel number corresponds lo the carousel number of the extraction cell. The total volume of the collected extract will depend on lhe extraction procedure employed and may range from 0.5 to 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

9.8 Extraction Parameters. Select the appropriate extraction parameters from Table 1, dependent upon the parameters of interest and enter them into the method screen of the instrument micro-computer. Save the operating parameters under an assigned method

number and employ these operating parameters when sample matrices of this type are extracted for the target parameters of interest.

Table 1.
Accelerated Solids Extraction
Operating Parameters for Selected Analysis

BNAs

Solvent:	Methylene Chloride : Acetone
Temperature:	100^{0}C.
Pressure:	1500 PSI
Siatic Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup	5 Min

PAH's

Solvent:	Methylene Chloride : Acetone
Temperature:	100^{0}C.
Pressure:	1500 PSI
Static Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup:	5 Min

Chlorinated Pesticides

Solvent:	Methylene Chloride : Acetone
Temperature:	100^{0}C.
Pressure:	1500 PSI
Static Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup	5 Min

PCB's

Solvent:	Methylene Chloride : Acetone
Temperature:	100^{0}C.
Pressure:	1500 PSI
Static Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup	5 Min

DRO

Solvent:	Methylene Chloride : Acetone
Temperature:	100^{0}C.
Pressure:	1500 PSI
Static Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup	5 Min

Chlorinated Herbicides

Solvent:	Methylene Chloride : Acetone
Temperature:	t00^{0}C.
Pressure:	1500 PSI
Static Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup	5 Min

Table 1 (cont'd)

PCBs in Fish tissue

Solvent:	Methylene Chloride : Acetone
Temperature:	100^{0}C.
Pressure:	1500 PSI
Static Time:	5 Min
Flush Volume:	60%
Purge Time:	60 seconds
Static Cycles:	1
Oven Heatup	5 Min

9.9 Initiate the extraction cycle by first loading the method and extraction schedule from the load method screen and pushing the enter key. When this step has been completed, push the start key to initiate the extraction sequence.

9.10 Collect each extract in a clean vial (see Sec. 9.6). Allow the extracts to cool after the extractions are complete.

9.11 Residual Water Removal. Prepare a sodium sulfate column in a small glass funnel. Pre-rinse the sodium sulfate with methylene chloride. pass the sample extract through the sodium sulfate, removing the co-extracted water. Collect the extract in an in-line Kuderna-Danish equipped with a jacketed concentrator tube.

9.12 The extract is now ready for concentration, cleanup, or analysis, depending on the extent of interferants and the determinative analytical finish to be employed. Excess water present in extracts may be removed by filtering the extract through a bed of anhydrous sodium sulfate. Refer to EOP 002 for detailed procedures.

9.13 If the phosphoric acid solution is used for the extraction of chlorinated herbicides, then the extractor should be rinsed by pumping acetone through all the lines of the system. The use of other solvents for these analytes may not require this rinse step.

10.0 QUALITY CONTROL

10.1 Reagents. All reagents used In the extraction process are carefully controlled by maintaining accurate records of purchase dates, opening dates, and shelf life. Any reagent that either contains interfering compounds or becomes contaminated with interfering compounds must be immediately discard and replaced with a lot which satisfies the interference free criteria.

10.2 Method Blank. Each extraction batch must contain a method blank that demonstrates that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a solid matrix method blank (e.g., clean sand). Each time samples are extracted, and when there is a change in reagents, a method blank needs to be extracted and analyzed for the compounds of interest. The method blank is processed through the extraction and analytical finish steps.

10.3 If the equipment or reagents contains interferences or target parameters which affect the analysts ability to report reliable data, the analysis must be immediaieiy stopped and the source of contamination identified and eliminaied before continuing with sample extraction.

10.4 A laboratory control spike (LCS) is extracted and analyzed with each batch of samples. LCS accuracy is used to determine if out of control performance on matrix spike/matrix spike duplicate samples is attributed to matrix effects. If the MS/MSD is out of control and the LCS is in control, matrix effects are attributed to the poor MS/MSD accuracy. If the LCS is out of control, then the laboratory is out of control and all sample analysis must be repeated.

10.5 A matrix spike or matrix spike/matrix spike duplicate (MS/MSD) samples must be extracted and analyzed with each batch of samples prepared by this procedure. The accuracy values for each compound are compared to the control limit values. If the results indicate an out of control situation, the performance of each individual compound in the MS/MSD is compared to the individual accuracy in the laboratory control spike. If the laboratory control spike accuracy is within control, the out of control MS/MSD performance is attributed to matrix related issues and the client is given the option of requesting repeat analysis.

10.6 Surrogate standards are added to all samples and quatity control samptes. Surrogate accuracy is monitored to determine if the analysis is in control. If surrogate accuracy falls outside the control limits, and attempts to determine the reasons for the out of control event are unsuccessful, the extraction must be repeated to verify either matrix affects or extraction error.

10.7 Refer to Project Specific Bench Notes(GC8081, GC8082, MS8270) for additional program or client specific QC requirements.

11.0 DOCUMENTATION

11.1 All the information required in the extraction logbooks must completed.

11.2 All standards preparation must be documented in the standards preparation logbook.

11.3 Equipment maintenance logs must be maintained.

12.0 DATA REVIEW & REPORTING

Not appticable.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 REFERENCES

14.1 B. Richter, Ezzell, J., and Felix, D., "Single Laboratory Method Validation Report. Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD"; Document 116064.A, Dionex Corporation, June 16, 1994.

14.2 B Richter, Ezzell, J., and Felix, D., "Single Laboratory Method Validation Report. Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) OPPS, Chlorinated Herbicides and PCBs usirig Accelerated Solvent Extraction (ASE)". Document 101 124, Dionex Corporation, December 2, 1994).

14.3 United States Environmental Protection Agency, "Method 3545A: Pressurized Fluid Extraction", Test Methods for Evaluating Solid Wastes, SW846 Final Update IV: Laboratory Manual, Physical/Chemical Methods, Revision 1, February 2007.

ACCUTEST LABORATORIES
Standard Operating Procedure

Lab Manager

QA Manager

Effective Date: 12/15/2010

TEST NAME DETERMINATION OF ORGANOCHLORINE PESTICIDES USING GC SYSTEM

METHOD REFERENCE SW846 8081B (Revision 2, February 2007)

Revised sections: Table 2, 3.2, Added Section 13.9

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of organochiorine pesticides and screening of polychlorinated biphenyls (PCBs) by gas chromatography with Electron Capture Detectors (ECD).

1.2 The method is applicable to extracts from solid and liquid matrices. The compounds listed in Table 1 are determined by a dual-column analysis system.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Liquid samples are extracted at neutrat pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted using Method 3545A, Pressurized Fluid Extraction or Method 3550C, Sonication. A variety of cteanup steps may be applied to the extract, depending dn the nature of the matrix interferences and the target analytes. Cleanups include Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.2 After cleanup, the extract is analyzed by injecting a 2-pL sample that is split between dual narrow-bore fused silica capillary columns that are mounted in a single gas chromatograph with electron capture detectors (GC/ECD).

2.3 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of compounds on two different column types (primary and confirmation).

2.4 If sensitivity permits, the positive hit should be confirmed by GC/MS method 8270D.

2.5 Once identified the compound is quantitated by external standard techniques with an average calibration factor generated from a calibration curve.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentraiion standard in the calibration curve. RL's may vary depending on matrix and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The different types of blanks are Method Blank, Instrument Blank, Storage Blank, and Sulfur Blank.

FIELD BLANK – an analytical sample prepared from organic-free water and carried through the sampling handling protocol serves as a check for contamination.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass Injected. The calibration factpr is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initiat calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the term's continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. A sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantifies of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second atiquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) – The minimum concentration of a substance that can be measured and reported with **99%** confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at **105**°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below **105** °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an tnterferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a posittve number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evaluation sample containing lab reagent grade water with internal standards and/or surrogate standards added. An insbument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outiined in the Accutest Health and Safety Pian and Personal Protection Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high cpncentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by coritaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to 'The Preparation of Glassware for Extraction of Organic Contaminants" SOP for practices utilized in the extraction departmeni.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary from source to source. Interferences such as sulfur and phthalate are treated with copper and alumina by organics preparation respectively.

6.3.1 The presence of elemental sulfur will result in broad peaks that interfere with detection of eariy-eluting organochiorine pesticides. Method 3660 is suggested for removal of sulfur.

6.3.2 Avoiding contact with any plastic materials and checking all solvents and reagents for phthatate contamination can best minimize interference from phthalate esters.

6.4 Waxes, lipids, and other high molecular weight materials can be removed by method-3640 (Gel Permeation Chromatography-GPC column cleanup).

6.5 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent.

6.6 In the case where an unusually concentrated sample is encountered, it should be followed by the analysis of an instrument blank. An instrument blank is a sample containing hexane with surrogate standards added at 20 ppb. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

7.0 SAMPLE PRESERVATION AND HOLDING TIME

7.1 PRESERVATION

7.1.1 Water Samples

7.1.1.1 Collect samples in 1 liter glass amber bottles without preservatives.

7.1.1.2 A liter of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike dupticates. Therefore, 3 liters of at least one sample in every group of 20 field samples are required for analysis to accommodate all quality control requirements.

7.1.2 Soil Samples

7.1.2.1 Samples are collected in a 300-ml amber glass sample bottle. No preservative is required.

7.1.3 Sample should be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

7.1.4 The samples must be protected from light and refrigerated at $\leq 6\ ^0C$ from the time of receipt until extraction and analysis.

7.2 HOLDING TIME

7.2.1 Aqueous sample must be extracted within 7 days of sampling.

7.2.2 Soil sample must be extracted within 14 days of sampling.

7.2.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS AND MATERIALS

8.1 GAS CHROMATOGRAPH SYSTEM

8.1.1 Gas Chromatograph – Agilent or Hewlett Packard Models 6890 and 5890. The analytical system is completed with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases. The capillary column is directly coupled to the source. The injection port is designed for splitless injection with capillary columns.

8.1.2 Columns

8.1.2.1 Column pair 1

8.1.2.1.1 30 m x 0.32 mm ID, 0.5 µm film thickness fused silica, D8-1701 narrow-bore capillary column or equivalent.

8.1.2.1.2 30 m x 0.32 mm ID, 0.5 pm film thickness fused silica, D8-5 narrow-bore capillary column.

8.1.2.2 Column pair 2

8.1.2.2.1 30 m x 0.32 mm ID, 0.5 pm film thickness fused silica, RTX CLPI narrow-bore capillary column or equivalent.

8.1.2.2.2 30 m x 0.32 mm ID, 0.25 µm film thickness fused silica, RTX CLPII narrow-bore capillary column or equivalent.

8.1.3 Detectors

8.1.3.1 Electron Capture Detectors (HP).

8.1.3.2 Micro Electron Capture Detectors (HP).

8.2 AUTOSAMPLER

8.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

8.3 DATA SYSTEM

8.3.1 MSD iinterfaced to the gas chromatograph which allows the continuous acquisition and storage on machine-readable media (disc) of all chromatographic data obtained throughout the duration of the analysis.

8.3.2 The ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration.

8.3.3 Legato Networker with lookup database on 4mm DAT tape for long term, off line magnetic storage of data.

8.4 SYRINGES

8.4.1 Manually held ul graduated syringes, various volumes (Hamilton or equiv.).

8.4.2 10 µt graduated, auto sampler (Hamilton or equiv.).

8.5 VOLUMETRIC FLASKS, Class A.

9.0 REAGENTS AND STANDARDS

9.1 Refer to Accutest Sample Preparation SOPs EOP001 and EOP040A for reagents and standards used for sample extraction.

9.2 Solvents - Ultra pure, chromatography graded Hexane.

9.3 Stock Standard Solutions

9.3.1 Two separate sources of commercially prepared standards with traceability documeniation are used.

9.3.1.1 Pesticides Mixtures containing one or more of the following compounds: alpha-BHC, beta-BHC, delta-BHC, gamma-BHC(Lindane), Heptachlor, Aldrin, Heptachlor Epoxide, Endosulfan I, Dieldrin, 4,4'-DDE, Endrin, Endosulfan II, 4,4'-

DDD, Endosulfan sulfate, 4,4—DDT, Methoxychlor, Endrin ketone, Endrin Aldehyde, alpha-Chlordane & gamma-chlordane.

9.3.1.2 Individual standards containing Toxaphene, Chlordane and Mirex.

9.4 Working Solutions

9.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3 for details.

9.5 Calibration Standards

9.5.1 Initial Calibration Standards

9.5.1.1 Calibration standards are prepared at a minimum of five concentrations, including surrogates, from the above working solutions. Suggested levels and preparations are shown in Table 4A.

9.5.1.2 Separate calibration standards are required for each multi-component target analyte (i.e., Toxaphene and Chlordane). Unless otherwise necessary for a specific project, such as Ohio VAP or the Dept. of Defense (DoD), a single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is employed. Refer to Table 4B and 4C for preparation scheme. Optional curves as shown on Table 4D and 4E may also be used for a multi-point calibration per project's specification.

9.5.2 Continuing Calibration Verification (CCV)

9.5.2.1 Continuing calibration checks containing all the single-component analytes are prepared at concentrations of **10** µg/l, 25 ug/l and **50** µg/l as described in Table 5. During analysis, these alternate concentrations are run to check the initial calibration.

9.5.2.2 In situations where only Toxaphene or Chlordane is of interest for a specific project and for Ohio VAP multi-level calibration checks of each multi-component analyte of interest may be prepared and analyzed throughout the analytical sequence.

9.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

9.6.1 Prepare the ICV standards from separate sources of stock standards from the calibration curve following the procedures in Table 6A and 6B.

9.6.2 The ICV must be analyzed immediately following the initial calibration.

9.7 Surrogates

9.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DGB) are used as surrogate standards for this method.

9.7.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

9.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of 40 pg/l of each surrogate compound.

9.8 Breakdown Evaluation Solution

9.8.1 The DDT and Endrin breakdown evaluation solution is prepared in hexane as outlined in Table 7.

9.9 Storage of Standards

9.9.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

9.9.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at ≤ 6°C in the dark.

9.9.3 Opened stock standard solutions must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicates a problem.

9.9.4 All other standards must be reptaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

10.0 CALIBRATION

10.1 Initial Calibration

10.1.1 The calibration range covered for all single-component analytes employs at least five of the following standards: 2, 5, 10, 25, 50, and 100* µg/l (*this point may be dropped if it exceeds the linear range of the Instrument). The method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentraiion standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentratidn standard. Calibration is performed for both the primary and secondary columns.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.3 Unless otherwise necessary for a specific project, the analysis of the multi-component analytes (such as: Toxaphene or Chlordane) employs a single-point calibration. This

single calibration standard is included with the initial calibration of the single component analytes for pattern and retention time recognition. For Ohio VAP and Dept. of Defense (DoD) projects an initial 5 point calibration is required for these analytes if there are positive hits.

10.1.4 Aliquot proper amount of each calibration standard into a 2-ml crimp top vial.

10.1.5 Each analyte is quantitatively determined using the external standard technique. The Calibration Factor (CF) is defined in Section 14.1.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each analyte of interest on each column. If any analyte exceeds the 20% RSD acceptance limit for a given calibration other calibration options, such as linear calibration not through the origin may be used or corrective action must be taken.

10.1.6.1 If the problem is associated with a standard, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, narrow the calibration range by replacing the low or the high calibration standard that cover a narrow range.

10.1.6.2.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

10.2 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.2.1 The initial calibration is verified with a second source calibration check standard from an external source (Section 9.6). At a minimum, it must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Section 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the ICV second source check or re-prepare using a fresh ampoule and reanalyze the ICV second source check standard.

10.2.2.2 If the %D criteria cannot be achieved after re-injection of the second source check standard. a new calibration curve must be prepared by making fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification (CCV)

10.3.1 Continuing calibration check standards (Section 9.5.2) musi be acquired at the beginning of each 12 hour shift prior to analyzing samples, after every 10 injections not to exceed 12 hours and at the end of the analysis sequence. Analysts shoutd atternate

the use of the two different concentration mixtures for calibration verification depending on the range of the curve.

10.3.2 For the continuing calibration to be valid, the percent difference (%D) must be less than 20 % for each compound of interest on each column.

10.3.3 Each sample analysis must be bracketed by periodic analyses of acceptable calibration verification standards followed by an instrument blank, run after 10 injections or 12-hours, whichever is more frequent. If %D criteria fails during a mid sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.4 When a calibration verification standard fails to meet the QC criteria all samples injected after the last standard that met the QC criteria must be evaluated to prevent misquantitations and possible false negative results. Re-injection of the sample extracts may be required.

10.3.4.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is <u>above</u> the initial calibration response, i.e. >20%.

10.3.4.2 If the analyte was detected in the specific samples analyzed during the analytical shift, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.5 Each subsequent injection of a continuing calibration standard must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is not in control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.0 RETENTION TIME WINDOWS

11.1 Retention time windows must be calculated for each analyte and surrogate on each GC column and whenever a new chromatographic column is installed, when a new Initial calibration is analyzed or when there are significant changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

11.2 Employ the following approach to establish retention time windows.

11.2.1 Make three injections of all single component standard mixture and multi-response products at approximately equal intervats during the 72-hr period.

11.2.2 Calculate the mean and standard deviation of the three absolute retention times-recording the retention time to three decimal places (e.g. 10.015 min) - for each single component pesticide.

11.2.3 For multi-response pesticides, choose five major peaks and calculate the mean and standard deviation of the three retention times for those peaks. The peak chosen should be fairly immune to losses due to degradation and weathering in the samples.

11.2.4 In those cases where the standard deviations of the retention time window for a particular pesticide is <0.01 minutes, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

11.2.5 The width of the retention time window for each analyte and surrogate is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation is employed, the width of the window will be 0.03 minutes.

11.2.6 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.0 PROCEDURE

12.1 Sample Extraction

12.1.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP001). Solid samples are extracted using Method 3545A, Pressurized Fluid Extraction (Refer to SOP: EOP040A) or Method 3550C, Sonication (Refer to SOP: EOP003).

12.2 Sample Cleanup

12.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to the appropriate SOPs for details.

12.2.1.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC cleanup - pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or florisil) may also be required following the GPC cleanup.

12.2.1.2 Method 3610 (alumina) may be used to remove phthalate esters.

12.2.1.3 Method 3620 (florisil) may be used to separate organochiorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

12.2.1.4 Method 3630 (silica gel) may be used to separate single component organochiorine pesticides from some interferants.

12.2.1.5 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should he removed by the technique described in Method 3660.

12.3 Instrument Conditions

12.3.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification should be approved by team leader/manager.

12.4 DDT and Endrin Breakdown Evaluation

12.4.1 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin aldehyde indicates breakdown.

12.4.2 Before the initial calibration and at the beginning of each 12-hour shift, inject 1 µl of an evaluation standard directly on column. (Refer to Section 9.8).

12.4.3 Calculate the percent breakdown for Endrin and DDT (Section 14.7) and save the breakdown report in the LIMS system.

12.4.4 If degradation of either DDT or Endrin exceeds 15%, injector maintenance should be completed before proceeding with calibration. Refer to EQA036-01 for GC system maintenance utilized in the lab.

12.5 Initial Calibration

12.5.1 See Section 10.1.

12.6 Initial Calibration Verification (ICV)

12.6.1 Refer to Section 10.2.

12.7 Continuing Calibration Verification (CCV)

12.7.1 Refer to Seciion 10.3.

12.8 Sample Analysis (Primary)

12.8.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a 1ul or 2 µl injection size. A splitiess injection technology is used.

12.8.2 Sample concentrations are calculated by comparing sample responses with the initial catibration of the system (Section 14.4). If sample response exceeds the limits of the initial calibration range, dilute the extract and reanalyze. Extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

12.8.3 Sample Injections may continue for as long as the calibration verification standards meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

12.8.4 If chromatographic peaks are masked by the presence of interferences, further sample cleanup is necessary. Refer to Section 12.2 for extract cleanup alternatives.

12.8.4.1 If extract cleanup is required, all QC samples must also be processed through the cleanup method.

12.9 Confirmation Analysis

12.9.1 Confirmation analysis is to confirm the presence of all compounds tentatively identified in the primary analysis.

12.9.1.1 All instrument performance quality control criteria for calibration and retention times must be satisfied on the confirmation analysis.

12.9.2 Each tentative identification must be confirmed using either a second GC column of dissimilar stationary phase or using another technique such as GC/MS.

12.9.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

12.9.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS, normally a concentration of approximately 10 ng/µl in the final extract for each single component compound is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

12.9.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns should be checked.

12.10 Sample Dilution

12.10.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

* Utilize screen data (specific project only).
* Utilize acquired sample data.
* Utilize the history program or approval from client/project.
* Sample characteristics (appearance).

12.10.2 If no lower dilution has been reported, the dilution factor chosen should keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

12.10.3 Preparing Dilutions.

12.10.3.1 Prepare sample dilutions quantitatively. Dilute a stored sample extract, if available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

12.10.3.2 Syringe dilutions. – Refer to Table 8 for dilutions. A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

12.10.3.3 Volumetric Flask Dilutions - Dilutions can also be made with a Class A volumetric flask. Measure the appropriate sample extract volume in a calibrated syringe and bring to final volume with dilution solvent in a Class A volumetric flask. Gently shake to disperse the extract throughout the solvent and transfer to auto-sampler vial for analysis.

12.11 Data interpretation

12.11.1 Qualitative identification

12.11.1.1 Analyst shall identify the targeted compounds with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected compound. The criteria required for a positive identification are:

12.11.1.1.1 The sample component must elute at the absolute retention time window (Refer to Section 11.0) for both primary and confirmation run.

12.11.1.1.2 For the multi-response pesticides, at least five major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. Identification of a multi-component analyte in the sample is based on pattern recognition in conjunction with the elution of these five peaks within the retention time windows of the corresponding peaks of the standard on both GC cotumns.

12.11.1.1.3 Be aware of matrix interfering effects on peak shape and relative peak ratios that could distort the pattern. Interpretation of these phenomena may require a highly experienced chromatographer or at least a second opinion.

12.11.2 Quantitative analysis

12.11.2.1 When a target compound has been identified, concentration (see section 14.4) will be based on the integrated area/or height of fhe peak and calculated by

external standard technique. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined.

12.11.2.2 For multi-response pesticides, usually the areas of 5 peaks are used for quantitation to calculate the calibration factors for those peaks, but fewer may be used depending on the extent of matrix interferences. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the resulting concentrations are averaged to provide the final result for the sample.

12.11.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. Report the lower result.

12.11.2.3.1 A program to perform the RPD calculation had been developed and incorporated into ENVIROQUANT software.

12.11.2.3.2 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are hoted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

12.11.2.3.3 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating "More than 40% RPD for detected concentrations between two GC columns".

13.0 QUALITY CONTROL

13.1 QC Requirements Summary

DDT and Endrin Breakdown Evaluation	Every 12-hour shift
ICV -Second Source Calibration	Following initial calibration
Continuing Calibration Checks	Every 12-hour shift or 10 injections (whichever is more frequent) and at the end of analysis sequence
Method Blank	One per extraction batch* or per day for a running batch
Blank Spike	One per extraction batch* or per day for a mnning batch
Matrix Spike	One per extractioh batch*
Matrix Spike Duplicate	One per extraction batch*
Surrogate	Every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

13.2 DDT and Endrin Breakdown Evaluation

13.2.1 Refer to Seciion 12.4.

13.3 Initial Calibration Verification (ICV) - Second Source Calibration Check

13.3.1 Refer to Section 10.2.

13.4 Continuing Calibration Verification (CCV)

13.4.1 Refer to Section 10.3.

13.5 Method Blank

13.5.1 The method blank is either DI water or sodium sulfate (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a mnning batch, a new method blank is required for each different extraction day. The method blank are then extracted and run through any clean-up procedures along with the other samples in that batch.

13.5.2 If the method blank contains a target analyte above its MDL, the entire batch must be re-extracted and re-analyzed.

13.5.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria, the entire batch must be re-extracted and re-analyzed.

13.6 Blank Spike

13.6.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. A separate blank spike may be needed if the sample requires Chlordane and/or Toxaphene. Il is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

13.6.1.1 For single-component analytes, the blank spike is prepared at 0.25 pg/l or 8.33 µg/kg on a dry weight basis.

13.6.1.2 For Toxaphene only analysis or per project specification, the blank spike is prepared at 5 µg/l or 187 µg/kg on a dry weight basis.

13.6.1.3 For Chlordane only analysis or per project specification, the blank spike is prepared at 4 µg/l or 133 µg/kg on a dry weight basis.

13.6.2 The blank spike recoveries should be assessed using in house limits..

13.6.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high and no hits reported in associated samples and QC batch the sample results can be reported with footnote (remark) and no further action is required.

13.6.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

13.6.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanatyze the sample batch.

13.6.3.3 If no problem is found, re-extract and reanalyze the sample batch.

13.7 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

13.7.1 One sample is randomly selected from each extraction batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results.

13.7.2 A separate matrix spike and matrix spike duplicate set may be needed if the sample requires Chlordane and/or Toxaphene. Matrix spikes are prepared by spiking an actual sample for a concentration of 0.25 µg/l or 8.33 µg/kg on a dry weight basis for pesticides, 5 µg/l or 167 µg/kg for Toxaphene, 4 µg/l or 133 µg/kg for Chlordane.

13.7.3 Assess the matrix spike recoveries and relative percent difference (RPD) against the in house control limits.

13.7.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. Matrix interference is assumed and the data is reportable. No further corrective action is required.

13.8 Surrogates

13.8.1 Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used as surrogate standards. All blanks, samples, QC samples, and calibration standards contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

13.8.2 The recoveries (refer to Seciion 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory.

13.8.3 If surrogate recovery is not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

13.8.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

13.8.3.2 Re-analyze the extract if calculation errors are not detected. If the surrogate recoveries for the re-analyzed extract are in control, report data from the re-analysis only.

13.8.3.3 If data from the reanalysis is also out of control, re-extract and reanalyze the sample.

13.8.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

13.8.3.5 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

13.8.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample should be reanalyzed when the retention time of any surrogate compound is outside the retention window.

13.8.4.1 Reanalysis may not be required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment should be approved by team leader or supervisor.

13.9 Refer to Project Specific Bench Notes (GC8081) for additional program or client specific QC requirements.

14.0 CALCULATION

14.1 Calibration Factor (CF).

$$CF = \frac{A_s}{C_s}$$

where:
A_s = Area of the peak for the compound being measured.
C_s = Concentration of the compound being measured (µg/l).

14.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

14.3 Percent Difference (% D).

$$\% D = \frac{|CF_{av} - CF_c|}{CF_{av}} \times 100$$

where:
CF_c = CF from continuing calibration (CBCHK).

14.4 Concentration (Conc.).

14.4.1 For water:

$$\text{Conc. } (\mu g/l) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{V_i}$$

14.4.2 For soil/sediment (on a dry weight basis, see EGN007):

$$\text{Conc. } (\mu g/kg) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.

14.5 Percent Recovery (% R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

14.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1 + C_2)} \times 100$$

where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

14.7 Percent Breakdown.

$$\text{\% Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where:
Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD

$$\% \text{ Breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area}}{\text{Total Endrin peak area}} \times 100$$

where:
Total Endrin degradation peak area = Endrin aldehyde + Endrin ketone.
Total Endrin peak area = Endrin + Endrin aldehyde + Endrin ketone.

15.0 DOCUMENTATION

15.1 The Analytical Logbook is a record of the analysis sequence; the togbook must be completed daily. Each instrument will have a separate logbook.

15.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

15.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

15.2.1 The Accutest Lot Number must be cross-referenced on the standard vial.

15.3 The Instmment Maintenance Logbook must be completed when any type of maintenance is perfomed on the instrument. Each instrument has a separate log.

15.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

15.5 Unused blocks of any form must be x'ed or z'ed by the analyst before submitting the data for review.

15.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

16.0 DATA REVIEW AND REPORTING

16.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

16.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

16.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

16.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

16.3 Chromatogram Review. The chromatogram of each sample is evaluated for target compounds.

16.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

16.3.1.1 Each sample may require the reporting of different target compounds. Review the login to assure that the correct target compounds are identified.

16.3.2 The compound must be identified on the primary and confirmatory column before assigning a qualitative identification.

16.3.3 Manual integration of chromatographic peaks must be identified by the analysts by initialing and dating the changes made to the report.

16.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposat of all waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.

17.2.2 Hazardous aqueous wastes

17.2.3 Chlorinated organic solvents

17.2.4 Non-chlorinated organic solvents

17.2.5 Hazardous solid wastes

17.2.6 Non-hazardous solid wastes

Table 1. Target Compound List and Reporting Limits			
Compound	CAS Np	Water (pg/l)	Soil (pg/kg)
alpha-BHC	319-84-6	0.02	0.67
beta-BHC	319-85-7	0.02	0.67
delta-BHC	319-86-8	0.02	0.67
Gamma-BHC (Lindane)	58-89-9	0.02	0.67
Heptachlor	76-44-8	0.02	0.67
Aldrin	309-00-2	0.02	0.67
Heptachlor epoxide	1024-57-3	0.02	0.67
Endosu1fan I	959-98-8	0.02	0.67
Dieldrin	60-57-1	0.02	0.67
4,4'-DDE	72-55-9	0.02	0.67
Endrin	72-20-8	0.02	0.67
Endosulfan II	33213-65-9	0.02	0.67
4,4'-DDD	72-54-8	0.02	0.67
Endosulfan sulfate	1031-07-8	0.02	0.67
4,4'-DDT	50-29-3	0.02	0.67
Methoxychlor	72-43-5	0.05	1.70
Endrin ketone	53494-70-5	0.05	1.70
Endrin aldehyde	7421-93-4	0.02	0.67
α-Chlordane	5103-71-9	0.02	0.67
γ-Chlordane	5103-74-2	0.02	0.67
Mirex	2385-85-5	0.02	0.67
Chlordane (technical)	12789-03-6	0.50	17.0
Toxaphene	8001-35-2	0.25	8.50

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/Electrdh Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*40 ml/min
Injection port temperalure	*280°C
Injection 1type	Splitless
Detector temperalure	*320°C
Column flow	2 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*160°C
Time 1	*2 minutes
Column temperature rate 1	*45 degrees/min
Temperature 1	*200°C
Column temperature rate 2	*7 degrees/min
Temperature 2	*260°C
Coiumn temperature rate 3	*50 degrees/min
Final temperature	*305°C
Time 3	*0.8 minutes
Total run time	10-20 minutes

*Parameter modiflcalion allowed for performance optimization as long as QC criteria are achieved.

Table 3. Pesticides and Surrogates Working Sblution	
Stock Solution	Volume Added
Pesticides Mixture (1,000 µg/ml)	0.1 ml
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	0.5ml
Mirex (1000ug/ml) (optional)	0.1ml
Hexane	9.4 ml (or 9.3 ml with Mirex)
Total	10.0 ml

Pesticides Mixture (10 pg/ml) and Surrogates (10 µg/ml) Working Solution: Prepared by measuring 0.1 ml of 1,000 µg/ml of pesticides mixture, 0.5ml of 200 µg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane. Note larger or smaller volumes of standards may be prepared, as needed using the same ratios. ICV is prepared in the same way, but a second source is used.

Table 4A. Pesticides Calibration Standsrd Solutions					
Solution	Working Solution	Concentration (µg/ml)	Volume Added (µl)	Final Volume in Hexane (ml)	Final Concentration(µg/l)
Standard A	Pesticides Mixture	10	500	50	100
	Surrogates	10			100
Standard B	Pesticides Mixture	10	250	50	50
	Surrogates	10			50
Standard C	Pesticides Mixture	10	125	50	25
	Surrogates	10			25
Standard D	Pesticides Mixture	10	50	50	10
	Surrogates	10			10
Standard E	Pesticides Mixture	10	25	50	5
	Surrogates	10			5
Standard F	Pesticides Mixture	10	10	50	2
	Surrogates	10			2

Standard A: Prepared by measuring 500 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard B: Prepared by measuring 250 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard C: Prepared by measuring 125 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard D: Prepared by measuring 50 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard E: Prepared by measuring 25 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard F: Prepared by measuring 10 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Table 4B. Toxaphene Calibration Standard Solution (20ug/ml)	
Stock Solution	Volume Added (µl)
Toxaphene stock (4000 µg/ml)	125
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100
Hexane	24775
Total	25000

Toxaphene (20 µg/ml) and Surrogates (0.80 µg/l) Calibration Solution: Prepared by measuring 125 µl of 4000 µg/ml of Toxaphene stock solution, 100 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4C. Chlordane Calibration Standard Solution (20 µg/ml)	
Stock Solution	Volume Added (µl)
Chlordane stock (2000 µg/ml)	250
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100
Hexane	24650
Total	25000

Chlordane (20 µg/ml) and Surrogates (0.80 µg/ml) Calibration Solution: Prepared by measuring 250 µl of 2000 µg/ml of Chlordane stock solution, 100 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4D. Multi-point Toxaphene Calibration Standards (optional)					
Solution	Stock Solution	Concentration (µg/ml)	Volume Added (µl)	Final Volume in Hexane (ml)	Final Concentration(µg/l)
Standard A	Toxaphene	20	3750	25	3000
	Surrogate Spiking	0.8	3750		120
Standard B	Toxaphene	20	2500	25	2000
	Surrogate Spiking	0.8	2500		80
Standard C	Toxaphene	20	1250	25	1000
	Surrogate Spiking	0.8	1250		40
Standard D	Toxaphene	20	625	25	500
	Surrogate Spiking	0.8	625		20
Standard E	Toxaphene	20	312.5	25	250
	Surrogate Spiking	0.8	312.5		10
Standard F	Toxaphene	20	62.5	25	50
	Surrogate Spiking	0.8	62.5		2

Standard A: Prepared by measuring 3750 µl of 20 µg/ml of Toxaphene stock solution, 3750 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard B: Prepared by measuring 2500 µl of 20 µg/ml of Toxaphene stock solution, 2500 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard C: Prepared by measuring 1000 µl of 20 µg/ml of Toxaphene stock solution, 1000 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard D: Prepared by measuring 625 µl of 20 µg/ml of Toxaµhene stock solution, 625 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard E: Prepared by measuring 312.5 µl of 20 µg/ml of Toxaphene stock solution, 312.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard F: Prepared by measuring 62.5 µl of 20 µg/ml of Toxaµhene stock solution, 32.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4E. Multi-point Chlordane Calibration Standards (optional)					
Solution	Stock Solution	Concentration (µg/ml)	Volume Added (µl)	Final Volume in Hexane (ml)	Final Concentration(µg/l)
Standard A	Chlordane	20	3750	25	3000
	Surrogate Spiking	0.8	3750		120
Standard B	Chlordane	20	2500	25	2000
	Surrogate Spiking	0.8	2500		80
Standard C	Chlordane	20	1250	25	1000
	Surrogate Spiking	0.8	1250		40
Standard D	Chlordane	20	625	25	500
	Surrogate Spiking	0.8	625		20
Standard E	Chlordane	20	312.5	25	250
	Surrogate Spiking	0.8	312.5		10
Standard F	Chlordane	20	62.5	25	50
	Surrogate Spiking	0.8	62.5		2

Standard A: Prepared by measuring 3750 µl of 20 µg/ml of Chlordane slock solution, 3750 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing lo 25 ml with hexane.

Standard 8: Prepared by measuring 2500 µl of 20 µg/ml of Chlordane stock solution, 2500 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard C: Prepared by measuring 1000 pl of 20 µg/ml of Chlordane stock solution, 1000 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard D: Prepared by measuring 625 µl of 20 µg/ml of Chlordane stock solution, 625 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing lo 25 ml with hexane.

Standard E: Prepared by measuring 312.5 µl of 20 µg/ml of Chlordane stock solution, 312.5 µl of 0.8 µg/ml pesticides surrogate sld spiking solution and bringing to 25 ml with hexane.

Standard F: Prepared by measuring 62.5 µl of 20 µg/ml of Chlordane stock solution, 32.5 µi of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 5. Continuing Calibration Check Solutions					
Checks	Working Solution	Concentration (µg/ml)	Volume Added (µl)	Final Volume in Hexane (ml)	Final Concentration(µg/l)
Solution 1	Pesticides Mixture	10	250	50	50
	Surrogates	10			50
Solution 2	Pesticides Mixture	10	50	50	10
	Surrogates	10			10
Solution 3	Pesticides Mixture	10	125	50	25
	Surrogates	10			25

Solution 1: Prepared by measuring 250 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Solution 2: Prepared by measuring 50 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Solution 3: Prepared by measuring 125 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Table 6. DDT and Endrin Breakdown Evaluation Standard	
Stock Solution	Volume Added (µl)
Pesticides Performance Evaluation Mixture (10-250 µg/ml)	50
Hexane	49950
Total	50000

DDT and Endrin Breakdown Evaluation Standard (10-250 µg/l): Prepared by measuring 50 µl of Pesticides Performance Evaluation Mixture (10-250 µg/ml) and diluting to 50 ml with hexane.

Table 7
Sample Dilution Table

All dilutions must be made using a 1ml calibrated syringe.

Dilution	Intact Sample	Solvent
1:2	500ul	500ul
1:5	200ul	800ul
1:10	100ul	900ul
1:20	50ul	950ul
1:25	40ul	960ul
1:50	20ul	980ul

Two Step dilution				
Dilution	Step 1		Step 2	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*
1:100	100ul	900ul	100ul	900ul
1:200	100ul	900ul	50ul	960ul
1:250	100ul	900ul	40ul	960ul
1:500	100ul	900ul	20ul	980ul

Three Step Dilution						
Dilution	Step 1		Step 2		Step 3	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*
1:1000	100ul	900ul	100ul	900ul	100ul	900ul
1:2000	100ul	900ul	100ul	900ul	50ul	950ul
1:2500	100ul	900ul	100ul	900ul	40ul	960ul
1:5000	100ul	900ul	100ul	900ul	20ul	980ul

Four Step Dilution								
Dilution	Step 1		Step 2		Step 3		Step 4	
	Intact Sampte	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*	*Sample Aliquot from Step 3*	*Solvent*
1:10,000	100ul	900ul	100ul	900ul	100ul	900ul	100ul	900ul
1:20,000	100ul	900ul	100ul	900ul	100ul	900ul	50ul	950ul
1:25,000	100ul	900ul	100ul	900ul	100ul	900ul	40ul	960ul
1:50,000	100ul	900ul	100ul	900ul	100ul	900ul	20ul	980ul

ACCUTEST LABORATORIES
Standard Operating Procedures

Lab Manager

QA Manager

Effective Date: 12/15/2010

TEST NAME SW846 8082A: DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

METHOD REFERENCE SW846 8082A (Revision 1, February 2007)

Revised Sections: 3.2, 13.5.2, 13.5.3, *Added* section 13.9

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of polychlorinated biphenyls (PCBs) as Aroctors, using dual open-tubular, capillary columns with electron capture detectors (ECD).

1.2 This gas chromatographic (GC) method applicable to the determination of the PCB Aroclors listed in Table 1 in extracts from solid and aqueous matrices.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Petroleum Products and organic wastes are diluted with an organic solvent and follow SW 846 Method 3580A. Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted with using Method 3545A, Pressurized Fluid Extraction.

2.2 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides.

2.3 After cleanup, the extract is analyzed by injecting a 1 or 2-µL aliquot into a gas chromatograph with dual narrow bore fused silica capillary columns and electron capture detectors (GC/ECD). The chromatographic data may be used to determine the seven Aroclors In Table 1.

2.4 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of PCBs on two different column types (primary and confirmation).

2.5 Once identified, the Aroclor is quantitated by external standard techniques with an average calibration factor generated from a calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. RL's may vary depending on matrix difficulties and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The types of blanks are Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INITIAL CALIBRATION - analysis pf analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards (or SMCs for VOA), that is carried throughoui the entire analytical procedure. The method btank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at **105**°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below **105** °C, including water. Percent moisture may be determined from decanted samptes and from samples that are not decanted.

REAGENT WATER - water in which an Interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two vatues, and is reported as an absotute vatue, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopicalty labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evatuation sample containing solvent and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personat Proteciion Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supen/isor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a poteniial health hazard. Exposure to these reagents must be reduced to the lowest possible tevel. The laboratory is responsible for maintaining a current awareness file of OSHA regutations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheeis must be made available to all personnel involved in these analyses.

5.3 Polychlorinated biphenyls have been classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned. Refer to 'The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

6.3 Interferences may be caused by contaminants that are co-extracted from the sample. The extent of the interferences will vary from source to source, which can be grouped into three broad categories.

6.3.1 Contaminated solvents, reagents, or sample processing hardware.

6.3.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

6.3.3 Compounds extracted from the sample matrix to which the detector will respond.

6.4 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determination.

6.4.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interference from phthalate esters.

6.4.2 Exhaustive cleanup of solvents, reagent and glassware may be required to eliminate background phthalate ester contamination.

6.4.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

6.5 Elemental sulfur is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Method 3660 is suggested for removal of sulfur.

6.6 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of an instrument blank to check for cross contamination.

7.0 SAMPLE PRESERVATION AND HOLDING TIME

7.1 PRESERVATION

7.1.1 Water Samples

7.1.1.1 Collect samples in 1 liter glass amber bottles without preservatives.

7.1.1.2 A liter of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike duplicates. Therefore, 3 liters of at least one sample in every group of 20 field samples are required for analysis to accommodate all quality control requirements.

7.1.2 Soil Samples

7.1.2.1 Samples are collected in a 300-ml amber glass sample bottle. No preservative is required.

7.1.3 Sample should be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

7.1.4 The samples must be protected from light and refrigerated at $\leq$ 6 °C from the time of receipt until extraction and analysis.

7.2 HOLDING TIME

7.2.1 Aqueous sample must be extracted within 1 year of sampling.

7.2.2 Soil sample must be extracted within 1 year of sampling.

7.2.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS AND MATERIALS

8.1 GAS CHROMATOGRAPH SYSTEM

8.1.1 Gas Chromatograph-Agilent or Hewlett Packard Model 5890 and 6890. The analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for splitless injection with capillary columns. The capillary columns are directly coupled to the detectors.

8.1.2 Columns

8.1.2.1 Column pair 1

8.1.2.1.1 30 m x 0.32 mm fused silica (0.5 µm film thickness) DB-1701 narrow-bore capillary column or equivalent.

8.1.2.1.2 30 m x 0.32 mm fused silica (0,5 µm film thickness) DB-5 narrow-bore capillary column or equivalent.

8.1.2.2 Column pair 2

8.1.2.2.1 30 m x 0.32 mm fused silica (0.5 µm film thickness) RTX CLPI narrow-bore capillary column or equivalent.

8.1.2.2.2 30 m x 0.32 mm fused silica (0.25 µm film thickness) RTX CLPII narrow-bore capillary column or equivalent.

8.1.3 Detectors

8.1.3.1 Electron Capture Detectors (HP).

8.1.3.2 Micro Electron Capture Detectors (HP).

8.2 AUTOSAMPLER

8.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

8.3 DATA SYSTEM

8.3.1 MSD interfaced to the gas chromatograph which allows the continuous acquisition and storage on machine readable media (disc) of all chrortiatographic dala obtained throughout the duration of the analysis.

8.3.2 The ENVIROQUANT dala system is capable of quantitation using multi-point calibration.

8.3.3 Lagato Networker wilh lookup database on 4mm DAT tape for long term, off line magnetic storage of data.

8.4 SYRINGE

8.4.1 Manually held ul-syringes, various volumes (Hamilton or equiv.).

8.4.2 10 µl graduated, auto sampler (Hamilton or equiv.).

9.0 REAGENTS AND STANDARDS

9.1 Refer to Accutest Sample Preparation SOPs EOP00t and EOP040A for reagents and standards used for sample extraction.

9.2 Solvents - Ultra pure, chromatography grade Hexane.

9.3 Stock standard solutions.

9.3.1 Two separate sources of commercially prepared standards with traceability documeniation are used. The standards contain Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260.

9.4 Working Solutions

9.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3A, 3B for details.

9.5 Calibration Standards

9.5.1 Initial Calibration Standards

9.5.1.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks in the other five Aroclor mixtures. As a result, a multi-point calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibration for each of the seven Aroclors. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260, including surrogates, by dilution of the above working solutions (Section 9.4) with hexane. Suggested levels and preparations are shown in Table 4A.

9.5.1.2 Separate calibration standards are required for the other five Aroclors. Unless otherwise necessary for a specific project, a single calibration standard near the mid-point of the expected calibration range of each remaining Aroclor is employed to determine its calibration factor and for pattern recognition. Refer to Table 4B for preparation scheme. Optional curves as shown on Table 4C may also be used for a multi-point calibration per project's specification.

9.5.2 Continuing Calibration Verification (CCV)

9.5.2.1 For Aroclor analyses, the continuing calibration checks should be a mixture of Aroclor 1016 and Aroclor 1260. Two standards at 500 µg/l and 1,000 µg/l are prepared as described in Table 5A. During the analysis, these two solutions are alternated to check the initial calibration.

9.5.2.2 In situations where only a few Aroclors are of interest for a specific project, the calibration checks of each Aroclor of interest may be prepared (Table 5B) and analyzed as the 1016/1260 mixture throughout the analytical sequence.

9.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

9.6.1 Prepare the ICV check standards from separate sources of stock standards from the calibration curve followtng the procedures in Table 6A, and 6B.

9.6.2 The ICV is prepared at **1,000** µg/l for each Aroclor and is analyzed immediately after and initial calibration.

9.7 Surrogates

9.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (**DCB**) are used as surrogate standards for this method.

9.7.2 A caltbration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed wtth each calibration solution to define a range similar to the target compounds.

9.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

9.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of **40** µg/l of each surrogate compound.

9.8 Storage of Standards

9.8.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

9.8.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at $\leq$ 6°C in the dark.

9.8.3 Opened stock standard solutions must be replaced after 6 monts or sooner if manufacturer's exptration date comes first or comparison with quality control check samples indicates **a** problem.

9.8.4 All other standards must be replaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

10.0 CALIBRATION

10.1 Initial Calibration

10.1.1 The method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 The initial calibration for this method consists of two parts, described below.

10.1.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detectors and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. The calibration range covered for Aroclor 1016 and Aroclor 1260 employs standards of 50, 250, 500, 1,000, 2,000, and 3,000 µg/t

10.1.2.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used lo determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture In Section 10.1.2.1 has been used to describe the detector response. The concentration of each Aroclor standard is near the mid-point of the linear range of the detector, usually at 1,000 µg/l. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of those 1016/1260 standards.

10.1.2.3 In situations where only a few Aroclors are of interest for a specific project, an initial calibration of a minimum of five standards of each Aroclors of interest instead of the 1016/1260 mixture may be performed.

10.1.3 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.4 Aliquot proper amount of each calibration standard into a 2 ml crimp top vial.

10.1.5 PCBs are quantitatively determined as Aroclors by the external standard technique. The Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards is calculated using the equation in Section 14.1.

10.1.5.1 Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found In both of these Aroclors. At least five sets of calibration factors will be generated, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture.

10.1.5.2 A minimum of 3 characteristic peaks must be chosen for each of the oiher Aroclors, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Thus, each single standard will generate at least three calibration factors, one for each selected peak.

10.1.5.3 Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 6 peaks should include at least one peak that is unique to that Aroclor.

10.1.5.4 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model chosen for this mixture must be applied to the other five Aroclors for which only single

standards are analyzed. If mutti-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate linearity.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each Aroclor of interest on each column. If any analyte exceeds the 20% acceptance limit for a given calibration, corrective action must be taken.

10.1.6.1 If the problem is associated with specific standards, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, narrow the calibration range by replacing one or more of the calibration standards that cover a narrow range.

10.1.6.2.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range. If the instrument response indicates signs of detector saturation, the concentration of the standard at the upper limit will be reduced. The changes to the lower end witl affect the overalt sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

10.2 Initiat Calibration Verification (ICV) - Second Source Calibration Check Standard

10.2.1 The initial calibration is verified with an ICV, a second source calibration check standard from an external source (Section 9.6). It must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Seciion 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the second source check. If the limit cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification (CCV)

10.3.1 Continuing calibration verificatiion (CCV) standards (Section 9.5.2) must be acquired at the beginning of each 12-hour shift, after every 10 injections not to exceed 12 hours and at the end of the analysis sequence. The 500 µg/l check standard is alternated with 1,000 µg/t standard for calibration verification.

10.3.2 For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

10.3.3 The percent difference (%D) (see seciion 14.3) must be less than 20% for each Aroclor of interest on each column.

10.3.4 Each sampte analysis must be bracketed by periodic analyses of acceptable calibration verification standards every 10 injections not to exceed 12 hours. If %D criteria faits during a mid sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.5 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.3.6 When a calibration verification standard fails to meet the QC criteria at the end of the analysis sequence, all samples injected after the last standard that met the QC criteria must be evaluated to prevent mis-quantitations, and re-injection of the sample extracts may be required.

10.3.6.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is <u>above</u> the initial calibration response.

10.3.6.2 If the anatyte was detected in the specific samples analyzed during the analyticat shift or sequence, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.7 Each subsequent injection of a continuing calibration standard during the 12-hour anatytical shift must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall ouiside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.0 RETENTION TIME WINDOWS

11.1 Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows must be calculated for each surrogate and at least 3 to 5 characteristic peaks of each Aroclor on each GC column, when a new initial calibration is run and whenever a new chromatographic column is installed, or when there are significant changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

11.2 Employ the following approach to establish retention time windows:

11.2.1 Make three injections of each Aroclor at approximately equal intervals during the 72-hr period.

11.2.2 For each Aroclor, choose three or five major peaks and calculate the mean and standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in the samples. Record the retention time to three decimal places (e.g. 10.015 min) for each Aroclor.

11.2.3 In those cases where the standard deviations of the retention time window for a particular Aroclor is 0.01 minutes or less, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

11.2.4 Apply plus or minus three times the standard deviations to retention time of each Aroclor standard (continuing calibration or middle level of initial calibration). This will be used to define the retention time window for the sample.

11.2.4.1 If default standard deviation of 0.01 minutes is employed, the width of the window will be 0.03 minutes.

11.2.5 Establish the center of the retention time window for each Aroclor and surrogate by using the absolute retention time for each Aroclor and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

11.2.6 When retention time windows are to be determined, analyze a standard containing DDT analogs to ensure that they do not elute at the same retention time as the last major Aroclor 1254 peak. The analyst must either adjust the GC conditions for better resolution, or choose another peak that is characteristic of the Aroclor and which does not elute at the same time as of the DDT analogs.

12.0 PROCEDURE

12.1 Sample Extraction

12.1.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP00 t). Solid samples are extracted using Method 3545A, Pressurized Fluid Extraction (Refer to SOP: EOP040A).

12.2 Sample Cleanup

12.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to appropriate SOPs for details.

12.2.1.1 Interferences by phthalate esters can be removed through the use of a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for

PCBs. This method should be used whenever elevated baselines or overiy complex chromatograms prevent accurate quantitation of PCBs.

12.2.1.2 Element sulfur, which may be present in certain sediments and industrial wastes, interfere with the electron capture gas chromatography of certain Aroclors. Sulfur should be removed by the technique described in Method 3660.

12.3 Instrument conditions.

12.3.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification should be approved by team leader/manager.

12.4 Initial calibration

12.4.1 Refer to Seciion 10.1.

12.5 Initial calibration Verification (ICV) -Second source calibration check standard

12.5.1 Refer to Section 10.2.

12.6 Continuing calibration Verifications (CCV)

12.6.1 Refer to Section 10.3.

12.7 Sample analysis (Primary)

12.7.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a tul or 2 µl injection size. A splitless injection technology is used.

12.7.2 Sample concentrations are calculated by comparing sample responses with the Initial calibration of the system (Section 14.4). If sample response exceeds the limits of the initial calibration range, dilute the extract and reanalyze. Extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

12.7.3 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the sample meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

12.7.4 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is wanranted.

12.7.5 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix.

12.8 Confirmation analysis.

12.8.1 Confirmation analysis is to confirm the presence of Aroclors tentatively identified in the primary analysis.

12.8.1.1 All instrument performance quality control criteria for calibration and retention time must be satisfied on the confirmation analysis.

12.8.2 Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS.

12.8.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

12.8.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS, normally a concentration of approximately 10 ng/pl in the final extract for each Aroclor is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

12.8.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns should be checked.

12.9 Sample Dilution

12.9.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sampie characteristics (appearance, odor).

12.9.2 If no lower dilution has been reported, the dilution factor chosen should keep the response of the largest peak for a target analyte In the upper half of the initial calibration range of the instrument.

12.9.3 Preparing Dilutions.

12.9.3.1 Prepare sample dilutions quantitatively. Dilute the stored sample extract If available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

12.9.3.2 Syringe Dilutions - A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughoui the solvent prior to loading on the auto-sampler tray for further analysis.

12.9.3.3 Volumetric Flask Dilutions – Dilutions can also be made with a Class A volumetric flask. Measure appropriate sample extract volume in a calibrated syringe and bring to a final volume with dilution solvent in a Class A volumetric flask. Gentiy shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

12.10 Dala interpretation

12.10.1 Qualitative identification

12.10.1.1 Analyst shall identify the target analytes with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected Aroclor. The criteria required for a positive identification are:

12.10.1.1.1 The quantitation of PCB resklues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

12.10.1.1.2 The target analytes must elute within the daily absolute retention time window on both primary and confirmation column.

12.10.1.1.3 For PCBs, at least five major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. This identification of PCBs as Aroclors is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of multi-component target analytes. Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte.

12.10.1.1.4 Be aware of matrix interfering effects on peak shape and relative peak ratios which could distort the pattern. Interpretation of this phenomenon may require a highly experienced chromatographer or at least a second opinion.

12.10.2 Quantitative analysis

12.10.2.1 Once the Aroclor pattern has been identified, compare the responses of at least 3 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each corresponding peak

and the linear calibration established from the multi-point calibration of the 1016/1260 mixture. A concentration (see section 14.4) based on the integrated area/or height of each of the characteristic peaks is determined and then those resulting concentrations are averaged to provide the final result for the sample.

12.10.2.2 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. The quantitation may then be perfomed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

12.10.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. The lower result is reported.

12.10.2.3.1 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instmment data system (or operator) during peak integration.

12.10.2.3.2 if no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating "More than 40% RPD for detected concentraiions between two GC columns".

13.0 QUALITY CONTROL

13.1 QC Requirements Summary

Initial Calibration	Whenever needed
Initiat Catibration Verification (ICV)	Following initial catibration
Continuing Calibration Verifications (CCV)	Every 12-hour shift , after every 10 samples and at the end of analysis sequence
Method blank	One per extraction batch*
Blank Spike	one per extraction batch*
Matrix Spike	one per extraction batch*
Matrix Spike Duplicate	one per extraction batch*
Surrogates	every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

13.2 Initial Calibration.

13.2.1 Refer to Section 10.1.

13.3 Initial Calibration Verif cation (ICV) -Second Source Calibration Check.

13.3.1 Refer to Section 10.2.

13.4 Continuing Calibration Verifications (CCV)

13.4.1 Refer to Section 10.3.

13.5 Method Blank.

13.5.1 The method blank is either Dt water or sodium sulfate (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank should be carried through all stages of the sample preparation and measurement.

13.5.2 If the method blank contains a target analyte above its MDL established by the laboraiory, the entire batch must be re-extracted and reanalyzed.

13.5.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria established by the laboratory, the entire batch must be re-extracted and reanalyzed.

13.6 Blank Spike (Laboratory Control Sample)

13.6.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. It is spiked with the same analyte at the same concentration as matrix spike. When the presence of specific Aroctors is not anticipated, the Aroclor 1016/1260 mixture may be appropriate choice for spiking. In situations where the other Aroclors are of interest for a specific project, the analyst may employ different spiking mixtures. The blank spike is prepared at a concentration of 2 pg/t or 66.7 pg/kg (on a dry weight basis) for each Aroclor.

13.6.2 The blank spike recoveries should be assessed using in house limits established by the laboratory.

13.6.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high and no hits reported in associated samples and QC batch the sampie results cari be reported with footnote (remark) and no further action is required.

13.6.3.1 Check to be sure that there are no errors In the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

13.6.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

13.6.3.3 If no problem is found, re-extract and reanalyze the sample batch.

13.7 Matrix Spike (MS) / Matrix Spike Dupticate (MSD).

13.7.1 One sample is randomly selected from each extraction batch and spiked in duplicate with select Aroclors to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, cleanup, and determinative procedures.

13.7.2 The MS and MSD should be spiked with the Aroclors of interest. If samples are not expected to contain target analytes, a matrix spike and matrix spike duplicate pair should be spiked with Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclor should be used for spiking.

13.7.3 Matrix spikes are prepared by spiking an actual sample at a concentration 2 µg/l or 66.7µg/kg on a dry weight basis.

13.7.4 Assess the matrix spike recoveries and relative percent difference (RPD) against the control limits established by the laboratory.

13.7.5 If the matrix spike accuracy of any individual Aroclor is out of control, the accuracy for that Aroclor in the blank spike must be within control. Matrix interference is assumed and the data is reportable. No further corrective action is required.

13.8 Surrogates.

13.8.1 Tetrachloro-m-xylene (TCMX) and Decachlrobiphenyl (DCB) are used as surrogate standards. All blanks, samples, matrix spikes, and calibration standards contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

13.8.2 The recoveries (Section 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory annually.

13.8.3 If surrogate recoveries are not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

13.8.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

13.8.3.2 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

13.8.3.3 If the data from the reanalysis is also out of control, re-extract and reanalyze the sample.

13.8.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

13.8.3.5 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

13.8.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample must be reanalyzed when the retention times for both surrogates are outside the retention time window.

13.8.4.1 Reanalyses are not required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment should be approved by a team leader or supervisor.

13.9 Refer to Project Specific Bench Notes(GC8082) for additional program or client specific QC requirements.

14.0 CALCULATION

14.1 Calibration Factor (CF).

$$CF = \frac{A_s}{C_s}$$

where:
A_s = Area of the peak for the compound being measured.
C_s = Concentration of the compound being measured (µg/l).

14.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

14.3 Percent Difference (% D).

$$\%D = \frac{|CF_{av} - CF_c|}{CF_{av}} \times 100$$

where:
CF_c = CF from continuing calibration (CBCHK).

14.4 Concentration (Conc.).

For water:

$$\text{Conc. } (\mu g/l) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{V_i}$$

For soil/sediment (on a dry weight basis, see SOP EGN007):

$$\text{Conc. } (\mu g/kg) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.

14.5 Percent Recovery (% R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

14.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1 + C_2)} \times 100$$

where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

15.0 DOCUMENTATION

15.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

15.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

15.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

15.2.1 The Accutest Lot Number must be cross-reference on the standard vial.

15.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

15.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

15.5 Unused blocks of any form must be x'ed and z'ed by the analyst before submitting the data for review.

15.6 Supervisory (or peer) perspnnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

16.0 DATA REVIEW AND REPORTING

16.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

16.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

16.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

16.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

16.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

16.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

16.3.1.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

16.3.2 The Aroclor must be identified on the primary and confirmatory column before assigning a qualitative identification.

16.3.3 Manual integration of chromatographic peaks must be identified by the analysts. An electronic signature is applied upon data review.

16.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of alt waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.

17.2.2 Hazardous aqueous wastes

17.2.3 Chlorinated organic solvents

17.2.4 Non-chlorinated organic solvents

17.2.5 Hazardous solid wastes

17.2.6 Non-hazardous solid wastes

Table 1. PCB Aroclors and Reporting Limits				
Compound	CAS Number	Water (µg/l)	Soil (µg/kg)	Oil (µg/kg)
Arochlor – 1016	12674-11-2	0.5	30	2000
Arochlor – 1221	11104-28-2	0.5	30	2000
Arochlor – 1232	11141-16-5	0.5	30	2000
Arochlor – 1242	53469-21-9	0.5	30	2000
Arochlor – 1248	12672-29-6	0.5	30	2000
Arochlor – 1254	11097-69-1	0.5	30	2000
Arochlor – 1260	11096-82-5	0.5	30	2000

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatdgraph/Electron Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*30 ml/min
Injection port temperature	*235 °C
Injection type	Splitless
Detector temperature	*320 °C
Column flow	*5 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*170 °C
Time 1	*2 min
Column temperature rate 1	*30 degrees/min
Temperature 1	*180 °C
Column temperature rale 2	*3.5 degrees/min
Temperalure 2	*240 °C
Column temperature rale 3	*10 degrees/min
Final temperature	*280 °C
Time 3	*5 min
Total mn fime	30-40 min

* Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 3A. Aroclors 1016/1260 Mixture and Surrogates Working Solution	
Stock Solution	Volume Added
Aroclor 1016/1260 (1,000 µg/ml)	500 µl
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100 µl
Hexane	fill to volume
Total	25.0 ml

- Aroclors 1016/1260 (20 µg/ml) and Sunogates (0.8 µg/ml) Working Solution: Prepared by measuring 500 µl of 1,000 µg/ml Aroclor 101/1260 and 100p of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 3B. Individual Aroclor* and Surrogates Working Solution	
Stock Solution	Volume Added
Individual Aroclor* (1,000 µg/ml)	500 µl
Pesticides Surrogate Sld Spiking Solution (200 µg/ml)	100 µl
Hexane	24.4 ml
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- Individual Aroclor (20 µg/ml) and Surrogates (0.8 µg/ml) Working Solution: Prepared by measuring 500 pl of 1,000 µg/ml each individual Aroclor, 100 pl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4A. Aroclors 1016/1260 Calibration Standard Solutions					
Standard	Working Solution	Concentration (µg/ml)	Volume Added (nl)	Final Volume In Hexane (ml)	Final Concentration(µg/l)
Standard A	Aroclors 1016/1260	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclors 1016/1260	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclors 1016/1260	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclors 1016/1260	20	3,750	25	3,000
	Surrogates	0.8			120

- Standard A: Prepared by measuring 62.5 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing lo 25 ml with hexane.
- Standard B: Prepared by measuring 312.5 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solutipn (Table 3A), and bringing to 25 ml with hexane.
- Standard C: Prepared by measuring 625 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.
- Standard D: Prepared by measuring 1,250 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing lo 25 ml with hexane.
- Standard E: Prepared by measuring 2,500 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing lo 25 ml wilh hexane.
- Standard F: Prepared by measuring 3,750 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml wilh hexane.

Table 4B. Single-Point Calibration Standard (1,000 ug/l) for Individual Aroclor*	
Stock Solution	Volume Added
Individual Aroclor*/Surrogale Working Solution (20 µg/ml/0.80µg/ml) (Table 3B)	1,250 µl
Hexane	23.75 ml
Total	25 ml

* Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Individual Aroclor Calibration Slandard (1,000 µg/l) and Surrogates (40 µg/l) Solution: Prepared by measuring 1,250 µl of individual Aroclor and surrogates working solution, containing 20 µg/ml of each corresponding Aroclor and 0.80 µg/ml of bolh surrogate compounds, and bringing to 25 ml wilh hexane.

Table 4C. Multi-point Calibration Standards for Individual Aroclor* (optional)					
Standard	Stock Solution	Concentration (µg/ml)	Volume Added (µl)	Final Volume in Hexane (ml)	Final Concentration(pg/l)
Standard A	Aroclor*	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclor*	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclor*	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclor*	20	3,750	25	3,000
	Surrogates	0.8			120

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Standard A: Prepared by measuring 62.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.
- Standard B: Prepared by measuring 312.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.
- Standard C: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.
- Standard D: Prepared by measuring 1,250 pl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.
- Standard E: Prepared by measuring 2,500 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.
- Standard F: Prepared by measuring 3,750 pl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

Table 5A. Continuing Calibration Check Solutions for Aroclors 1016/1260					
Checks	Working Solution	Concentration (ng/ml)	Volume Added (nl)	Final Volume in Hexane (ml)	Final Conceritration (ng/l)
Solution 1	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40

- Solution 1: Prepared by measuring 625 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

Table 5B. Continuing Calibration Check Solutions for Individual Aroclor*					
Checks	Working Solution	Concentration (ng/ml)	Volume Added (µl)	Final Volume In Hexane (ml)	Final Cbncentration (ng/l)
Solution 1	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40

* Aroclor: 1221, 1232, 1242, 1248, 12541262, & 1268

- Solution 1: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

Table 6A. Second Source Calibration Check Standard for Aroclors 1016/1260 (1,000 µg/l)	
Stock Solution	Volume Added
Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution	1,000 µl
Hexane	24 ml
Total	25 ml

- Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution: Prepared by measuring 250 µl of 1,000 µg/ml Aroclors 1016/1260 mix solution (2nd source), 125 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane.

- Aroclors 1016/1260 (1,000 µg/l) and Surrogates (100 µg/l) Solution: Prepared by measuring 1,000 µl of Aroclors 1016/1260 (25 µg/ml) and surrogates (2.5 µg/ml) working solution and bringing to 25 ml with hexane.

Table 6B. Second Source Calibration Check Standard for Individual Aroclor* (1,000 µg/l)	
Stock Solution	Volume Added
Individual Aroclor* (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution	1,000 µl
Hexane	24 ml
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- Individual Aroclor (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution: Prepared by measuring 250 µl of 1,000 µg/ml each individual Aroclor stock solution (2nd source), 125 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane.

- Individual Aroclor (1,000 µg/l) and Surrogates (100 µg/l) Solution: Prepared by measuring 1,000 µl of each individual Aroclor (25 µg/ml) and surrogates (2.5 µg/ml) working solution and bringing to 25 ml with hexane.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Nancy Cole

QA Manager:

Effective Date: 5/12/11

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES

REFERENCE: EPA 245.1, revision 3.0 (1994) and SW846 7470A (modified)

Revised Sections: 8.1, 11.1(all), 11.4, 11.5, 11.7, 11.10, 16.1 Added Section 12, renumbered remaining sections

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury for alt potable and non-potable water samples. This SOP is based on the May 1994 revision of EPA method 245.1. The reporting limit for mercury water samples based on the procedures outlined in this SOP, is 0.0002 mg/l.

1.2 Aqueous wastewater may also be analyzed following method 7470A. The modification to this method are a direct scale-down of the reagents and the use of an automated analyzer.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a ceil positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound thai meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samptes in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. The calibration check standard must be run at a frequency of 10 percent or less.
The mid-level calibration check standard criteria is either ± 5 or ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is ouiside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.
SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.
MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sampie should be assessed. The duplicate RPD is calculated as shown beiow. Assess laboratory performance against the controi limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate timits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amouni of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in

the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amouni is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to documeni the precision and bias of a method in a given sample matrix.

$$\frac{\text{(MS Result - MSD Resulil) x t00}}{\text{(MS Result + MSD Result)/2}} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.
METHOD DETECTION LIMITS (MDLS). The minimum concentraiion of a substance that can be measured and reported with 99% confidence that the analyte concentraiion is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentraiion of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.
REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes In solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively dituting a standard solution to produce working standards which cover the working range of the instrument. Standards shoutd be prepared at the frequency specified in the appropriate section. The catibration standards should be prepared using the same type of acid or solvent and at the same concentration as wilt result in the samples following sample preparation. This is applicabte to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must foltow normat safety procedures as outtined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contaci any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in Ihis method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsibte for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhatation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All water samples must be preserved by acidification with nitric acid to a pH of 2 or lower and stored in a polyethylene or glass container.

6.2 All samples must be analyzed within 28 days of the date of collection.

7.0 INTERFERENCES

7.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide as sodium sulfide as high as 20 mg/l do not interfere with mercury recoveries when following this method. High copper concentrations (> 10 mg/l) may also interfere with mercury recoveries.

7.2 Samples that are high in chloride such as seawater, brine, and industrial effluent may require as much as 25 ml of additional permanganate. NOTE: When chloride concentrations are high, hydroxylamine sulfate and stannous sulfate should be used in place of the corresponding chlorides.

7.3 Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

8.0 APPARATUS

8.1 Two Leeman instrumenis are available for analysis. One is a Leeman Hydra II AA automated analyzer and the other is a Leeman Hydra AA automated analyzer. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance Is outlined below.

8.1.1 Change the sample tubing as needed.

8.1.2 Change the drying tubing as needed.

8.1.3 Clean the exterior of the instrument as needed.

8.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

8.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

8.2 Heating Equipment.

8.2.1 Graphite heating block. Capable of heating at 95 °C for 2 hours.

8.3 Digestion Bottles. Disposable plastic digestion tubes are used with the graphite heating block.

8.3.1 Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

8.4 Calibrated glass tubes with verified 60.0 mi and 100.0 ml final volume calibration mark for bringing graphite heating block digestates to their final volume. (The 100 mi calibration is only required for soil digestions).

8.4.1 At a minimum of once per year, the calibration of these bottles must be verified and documented in the Hg Bottle calibration log following the procedure outlined below.

8.4.2 Carefully measure 60.0 ml of room temperature (20 to 25 deg. C) deionized water with a class A to deliver volumetric cylinder and pour into the calibrated Hg bottle.

8.4.3 If the bottom of the meniscus is on the calibration line, then the bottle passes calibration and can be used.

8.4.4 If the bottom of the meniscus is not on the line, then the bottle should be removed from service and replaced with a newly calibrated bottle. New bottles are calibrated following the same procedure as above, except that a line must be etched into the bottle at the bottom of the meniscus of the 60 ml of DI water.

8.4.4.1 Two different lines for the same volume (i.e. 60 ml) cannot be etched on the same bottle as that may lead to confusion in the measurement of the final volume.

8.4.5 Repeat the steps in 8.4.2 through 8.4.4 using a 100 ml final volume instead of the 60 ml final volume.

8.5 Class A, to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

8.6 Automatic pipettor bottles. Refer to EQA063 for calibration information.

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed.

9.1 Sulfuric acid, concentrated.

9.2 Nitric acid, concentrated. This acid must have a low mercury content.

9.3 Dilution acid. To approximately 400 ml of DI water, add 33.4 ml of concentrated sulfuric and 16.6 ml of concentrated nitric. Dilute to a final volume of 1000 ml. This dilution acid is used for making ditutions of digested samples.

9.4 Stannous chloride. Add 7.5 mi of concentrated sulfuric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix weil. Add 50 g of stannous chloride and dissolve. Make sure that this solution is dissolved whiie in use.

9.4.1 Stannous sulfate may be used in place of stannous chloride.

9.5 Sodium chloride-Hydroxylamine hydrochloride. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

9.6 Potassium Permanganate, 5 percent solution, w/v. Add 50 g of potassium permanganate to 1000 ml of water and mix well. Caution - Potassium permanganate is a strong oxidizing agent. Handle with care.

9.7 Potassium Persulfate, 5 percent solutipn, w/v. Dissolve 50.0 g of potassium

persulfate in 1000 ml of water and mix well. Caution - Potassium persulfate is a strong oxidizing agent. Handle with care.

9.8 Mercury standard solutions.

9.8.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipet or autopipel, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 mi of water and 2.0 mi of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

9.8.1.1 The 10 ppm external source should be made up following the directions in 9.8.1.

9.8.2 40.0 ppb Hg solution. Using an autopipel, add 0.400 ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 mi of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.8.2.1 The 40.0 ppb external source should be made up following the directions in 9.8.2.

9.8.3 4 ppb Hg solution. Using volumetric pipets or autopipets, add 10.0 ml of 40.0 ppb Hg solution to a 100 ml volumetric flask conlaining approximately 75 mi of Di water and 2.0 mi of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

10.0 WATER DIGESTION FOR GRAPHITE HEATING BLOCK

Below is a slep-by-step procedure for the digestion and analysis of water samples for mercury.

10.1 If necessary, acid rinse disposable digestion tubes with 10% nitric acid and deionized water before use.

10.2 Make up a standard curve consisting of 5 standards and a blank. Suggested concentraiions are shown below. Aii standards are made up to a final volume of 40 mi. Different concentraiions may also be used, as long as all of the method requirements are met. Make sure to clearly label each bottle. Calibration standards must be prepared fresh with each digestion batch.

ml of 4 ppb Hg solution	ml of 40 ppb Hg solution	Ml of DI water	Total ug of Hg	ug/L of Hg
0.000	0.000	40	0.000	0.000
2.00	0.000	38.0	0.008	0.20
5.00	0.000	35.0	0.020	0.50
0.00	1.00	39.0	0.040	1.00
0.00	2.50	37.5	0.100	2.50
0.00	5.00	35.0	0.200	5.00

10.3 Samples. For each sample, homogenize the sample well and measure out a representative 40.0 ml aliquot of the sample into the digestion tube using a class A, to deliver, graduated cylinder. A smaller volume may be used if there are matrix problems or high levels of mercury in the sample.

10.4 Make up additional quality control samples as shown below, using a final volume of 40 ml for each check standard. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the methods) Make sure to clearly label each bottle. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve. The CCV must be made from the same source as the calibration curve. A low check standard at the level of the CRDL (0.20 ug/l) is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	ml of 40 ppb Hg solution	ml of DI water	Total ug of Hg
CCV Check(s)	2.5	37.5	0.25
MB	0.0	40	0.0
MS	2.0	(a)	0.20 (b)
MSD	2.0	(a)	0.20 (b)
ICV	3.0	37.0	0.30
LCS	2.0	38.0	0.20

a (a) 40 ml of sample
(b) plus the level of Hg in the sample.

10.5 To all samples, QC, and standards add the reagents listed below, swirling the samples well after each addition of reagent. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

- 2.0 ml of conc. sulfuric acid.
- 1.0 ml of cone. nitric acid.
- 6.0 ml of 5% permanganate solution.

Wait 15 minutes, then

- 3.2 ml of potassium persulfate solution.

10.5.1 All of the additions shown can be done with a bottle pipettor which must be accurate to within a range of 90 to 110%.

10.6 Cap the samples and place them in the graphite heating block and heat for 2 hours at 95 °C. Record the digestion times and temperature.

10.7 Enter the prep data into the LIMS system, double checking all volumes and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculations.

11.0 COLD VAPOR ANALYSIS PROCEDURE HYDRA AA

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators' manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying tine and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 In the software, go to the Runner section and select the control tab. Click on the Hg lamp and the pump. The gas will turn on automatically when the pump is turned off. If can also be turned on separately if necessary. The pump rates and gas pressure are set in the protocol. Refer to the Instrument maintenance manual for more information on setting up a new protocol. If the Hg lamp needs to be optimized, it can be done using the tab adjust on this page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the tines. Do not overtighten.

11.1.4.1 In the software, go to the Utility tab and pick the gas control test option. The output should be approximately 7 psi and the input should be between 60 to 90 psi. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.5 Start a batch to save your data.

11.1.5.1 Go to the sample runner tab and click on start new batch. The batch name is limited to 8 characters. The batch should normally be named H1 or H2 followed by the month and date, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument 2 for 3/24/03 would be named H20324w1. The reattime print option can also be turned on from this tab.

11.1.6 Set up autosampler racks containing the samples that are going to be run.

11.1.6.1 Go to main tab and click on the rack editor button. Enter your samples and the appropriate QC. CCV and CCB checks can be entered in the macro column. This tab may also be reached by

clicking on the autosampler icon at the top of the page.

11.1.7 Set up the calibration.

11.1.7.1 Enter or verify the standard values. From the runner menu click on the standard tab. Click the buttons to the left of the standards that are to be run. Also click on the number of replicates to be run for each standard. Normally one replicate is run per standard. The standard concentrations are defined under the database menu under the line Info tab. The check standard concentrations and acceptance ranges are also defined under this line info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Add hydroxylamine hydrochloride to all samples and standards as outlined below.

11.2.1 Add 2.4 ml of hydroxylamine hydrochloride solution to each standard and sample and swirl until the solution has been completely decolorized. Transfer to a calibrated glass cylinder and dilute to a final volume of 60 ml and swirl to mix.

11.2.2 They hydroxylamine hydrochloride can be added using a bottle pipettor which is accurate in a range of 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check ali transfers. Let ali samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

11.4.1 Turn on the real time report by checking the real time printing option on the runner menu either under main or under sample. Then go to the runner menu and the standard tab. Push the standard auto button. The calibration curve will be run by the autosampler. When the curve is complete, go to the database menu and click the calibration curve tab. Check to make sure that all acceptance criteria are met and then accept the curve. See section 13.3 for calibration curve criteria. Make sure that the curve is prinied as soon as it is accepted.

11.5 After the calibration has been accepted, start to run the samples.

11.5.1 Go to the runner menu and the sample tab. Pick the autosampler rack that is to be run and type in the start cup and the end cup. Then push the button for run auto.

11.6 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see Seciion 9.3) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.7 Both paper and electronic reports can be generated using the reporl option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

11.7.1 Go lo the data base menu and pick the report tab. Make sure that the correct report specification has been chosen (normally Accutest). Pick the batch that is to be printed and then push the generate report button. Generate both the electronic reports (prn file) and prinied reports (report) from this menu.

11.8 The calculations are done in the LIMS as described below. A final volume of 40.0 mi is used for calculation purposes for graphite heating block digestions. (The volume of 60.0 ml is factored out since all standards and samples are brought up lo the same final volume and standard concentrations are calculated based on 40.0 ml.)

Final sample concentration in mg/L =

$$\frac{\text{concentration in the digestate in ug/l x final volume in ml}}{\text{Initial volume in ml}}$$

11.9 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.10 Shut down the instruments.

11.10.1 To shut down the Hydra AA instrument, move the stannous chloride line from the stannous chloride bottle to the rinse container. Let the system rinse with 10% nitric for several minutes. Then switch the bath to DI water and let rinse for several more minutes. Then empty the rinse bath and let the pump and gas run until the lines are completely dry. Go to Taskmaster and select the standby mode option. Release the tension on aii of the pump clamps.

12.0 COLD VAPOR ANALYSIS PROCEDURE HYDRA AA II

12.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional Instructions are available in the instrument operators' manual.

12.1.1 Turn on the nitrogen and adjust lo 60 to 90 psi. Turn on the instrument power if it is not already on.

12.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure thai il is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler iine and the stannous chloride line in the rinse container.

12.1.3 Turn on the analyzer and allow it to warm up.

12.1.3.1 For the Hydra AA II, open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump Individually on the Instrument Control Page.

12.1.4 Tighten the pump clamps until the fiow is coming evenly through the lines. Do not overtighten.

12.1.4.1 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

12.1.5 Start a batch to save your data.

12.1.5.1 Create a new chapter (Data File) by clicking Anatysis. The batch should normally be named H5 followed by the month date and year, fotlowed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

12.1.6 Set up autosampler racks containing the samples that are going to be run.

12.1.6.1 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro coiumn of the sequence page.

12.1.7 Set up the calibration.

12.1.7.1 Go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Aiso select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always ctick apply when any changes are made in a tab.

12.2 Add hydroxytamine hydrochloride to ail samples and standards as outlined beiow.

12.2.1 Add 2.4 ml of hydroxylamine hydrochloride solution to each standard and sampie and swirl until the solution has been completely decolorized. Transfer to a catibrated glass cylinder and dilute to a final volume of 60 mi and swirl to mix.

12.2.2 They hydroxylamine hydrochloride can be added using a bottle pipettor which is accurate in a range of 90 to 110%.

12.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

12.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Documeni icon, then choose HG5-PDF. Rename the file as MA*****_cal.

12.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (ie. ICV) and click start from here.

12.6 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see Section 9.3) and reanalyzed. it is recommended that any sampte analyzed after a sampie with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

12.7 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports shoutd be transferred into the LIMS system where the final catculations are done.

12.7.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click GK. Glick on chapter in order to select all samples. Then click report output and then csv.fiie. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

12.8 The calculations are done In the LIMS as described below. A final volume of 40.0 mi is used for calculation purposes for graphite heating block digestions. (The volume of 60.0 ml is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calcutated based on 40.0 ml.)

Final sample concentraiion in mg/L =

$$\frac{\text{concentration in the digestate in ug/t x final volume in ml}}{\text{Initial volume in ml}}$$

12.9 Review the data in the LIMS, adding comments and accepting resuits as appropriate.

12.10 Shut down the instruments.

12.10.2 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the

system rinse with 10% HNO3 for several minutes. Then switch the iine to DI water bottie and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

13.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

13.1 Instrument Detection Limits (IDLs). The instrument detection limits must be done a minimum of once per year or when instrument conditions change significantly. The IDL is generated by running 10 replicates of a digested blank. The IDL is then defined as 3 times the standard deviation of the 10 replicates of the blank.

13.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate atiquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's I value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

13.3 instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards should be prepared fresh with each preparation batch. A minimum of a blank and 5 standards are required. The correlation coefficieni of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met. Resioping is acceptable as long as it is immediately preceded and immediately followed by a complaint CCV and CCB.

13.4 Linear Dynamic Range (LDR). For each instrument, the upper limit of the linear dynamic range must be established. A linear calibration should be prepared from 3 standards, pne of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10 percent below the true value of the standard. Sample concentrations that are greater than 90% of the determined upper LDR limit must be analyzed using dilutions. The LDR should be verified annually or whenever there is a significant change in the instruments analytical performance.

13.5 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV)). At a minimum of once per quarter, a standard from a different source than the calibration standard must be analyzed. Normally this is analyzed at the beginning of the run <u>after</u> the CCV and CCB checks. The ICV must be within 10 percent of the true value. It is recommended that this standard be analyzed with each run so that it is included with ali client reports. For SW846 7470A, this standard should be at a concentration near the

midpoint of the calibration curve. If the ICV is outside of the acceptance limits, then the problem must be corrected and the ICV reanalyzed and shown to be within QC limits before any samples can be reported. All reported samples must be bracketed by an ICV which meets acceptance criteria.

13.5.1 If the ICV is biased high and all sample results are < RL, then, at the discretion of the data reviewer, data may be reported.

13.6 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

13.7 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample (spike blank) with each set of samples. A minimum of one lab control sample is required for every 20 samples. For a running batch, a new lab control sample is required for each different digestion day. For method 245.1, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 85 to 115 percent. For method 7470A, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. In either case, if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. If the lab control recovery is low or there are samples above the reporting limit, then all affected samples must be redigested and reanalyzed.

13.8 Matrix Spike.

13.8.1 For method 245.1, the laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be within the limits of 70 to 130. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

13.8.2 For method 7470A, the laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The laboratory should assess the matrix spike recovery against limits of 75 to 125. (In house control limits are also generated on an annual basis and are used to support the default limits.) An exception to this rule occurs where the sample concentration exceeds the spike concentration by a factor of 4 or more. If the matrix spike fails this criterion, then the sample should be flagged as showing possible matrix interferences.

13.8.3 Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated

as zero. Refer to the calculation shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

13.9 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the sample should be assessed. The calculations for both rpds are shown below.

13.9.1 For method 245.1, the control limits for the matrix spike duplicates or the duplicates are calculated on an annual basis and are used to assess whether a matrix spike duplicate or a duplicate is in control. If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

13.9.2 For method 7470A, the duplicate or matrix spike duplicate RPD must be assessed against a limit of 20% RPD. (In house control limits are also generated on an annual basis and are used to support the default limits.) If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

13.9.3 Both the duplicate amouni and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculations shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \text{\% RPD}$$

or

$$\frac{\text{(|MS Result - MSD Result|)} \times 100}{\text{(MS Result + MSD Result)/2}} = \text{MSD RPD}$$

13.10 Continuing Calibration Verification. (Aiso known as the instrument performance check solution.) The CCV must be from the same source as the calibration curve.

13.10.1 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sampie and at the end of the sampie run. If the CCV solution is not within a method specified range of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentraiion

should be at or near the mid-range of the calibration curve.

13.10.1.1 For method 245.1, the CCV must be within 10 percent of the true value.

13.10.1.2 For method 7470A, the CCV must be within 20 percent of the true value.

32.10.2 The iCCV check must aiso be analyzed at the beginning of the run, immediately after the instrument is catibrated. For method 245.1, this first check must be within 5 percent of the true value. If it is not and there is not a problem with the standard solution, the instrument should be recalibrated and rechecked.

13.10.2.1 This check is not required for method SW846 7470A.

13.11 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting timit, then no samples can be reported in the area bracketed by the failing CCB.

13.12 CRA (Low) Check. For ail runs, a low check at the level of the CRDL (0.20 ug/l) or reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. No specific acceptance criteria are listed in any of the methods for this standard at this time. An in-house criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then ali samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

13.12.1 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

13.12.2 Some client may require additionat bracketing low checks to be analyzed. Client specific limits may also be required. Check with the area supervisor or manager for more information.

14.0 DOCUMENTATION REQUIREMENTS

Refer to the taboratory Quatity Assurance Manual for additional documentation requirements.

14.1 Sample Worksheets. Digestion data sheeis for the Hg water samples must show aii digestion information inctuding the sampie ID's, sample volumes, bottle numbers, start times, end times, and pressure or temperature, as appropriate for alt digestions. The digestion method (i.e digestion block) must be indicated on the digestion sheet. Alt sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the

samples or the digestion procedure should be noted in the Commenis sections. Make sure also that all dilutions are clearly documented.

14.2 Standards and Reagents. All stocks and reagents must be recorded in the reagent logbook. All standards should be recorded on the digestion log with the samples.

14.3 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

14.4 Annual bottie calibration verifications must be documented in the Mercury Bottle catibration tog.

15.0 DATA REVIEW AND REPORTING

15.1 Ail samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and It is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

15.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

15.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. instrument data is transferred electronically.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform aii procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. Aii safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. Ali method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS 004. This documeni describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes.

16.2.3 Chlorinated organic solvents.

16.2.4 Non-chlorinated organic solvents.

16.2.5 Hazardous solid wastes.

16.2.6 Non hazardous aqueous wastes.

17.0 ADDITIONAL REFERENCES

17.1 Leeman Hydra II AA instrument manual.

17.2 Leeman Hydra AA instrument manual.

Accutest Laboratories
Standard Operating Procedure

Lab Manager Nancy Cole

QA Manager [illegible] for [illegible]

Effective Date: 9/12/11

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) USING SOLID STATE ICP.

METHOD REF: SW846 6010C

Revised Sections: 1.2, Tables 1, 2, 3, 4, and 5

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of metals in water, wipes, sludges, sediments, and soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge, wipe or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

1.2 A variety of metals can be analyzed by ICAP. These include, but are not limited to, Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, S, Se, Si, Ag, Na, Sr, Tl, Sn, Ti, Pd, V, W, Zn, and Zr.

2.0 SUMMARY

2.1 Prior lo analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This SOP describes operation of the ICAP 6500 Spectrometer following method SW846 6010C.

2.2.1 This inductively coupled argon plasma optical emission specfrometers (ICP-OES) uses an Echeiie optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Control of the spectrometer is provided by PC based ITEVA software.

2.2.2 In the instrument, samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored the solid state detector.

2.2.3 Background correction is required for trace element determination. Background must be measured adjacent lo analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in

background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical resuit. Interferences which cannot be addressed with background correciion must be corrected using the appropriate interelement correction factors.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limits for this method have been established at the concentrations listed in Table 1. Reporting limits may vary depending on client needs and lab protocols, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. In addition, the reporting limits must always be greater than the MDL. Refer to the scheduling sheets and check with the metals supervisor for further information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent during an analysis mn, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is ± 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run with each calibration. For this method, the external check standard criteria is ± 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. Assess laboratory performance against the control limits of 80 to 120 percent. in house limits should also be generated once sufficient data (usually a minimum of 20 to 30 analyses) is available to support the default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control or spike

blank is ouiside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE DUPLICATE: A matrix spike duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike should be assessed. A duplicate may be used in place of the matrix spike duplicate on client request. The matrix spike duplicate RPD is calculated as shown below. The control limit for the duplicate is 20% rpd. if a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix SpikeDuplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the default limits of 75 to 125 percent. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amouni, then the sampte cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each differeht digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less than ½ of the reporting limit for that parameter. If the method blank contains levels over this levei, then the samples must be redigested and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required timit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sampie preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank Is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent

blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the curreni specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified In the appropriate seciion. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analysis.

LOW LEVEL CALIBRATION VERIFICATION fCRI or LLCCV). The LLCCV or CRI standard is a check standard containing the elements of interest at (or below) the reporting tevel for each element. For this method, the CRI (LLCV) must be ahalyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outiined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contaci the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemicai must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a curreni awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheeis must be made available to ail personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Ali water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples should be stored in a refrigerator at 4 degrees C.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace melals determinations by ICP. These interferences are discussed below.

7.2 Spectral Interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections for these Interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

7.3 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by using an internal standard, by making sample dilutions or by analyzing a sample using the method of standard additions.

7.4 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

8.0 EQUIPMENT AND SUPPLIES

8.1 Currently there are two solid state ICPs available for use in the lab. Both are Thermo 6500 ICP units. These units have been optimized to obtain low detection limits for a wide range of elements. Since they are solid state systems, different lines may be included for elements to obtain the best analytical results. However, the lines which are normally included in the normal analysis program are shown in Table 2.

8.2 Instrument autosamplers. For random access during sample analysis.

8.3 Class A volumetric glassware and pipets.

8.3.1 All glassware must be washed with soap and lap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. It must then be rinsed at least 3 times with deionized water.

8.4 Glass autosampler tubes

8.4.1 Autosampler tubes must be washed wilh soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. They must then be rinsed al least 3 times with deionized water.

8.5 Autopipeters with tips. These must be calibrated and ohecked as outlined in the autopipeter SOP, EQA004.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless othenwise specified. Deionized water must be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For

acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric Acid, Baker instra-analyzed or equivalent.

9.4 Standard stock solutions available from Absolute, Inorganic Ventures, MV Laboratories, Ultra Scientific or equivalent. Note: All standards must be ICP quality standards.

9.5 Calibration Standards. These can be made up by diluting the stock solutions lo the appropriate concentrations . It is recommended that fresh calibration standards should be prepared a minimum of every two weeks. They must be monitored on a daily basis by comparison lo an ICV. Standards which are going to be stored for several days should be transferred to FEP fluorpcarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.5.1 Standards should be approximately matrix matched to the samples. For most samples, a 5 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, then the matrix of the standards should be modified or the samples should be diluted so that they are in a similar matrix to the curve.

9.5.2 Standards should be prepared so that there is minimal spectral interference between analytes.

9.5.3 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. The standard curve consists of a blank and 3 non-zero standards at the levels shown in Table 3.

9.6 Calibration/Rinse Blank. The calibration blank is prepared by diluting a mixture of 50 ml of concentrated nitric acid and 50 ml of concentrated hydrochloric acid to a final volume of 1 liter with deionized water.

9.7 Analytical Quality Control Solutions. All of the solutions below are prepared by adding either mixed or single element metals solutions lo a solution containing 5 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. All of these solutions should be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.7.1 Initial Calibration Verification solution. This standard solution must be made from a different source than the calibration curve. The values for each element should be near the midpoint of the calibration curve. This solution is used to verify the accuracy of the initial calibration. See Table 4 for suggested ICV concentrations.

9.7.2 Continuing Calibration Verification solution. The metals concentrations for this standard should be at approximately the mid-point of the calibration curve for each element. This standard should be prepared from the same source that is used for the calibration curve. See Table 4 for suggested CCV concentrations.

9.7.3 Interference Element Check Solutions. These solutions should be used on a periodic basis to check the interfering element corrections on the instrumenis. Note: If interferences from different elements than those listed below are a problem, the interfering element solutions may be modified. Two acceptable solutions are outiined below.

9.7.3.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements.

Al	500 mg/L
Ca	400 mg/L
Fe	200 mg/L
Mg	500 mg/L

9.7.3.2 ICSAB Solution. The ICSAB solution contains both the interferenis and the analytes of interest. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements

Ag	1.0 mg/L	Zn	1.0 mg/L
Ba	0.50 mg/L	As	1.0 mg/L
Be	0.50 mg/L	Se	1.0 mg/L
Cd	1.0 mg/L	Sb	1.0 mg/L
Co	0.50 mg/L	Tl	1.0 mg/L
Cr	0.50 mg/L	Mo	0.5 mg/L
Cu	0.50 mg/L	Pd	0.5 mg/L
Mn	0.50 mg/L	Al	500 mg/L
Ni	1.0 mg/L	Ca	400 mg/L
Pb	1.0 mg/L	Fe	200 mg/L
V	0.50 mg/L	Mg	500 mg/L
W	0.50 mg/L	Zr	0.50 mg/L

9.7.4 CRI Standards (also referred to as LLCCV). The CRI standard must contain the elements of interest at (or below) the reporting limit for each element. The CRI level is at the reporting limit as shown in Table 1. This should be prepared by diluting calibration standard(s) to the reporting limit level for each element. They should be made in the same matrix as the calibration standards. Note: The CRI must be verified at the RL before any dilutions are applied

9.8 Matrix Spike and Spike Blank Solution (For soil samples). The final concentrations suggested for the matrix spike and spike blank solutions are shown in Table 5. The spiking solution is prepared by adding either mixed or single element metals solutions to a solution containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. Two mis of this stock solution should be added to the spike blank and the matrix spike before they are digested and brought to a final volume of 100 ml.

9.9 Matrix Spike and Lab Control Solution (For aqueous samples and TCLP leachates).

9.9.1 The final concentrations suggested for the matrix spike are shown in Table 5. Two spiking solutions, which are used for aqueous samples and TCLP leachates respectively, are prepared by adding either mixed or single element metals solution to solutions containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. 0.5 ml of the resulting stock solution is added to the matrix spike sample before they are digested.

9.9.2 A lab control sample should be digested and analyzed for every batch of 20 samples or less. The LCS is prepared by adding either mixed or single element metals solutions to DI water and bringing up to a fixed final volume. For TCLP samples, the lab control should be made using blank leachate solution rather than DI water. 50 ml of this solution is digested and brought to a final volume of 50 ml. In situations where any odd elements, such as B, Si, Sr, Sn, and Pd, is of interest for a specific prpject, besides a lab control, a spike blank is also digested.

9.10 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary

9.11 Internal Standard Solution (with matrix modifier). To a 1 liter flask containing approximately 800 ml of DI water, add 10.0 ml of 10,000 mg/l Lithium solution, 5.0 ml of 10000 mg/l indium, and 1.000 ml of 10000 mg/l yttrium. Add 50 ml concentrated nitric acid and 50 ml concentrated hydrochloric acid and bring to a final volume of 1000 ml and mix well. This solution is added to all samples and standards as the Instrument is running using a split line on the peristallic pump

10.0 PROCEDURE

10.1 Gerieral procedure on how to operate the SS Trace t is described below. Refer to the Thermo 6500 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, the dehumidifier is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Set up the pump tubing and engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction probiems and sample carryover.) If internal standard is being used, make sure that sufficient internal standard solution is prepared.

10.6 Start up the instrument following the sequence shown below.

10.6.1 Double click the ITEVA Controt Center Icon on desktop. Type admin in User Name field, and then click OK.

10.6.2 Once the ITEVA Control Center window is opened, click on Plasma Icon at status bar area. Then click on Instrument Status to check the interiock indicators (torch compartment, purge gas supply, plasma gas supply, water flow and exhaust should

be in green; drain flow and busy should be in gray) and the Optics Temperature. (It should be around 38°C.) Click on the Close box.

10.6.3 Click Plasma On. When the plasma is on, click close. Let the instrument warm up for 15 to 20 minutes before starting the analysis. New tubing may take an hour to stabilize .

10.7 Torch Alignment and Auto Peak

10.7.1 If the torch has been cleaned, then it has to be realligned after it is replaced

10.7.1.1 Open the method and then click on Sequence tab, then click on List View Icon until you reach rack display.

10.7.1.2 Go to S-6 position (you can assign any position in the rack for torch alignment), then right click to select Go to empty sample S:6. (Now, the autosampler tip moves from Rinse to this position)

10.7.1.3 Click on Analysis tab, then select Torch Alignment from Instrument drop down menu. There will be a pop up dialog box present. Click RUN. Then there will be another dialog box pop up (This is a reminder for Torch Alignment Solution (2 ppm Zn)), click Ok. Now, the instrument is initiating an automated torch alignment. It takes about 7 minutes to complete this step. Progress is indicated in the progress bar.

10.7.1.4 After Torch Alignment is done, click Close. Click on Sequence tab, then follow by List View Icon.

10.7.1.5 Go to Rinse position at rack display, right click to select Go to rinse and let it rinse for 2 minutes.

10.7.2 Perform Auto Peak.

10.7.2.1 it is recommended that the Auto Peak Adjust procedure be performed monthly or whenever the peak shape has shifted for any element. A standard that contains all of the lines of interest is used and the system automatically makes the appropriate fine adjustment. (CCV solution is used for this process.)

10.7.2.2 Click Sequence tab, then click on List View Icon till the rack is displayed.

10.7.2.3 Go to S-5 position (you can assign any position in the rack for auto peak adjust), then right click to select Go to empty sample S:5. (Now, the autosampler tip moves from Rinse to this position). Click on Analysis tab. All elements' result is showed in the display area. From Instrument drop down menu, select Perform Auto Peak. There will be a pop up dialog box present. Highlight _All Elements_, then click RUN. Then there will be another dialog box pop up (This is a reminder for Perform Auto Peak Solution), click Ok. Now, the instrument is performing auto peak adjust. It takes about 5 minutes to complete this process. The Auto Peak dialog box will show a green "√" in front of All Elements, which indicates Auto Peak is completed.

10.8 Open the method and start up the run.

10.8.1 Glick on **Analyst** Icon at the workspace. Go the Method and choose Open from the drop down menu. Select the method with a Revision (usually select the last revision used).

10.8.2 Go to Method tab at the bottom of left-hand corner to click on **Automated Output** at the workspace area. Type a filename in Filename field in the dala display area (i.e.: SA073107M1: starts with SA, then follow by MM-DD, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs).

10.8.3 Click on Sequence tab at the bottom of left-hand corner. From **Auto-Session** drop down menu bar, click on New Autosampler to create a sequence. This will pop up a dialog box , then click on New and fill number of samples (i.e.: 100) in the Number of Samples field and the sample ID (usually leave this field empty) in Sample Name field. Type a sequence name (i.e.: SEQ073107M1: starts with SEQ, then MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs) in the Sequence Name field. Click OK, then put in "0" on Settle Time Between Sequences box, click OK.

10.8.4 Right click on **Untitled** (CETAC ASX-520 Enviro 5 Named Rack is the rack that currently using) at the workspace area, click on **Auto-Locate ALL** to locate all samples.

10.8.5 Double click on **Untitled** again, then click on the sequence name (i.e.: SEQ073107M1), on the data display area, type the sequence in Samplename column, dilution factor (if needed) in CorrFact column, check the box in front of Check column, and select an appropriate check table.

10.8.6 Once done with creating sequence, go to **Method** drop down menu and save all changes as Save **As**. There will be a Save a Method dialog box present, go to Save Option to check on "Ovenwrite Method and bump revision number" box, then click OK.

10.8.7 Go to Sequence tab, click on **List View** Icon from tool bar, then click on Connect **Autosampler to PC** and **Initialize** icon. (Now, the autosampler tip is up and sits on the top of the rinse cup.)

10.8.8 The sequence includes the calibration and run quality control.

10.8.8.1 Calibrate the instrument as outlined below using the standards shown in Table 3. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the autosampler program or they may be run separately. A correlation coefficient of 0.998 or better must be obtained using a first order curve fit. Second and third order curve fits are not acceptable.

10.8.8.2 Run the CRI (**LLCCV**) solution after the calibration is completed and before any samples are analyzed.

10.8.8.2.1 For all samples, the CRI check solution must be at the reporting limit for each element. If special client reporting limits are requested, then low checks corresponding to those reporting limits must also be analyzed.

10.8.8.2.2 Method limits of 70 to 130% are applied to the CRI standard, but tighter criteria may be needed in some client or project specific situations.

10.8.8.3 Then continue by analyzing the ICV check standard followed by the CCV, CCB, ICSA, ICSAB, and CCV, CCB every 10 samples. (An ICB may be run following the ICV, but is not required.) For mixed runs (EPA 200.7 and SW846 6010C), the first CCV is designaied the ICCV. For samples and quality control, insert the list pointer after a space after the sample. Check with the metals supervisors for additional information on the use of listpointers. In general, listpointer 2 refers to the SW846 6010 method and listpointer 1 refers to EPA 200.7 method.

10.8.8.3.1 For the ICV, all elements to be reported must be within 10 percent of the true values. After the ICV (and ICB, if run) and before any actual samples are analyzed, the CCV and CCB must be analyzed. For the CCV, all elements to be reported must be within 10 percent of the true values. For both ICV and CCV, all replicates exceed 5 times the reporting limit should have a relative standard deviation of less than 5 percent. Both ICB and CCB results should be less than the reporting limits for the every element.

10.8.8.4 Before analyzing any real samples, an Interference check solution must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions should contain less than two times the absolute value of the reporting limit for each element.

10.8.8.5 If the interfering element solution is not within specifications and that element must be reported, then new interfering element correction (IEC) factors will need to be generated following the procedure outiined in Seciion 11 below. If new IEC's are generated, then the run must be restarted from the ICSA, ICSAB quality control samples and new CCV checks must be run before any samples can be reported.

10.8.8.6 After the initial analytical quality controi has been analyzed, the samples and the preparation batch quality control should be analyzed. Each sample analysis should be a minimum of 2 readings using at least a 5 second integration time. For samples containing levels of elements greater than apprpximately 5 times the reporting limits, the relative standard deviations for the replicates should be less than 5%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element should be evaluated by the data reviewer and footnoted if

necessary. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.8.8.7 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for the required period of lime to ensure that analyte memory effects are not occurring. A time of 120 seconds is recommended for most analyses with the current autosampler set-up.

10.8.8.8 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples during an analysis run, whichever is more frequent, and at the end of the sample run.

10.8.8.9 If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element. Additionally, for the elements with a CCV greater than 5 times the reporting limit, the relative standard deviation for the replicates should be less than 5 percent.

10.8.8.10 The CCB results must be less than the reporting limit or limit of quantitation for each desired target analyte. ff this criterion is not met, then no samples can be reported in the area bracketed by the failing CCB for the failing element and all samples should be submitted for reanalysis.

10.8.8.10.1 However, if the samples are high relative to the CCB (> 10 X the CCB level) and a higher reporting limit is acceptable for the flnal end use of the data, then the samples may be evaluated using a higher reporting limit to meet the CC8 criteria. This must be clearly documented on the run if a higher reporting limit is applied.

10.8.8.10.2 In addition, at the reviewer's discretion, samples that are < RL may be reported when the CCB is biased high. Analysis should assume lhat samples bracketed by a failing CCB must be reanalyzed unless instructed otherwise.

10.8.8.10.3 If a CCB fails, if possible, the analyst should stop the run and run a new CCV, CCB pair before proceeding with the analysis of any additional samples.

10.8.8.11 For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution should be prepared. Normally the sampie used for the serial dilution is the sample lhal is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample is greater than 50 times the reporting limit for that element before dilution (or 10 times the reporting limit after dilution) and the sample results are within the linear range. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown beiow

10.8.8.12 If the matrix spike or matrix spike duplicate is out of acceptable limits, then it is recommended lhat post-digest spikes be prepared to determine potential interferences. For the post-spike, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noled in the quality control summary report.

10.8.8.13 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines wilh an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

10.8.8.14 For the interelement spectral interference corrections to remain valid durirg sample analysis, the interferent concentration must not exceed its linear range. If the interferent exceeds its linear range or its correction factor is big enough lo affect the element of interest even at a lower coricentration, sample dilution with reagent blank and reanalysis is required. In these circumstance analyte detection limits are raised. Check with metals supervisor for more information.

10.8.8.15 Anytime that the interference is large relative to the sample, dilution may be required. Check with the metals supervisor for more information.

10.8.8.16 For any readings where the internal standard is ouiside of the range of 70 to 130% of the internal standard level in the calibration blank, then the sample should be diluted until the internal slandard is within that range.

10.8.9 The CRI (LLCCV) must be analyzed at the end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all samples for that element in the concentraiion range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV crileria are rhet. Multiple levels of CRI checks may be analyzed if different reporting limits are being applied to samples on the run.

10.8.9.1 More frequent CRI (LCCV) checks may be analyzed during the course of the mn if system stability at the low end of the calibration is questionable or if the lab wants lo ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

10.8.9.2 It is recommended that the CRI check be run bracketing every 4 lo 8 hour period of analysis. II may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

10.8.10 This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required to meet other method and/or client requirements. Run the ICSA and ICSAB solutions every 8 hours unless otherwise

instmcted by the metals lab supervisor or manager. Note: The decision can also be made that the 8 hour ICSA/iCSAB was not required at the time of review. Because the 8 hour ICSA/ICSAB is a project specific requirement, the data reviewer can accept data where the ICSA/ICSAB was not run every 8 hours for any project that does not carry the specific 8 hour requirement.

10.8.11 After the instrument is optimized, click Run Auto-Session icon to start the run.

10.8.12 ff you need to add or delete samples once the run is started, follow the steps shown below.

10.8.12.1 Adding Samples.

10.8.12.1.1 Click on Sequence tab, then click on List View Icon at the tool bar. There is the sequence table on the data display area.

10.8.12.1.2 Click on Add Samptes Icon. This will pop up the dialog box, then fill number of samples that need to add in field. Click **OK**. By doing this, samples will be added at the end of sequence without a location the rack.

10.8.12.1.3 Go to the added samples, on the to position ID column, assign a number for each sampie. This number will be the position in the rack. On the Samplename column, type in sampie IDs, fill in Corr Fact (if needed) and Check Table.

10.8.12.1.4 The added samples will be analyzed at the end of the original sequence run order unless you assign them to run under different order.

10.8.12.2 Deleting Samples.

10.8.12.2.1 Click on Sequence tab, then click on List View Icon under the sequence display area.

10.8.12.2.2 To the sample that need to be deleted, on the to position ID column, change the number to "0". By doing this, that sample will be unlocated in the rack and the autosampler tip will go to the next sample.

10.9 When the analysis is completed export the data to LIMS following the procedure outlined below.

10.9.1 Double click on ePrint Icon on desktop. There will be a LEADTOOLS ePRINT dialog box pop up, then click Finish Jobs and **OK** boxes.

10.9.2 Double click the PDF Icon on desktop, the PDF file will present as Document_#. Right click on that file, select Rename to change the file name to an assigned analytical run ID. (i.e.: MA8324). This is the raw data for MA8324.

10.9.3 Drop the raw data lo Lims.

10.9.4 By completing above steps, the raw data (i.e: MA8324) can be pulled up in the Raw Data Search function.

10.10 The data must be reviewed in the LIMS as outiined in the inorganic data review SOP, EQA034. Calculations for water samples are done automatically in the LIMS using the equation shown below.

original sample concentraiion of metal (µg/l) =

$$\frac{\text{(conc. in the digestate (uo/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.11 Aft the end of the analysis day, the ICP must be brought down using the following sequence:

10.11.1 Place the autosampler tip in rinse cup and rinse in a mixed solution of 5% nitric acid and 5% hydrochloric acid for 10 minutes and in DI water for 20 minutes. Note: A stronger acid may be needed depending on the matrix of the samples that were analyzed.

10.11.2 Turn off the plasma by click on the Plasma Icon and click on Plasma Off.

10.11.3 Close all ITEVA programs/ windows.

10.11.4 Release the tension on the sample pump platen.

10.11.5 Switch off recirculating chiller.

11.0 PROCEDURE FOR GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

11.1 All IEC's must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. It is recommended that elements with frequent high concentrations or with large IEC's should be checked more frequently.

11.2 Calculate the IEC correction factors and enter them into the melhod. Verify lhal the recalculated sampie results are within QC limits. Calculate the correction factor using the equation shown below. This conection factor must be added lo the correction factor already in place in the method for a given element,

$$\text{IEC} = \frac{\text{Concentration Resuit of the element with the interference}}{\text{Cbncentration result of the interfering element}}$$

11.3 Analyze the ICS/VICSAB solutions and/or SIE solutions and verify lhat the combined standards are wilhin QC limits. ff they are not, make additional changes to the IEC factors and then re-verify both the individual and combined solution values.

11.4 Save and update the melhod.

11.5 Interfering element correction factors saved as raw data along with the run printouts on a daily basis so that the tEC's for a given run are traceable.

12.0 QC REQUIREMENTS

12.1 This section outiines the minimum Q/VQC operations necessary to satisfy the analytical requirements for method SW846 6010C.

12.2 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked al approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instmment Detection Limits (IDLs). Instrument Dection Limits (IDLs). It is required that IDL's be completed a minimum of every 3 months for all analytes or whenever instrument conditions have significantiy changed. The Instrument Detection Limits (in ug/L) are determined by analyzing 7 replicates of a reagent blank solution on 3 non-consecutive days. The IDL is defined as 3 times the average of the standard deviations of the 3 days. For the IDL, each measurement shall be performed as though il were a separate analytical sample (I.e., each measurement shall be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs shall be determined and reported for each wavelength used in the analysis of the samples.

12.4 Linear Calibration ranges. The upper limit of the linear calibration ranges should be established for each analyte by determining the signal responses from a minimum of three concentration standards, one pf which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined whenever there is a significant change in instrument response and every six months for those analytes that periodically approach their linear limit.

12.4.1 For work following the Army Corp of Engineers Shell documeni, the iinear range cannot exceed the level of the high calibration standard on that run. All elements to be reported that exceed the high standard must be reanalyzed on dilution and the resuits reported from the dilution.

12.5 initial Calibration Verification (ICV) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV may be followed by the analysis of the ICB, although this is not required by the method.

12.5.1 For the ICV, all elements lo be reported must be wilhin 10 percent of the true value and the replicates that exceed 5 times the reporting limit should have a relative standard deviation of less than 5 percent. The ICV must be from a different source than the calibration standards and must be near the mld-poinl of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing thai it meets QC criteria.

12.5.2 ff an ICB is analyzed, than ail elements to be reported must be less than the RL (LLOQ). If the ICB is outside of criteria, then the problem must be identifled and

corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria. Analysis of a CCB before running any reportable samples can be used to verify that the system meets calibration blank requirements.

12.6 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run.

12.6.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. The CCV should be made from the same source as the calibration standards at a concentration near the mid-level of the calibration curve. If an element does not meet the recovery criteria of the CCV (90 to 110%), than no samples can be reported for that element in the area bracketed by the CCV.

12.6.1.1 If the replicate rsd is high, but all replicates are within the recovery limits, then the results can be accepted at the discretion of the reviewer.

12.6.2 For the CCB, all elements to be reported must be less than the reporting limit (LLOQ). If an element does not meet this criteria, then no samples can be reported for that element in the area bracketed by the CCB.

12.7 interference Check Standard. An interference check standard must be analyzed at the beginning of each analytical run. For all spiked elements, the analyzed results must be within 20 percent of the true values. For unspiked elements, the interfering element solutions should contain less than the absolute value of two times the reporting limit for each element. If this criteria is not met, then no samples containing the elements in question can be reported in the area bracketed by this QC unless the samples contain no significant interferents. This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required due to meet other method and/or client requirements. Run the ICSA and ICSAB solutions every 8 hours unless otherwise instructed by the metals lab supervisor or manager. Note: The decision can also be made that the 8 hour ICSA/ICSAB was not required at the time of review. Because the 8 hour ICSA/ICSAB is a project specific requirement, the data reviewer can accept data where the ICSA/ICSAB was not run every 8 hours for any project that does not carry the specific 8 hour requirement.

12.8 Low Level Calibration Verification (CRI or LLCCV). The CRi standard containing the elements of interest at (or below) the reporting level for each element. The CRI (LLCV) must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. if an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

12.8.1 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab

wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

12.8.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

12.9 Method Blank. The laboraiory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank is considered acceptable.

12.9.1 The default SOP limit for the method blank is that is must be less than one half of the reporting limit.

12.9.2 In addition, the blank is considered acceptable if it is less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater.

12.9.3 If the method blank does not meet criteria, then it can be reanalyzed along with any associated samples. If It is still unacceptable, then all associated samples must be redigested and reanalyzed along with the other appropriate batch QC samples

12.10 Lab Control Sample or Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboraiory should assess laboratory performance of the lab control and spike blank against recovery limits of 80 to 120 percent. In house lab control ahd spike blank limits may also be generated to support these default limits. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.10.1 If solid lab controls are used, then the manufacturer's limits should be applied.

12.11 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Recoveries should be assessed against default limits of 75 to 125 percent. In house limits may be generated for this method for informational purposes only. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote and it is recommended that a post-digest spike be analyzed for the out of control element(s). If the matrix spike amount is less than one fourth of the sample amouni, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result) / Amount Spiked) x 100 = matrix spike recovery

12.11.1 If a post-digest spike is required, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the

matrix spike recovery or otherwise noled in the quality controi summary report. If the post-spike recoveries are out of the range of 80 to 120%, then the matrix spike results should be footnoted with a comment lhat the post-digest spike recovery indicates possible matrix interference.

12.12 Matrix Spike Duplicate (MSD) or Matrix duplicate (DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the MSD and the MS or between the DUP and the sample should be assessed. The rpd is calculated as shown below. The control limit for the duplicate rpd is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated lo the IDL for any given element. Any value less than the IDL is treated as zero.

12.12.1 If a MSD or duplicate is out of control, then the data should be checked carefully to confirm that the high rpd for a given element is not a result of an analytical problem. if an analytical problem ls suspected, the MSD or duplicate must be reanalyzed for confirmation. If the initial and reanalysis are in agreement (wilhin 20%), then the high rpd is a resuli of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement due lo an analytical problem, then any affected samples in the associated batch should also be reanalyzed for that element.

12.12.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate should be redigested for confirmation, unless the sample matrix is such lhat the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate should be fiagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch should be digested and reanalyzed.

12.12.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) should be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

12.12.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

12.13 Serial Dilution. A serial dilution is required on a frequency of one in 20 samples. For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution should be prepared. Normally the sample used for lhe serial dilution is the sample lhat is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution should agree wilhin 10 percent of the true value as long as the sample is greater than 50 times the

reporting limit for that element before dilution (or 10 times the reporting limit after dilution) and the sample results are within the linear range. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below.

$$\frac{100 \times ((\text{Sample result} - \text{Serial dilution result}))}{\text{Sample result}} = \text{Serial dilution percent difference}$$

12.14 Post Digestion Spike Addition. Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike should be performed. Recovery limits of 80 to 120 percent should be used to assess post-digest spikes.

12.15 IEC Correciion Factor Generation. All interfering element correction factors (IEC's), must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly.

12.16 Lower Limit of Quantitation check sample (LLQC). The LLQC is a sample at the reporting limit that is taken through the entire preparation and analytical process. This standard must be analyzed when reporting limits are initial established and on an as needed basis after that. The LLQC is equivalent to the LOQ (Limit of quantitation) standard which must be analyzed quarterly for the DOD QSM 4.1 program. The limits of quantitation are verified when all analytes in the LLQC sample are detected within 30% of their true value. if the limits cannot be verified at the spiked level, then the quantitation limit must be adjusted to a level where verification is successful.

12.17 Calibration Curve. The calibration curve should be prepared daily using a minimum of a calibration blank and three non-zero standards that bracket the desired sample concentration ranges. The calibration curve must have a correlation coefficient greater than or equal to 0.998 and must be verified with initial low level and mid level calibration verification standards before any samples can be analyzed. ff the curve does not meet the correlation coefficieni requirements or is not verified as described in section 12.5 or 12.8, then no results can be reported for those elements which did not meet quality control criteria.

13.0 CALCULATIONS

13.1 For water samples, the following calculations should be used. Refer to the QC section for the calculations to be used for the QC samples.

original sample concentration of metal (µg/l) =

$$\frac{(\text{conc. in the digestate (ug/l)}) \times (\text{final digestate volume (ml)})}{(\text{Initial sample volume (ml)})}$$

13.2 For soil samples, the following calculations should be used.

concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

14.0 DOCUMENTATION REQUIREMENTS

14.1 If any samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All Instrument data should be exported to the LIMS system and a copy of the run log should be included in the logbook by the instrument.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. A copy of any outside maintenance reports should also be kept in the log. In addition to the maintenance, the maintenance log should also contain daily information on such items as the profile intensity. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error and a reason for the correction. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 INSTRUMENT MAINTENANCE

15.1 Recommended periodic maintenance includes the items outlined below.

15.1.1 Change the pump tubing weekly or as needed.

15.1.2 Clean the filler on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

15.1.3 Clean the radial view quartz surface weekly or more often if needed.

15.1.4 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

15.1.5 Change the sampler tip as needed (every one to two months).

15.1.6 Clean the recirculating pump lines every 3 months or more often if needed.

15.1.7 Clean the slides on the autosampler with methanol and wipe them with a KimWipe saturated with Teflon spray a minimum of once per day.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

17.0 ADDITIONAL REFERENCES

17.1 Refer to other SOP's for ICP analysis (CLP and EPA 200.7 for both DW and WW).

TABLE 1: NORMAL REPORTING LIMITS BY ELEMENT			
Analyte	Water & Wipe Reporting Limit (µg/l)	Soil Reporting Limit (mg/kg)	TCLP Reporting Limit (mg/l)
Aluminum	200	50	
Antimony	6	2	
Arsenic	3	2	0.50
Barium	200	20	1.0
Beryllium	1	0.2	
Cadmium	3	0.5	0.005
Calcium	5000	500	
Chromium	10	1	0.010
Cobalt	50	5	
Copper	10	2.5	
Iron	100	50	
Lead	3	2	0.50
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	10	4.0	
Potassium	10000	1000	
Selenium	10	2	0.50
Silver	10	0.5	0.010
Sodium	10000	1000	
Thallium	2	1	
Vanadium	50	5	
Zinc	20	2	
Boron	100	10	
Molybdenum	20	1	
Palladium	50	5.0	
Sulfur	50	NA	
Silicon	200	20	
Strontium	10	1	
Tin	10	5	
Titanium	10	1	
Tungsten	50	5	
Zirconium	10	2	

TABLE 2: ANALYTICAL LINES ON THE SSTRACE1 AND SSTRACE2	
Element	Wavelength
Al	396.1
As	189.0
Ca	317.9
Fe	259.9
Mg	279.0
Mn	257.610
Pb	220.3
Se	196.0
Tl	190.8
V	292.4
Ag	328.0
Ba	455.4
Be	313.0
Cd	228.8
Co	228.6
Cr	267.7
Cu	324.7
K	766.4
Na	589.5
Ni	231.6
Sb	206.8
Zn	206.2
B	208.9
Mo	202.0
Pd	340.4
S	182.0
Sr	407.7
Sn	189.9
Ti	334.9
Si	212.4
W	207.9
Zr	339.1

TABLE 3: CALIBRATION STANDARD LEVELS in ug/l				
Element	STD A (Blank)	STD B	STD C	STD D
Ba	0	1000	2000	4000
Be	0	1000	2000	4000
Cd	0	1000	2000	4000
Cr	0	1000	2000	4000
As	0	1000	2000	4000
Se	0	1000	2000	4000
Pb	0	1000	2000	4000
Tl	0	1000	2000	4000
Mn	0	1000	2000	4000
Co	0	1000	2000	4000
Zn	0	1000	2000	4000
Cu	0	1000	2000	4000
Ni	0	1000	2000	4000
Sb	0	1000	2000	4000
Mo	0	1000	2000	4000
B	0	1000	2000	4000
Sn	0	1000	2000	4000
Ti	0	1000	2000	4000
Ag	0	125	250	500
V	0	1000	2000	4000
Sr	0	1000	2000	4000
Si	0	2500	5000	10000
Pd	0	1000	2000	4000
W	0	1000	2000	4000
Zr	0	1000	2000	4000
S	0	1000	2000	4000
Al	0	20000	40000	80000
Ca	0	20000	40000	80000
Fe	0	20000	40000	80000
Mg	0	20000	40000	80000
K	0	20000	40000	80000
Na	0	20000	40000	80000

TABLE 4: ICV, and CCV LEVELS		
Element	ICV Suggested Level In ug/l	CCV Suggested Level In ug/l
Al	40000	40000
As	2000	2000
Ca	40000	40000
Fe	40000	40000
Mg	40000	40000
Mn	2000	2000
Pb	2000	2000
Se	2000	2000
Tl	2000	2000
V	2000	2000
Ag	250	250
Ba	2000	2000
Be	2000	2000
Cd	2000	2000
Co	2000	2000
Cr	2000	2000
Cu	2000	2000
K	40000	40000
Na	40000	40000
Ni	2000	2000
Sb	2000	2000
Zn	2000	2000
B	2000	2000
Mo	2000	2000
Pd	2000	2000
Sr	2000	2000
Sn	2000	2000
Ti	2000	2000
Si	5000	5000
W	2000	2000
Zr	2000	2000
S	2000	2000

TABLE 5: SUGGESTED CONCENTRATIONS OF METALS IN THE MATRIX SPIKE AND SPIKE BLANK			
Element	**Soils Final Concentration in mg/kg**	**Aqueous Final Concentration in µg/l**	**TCLP Leachates Final Concentration in mg/l**
Ag	10	50	0.05
Al	5400	2000	
As	400	2000	2.0
B	100	2000	
Ba	400	2000	10.0
Be	10	50	
Ca	1250	25000	
Cd	10	50	0.05
Co	100	500	
Cr	40	200	0.20
Cu	50	250	
Fe	5200	1000	
K	1250	25000	
Mg	1250	25000	
Mn	100	500	
Mo	100	2000	
Na	1250	25000	
Ni	100	500	
Pb	100	500	2.0
Sb	100	500	
Se	400	2000	2.0
Tl	400	2000	
V	100	500	
Zn	100	500	
S	NA	2000	
Sn	100	2000	
Sr	100	2000	
Ti	100	2000	
Si	200	4000	
Pd	100	2000	
W	100	2000	
Zr	100	2000	

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager Nancy Cole

QA Manager

Effective Date: _____

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR SOIL SAMPLES

REFERENCES: SW846 7471B

Revised Sections: 7.1, Section 11 (all), Section 12 (all), 13.7, 14.2, 17.1, 17.2

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury in soils, sediments, bottom deposits, and sludge type materials. The reporting limit for mercury soil samples, based on a 0.6 g sample size, is 0.033 mg/kg.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. Recovery requirements vary by method. For this method a recovery from

80 to 120% Is required. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercialty available. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample Is digested at a minimum of 1 In 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is catculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. if the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

STANDARD CURVE: A plot of cpncentrations of known analyte standards versus the instmment response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation.

LOWER LIMIT OF QUANTITATION CHECK (also referred to as CRI, CRA, or LLQC). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A method criterion of 70 to 130% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All solid samples should be stored at 4 ± 2°C until the time of digestion.

6.2 All samples should be analyzed within 28 days of the date of sampling.

7.0 APPARATUS

7.1 Two Leeman instruments are available for analysis. One is a Leeman Hydra II AA automated analyzer and the other is a Leeman Hydra AA automated analyzer. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

7.1.1 Change the sample tubing as needed.

7.1.2 Change the drying tubing as needed.

7.1.3 Clean the exterior of the instrument as needed.

7.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

7.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

7.2 Graphite heating block. Capable of heating at 95 ± 3 °C for 2 hours.

7.3 Digestion Bottles . Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

7.4 Calibrated glass lubes with verified 60.0 ml and 100.0 ml final volume calibration mark for bringing graphite heating block digestates to their final volume. (The 60.0 ml calibrallon is only required for water digestions).

7.4.1 At a minimum of once per year, the calibration of these bottles must be verified and documented in the Hg Bottie calibration log following the procedure outlined below.

7.4.2 Carefully measure 60.0 ml of room temperature (20 to 25 deg. C) deionized water with a class A to deliver volumetric cylinder and pour into the calibrated Hg bottle.

7.4.3 If the bottom of the meniscus is on the calibration line, then the bottie passes calibration and can be used.

7.4.4 If the bottom of the meniscus is not on the line, then the bottle should be removed frpm service and replaced with a newly calibrated bottle. New bottles are calibrated following the same procedure as above, except that a line must be etched into the bottle at the bottom of the meniscus of the 60 ml of DI water.

7.4.4.1 Two different lines for the same volume (i.e. 60 ml) cannot be etched on the same bottle as thai may lead to confusion in the measurement of the final volume.

7.4.5 Repeat the steps in 7.4.2 through 7.4.4 using a 100 ml final volume instead of the 60 ml final volume.

7.5 Class A , lo deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outiined above.

7.6 Analytical Balance, 4 place. Calibration must be verified daily before use with NIST traceable weights.

7.7 Automatic pipettor bottles. The calibration on these bottles must be verified as outlined in EQA063.

7.8 Volumetric pipets, class A.

8.0 REAGENTS

All chemicals listed below are reagent grade unless othenwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed. Different reagents are required for the different healing techniques.

8.1 Digestion Block Reagents.

8.1.1 Aqua Regie: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated nitric.

8.1.1.1 Make sure to only prepare the amouni of acid that will be needed for the prep and analysis.

8.1.1.2 This preparation must be done in a hood.

8.1.2 Dilution Acid: To approximately 800 mi of DI water, add 37.5 ml of concentrated HCl and 12.5 ml of concentrated nitric acid. Dilute to 1000 ml with DI water and mix well. This dilution acid is used for making dilutions of digested samples from the digestion block digestion procedures.

8.1.3 Potassium permanganate, 5% solution: Dissolve 50 g of potassium permanganate in 1000 ml of DI water. Caution - Potassium permanganate is a strong oxidizing agent. Handle with care.

8.1.4 Stannous chloride. Add 7.5 ml of concentrated sulfuric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride and dissolve. Make sure that this solution is dissolved while in use.

8.1.4.1 Stannous sulfate may be used in place of stannous chloride.

8.1.4.2 If clogging occurs during analysis using the automated analyzer, then a less concentrated solution may be used.

8.1.5 Sodium chloride-Hydroxylamine hydrochloride or Sodium chloride-Hydroxylamine hydrosulfate. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

8.2 Mercury standard solutions.

8.2.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 mi of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water ahd mix well. This standard may be held for up to 28 days.

8.2.1.1 The 10 ppm external source should be made up using a different mercury stock, and following the directions in 8.2.1.

8.2.2 100 ppb Hg solution. Using a 1.00 mt volumetric pipette, add 1.00 mt of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

8.2.2.1 The 100 ppb external source should be made up following the directions in 8.2.2.

8.2.3 10 ppb Hg solution. Using a 10.0 ml volumetric pipette, add 10.0 ml of 100 ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.0 INTERFERENCES

9.1 Potassium permanganate is added to eliminate possible sulfide interferences. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. High copper concentrations (> 10 mg/kg) may also interfere wilh mercury recoveries.

9.2 Samples that are high in chlorides may require additional permanganate because, during the oxidation step, chlorides are converted lo free chlorine, which also absorbs radiation at 254 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and analyzed. This may be accomplished by using an excess of the hydroxylamine hydrosulfale.

9.3 Certain volatile organics may also absorb at this wavelength and can interfere.

10.0 GRAPHITE DIGESTION BLOCK PROCEDURE FOR SOIL DIGESTION

10.1 Make up a standard curve consisting of 5 standards and a blank. Suggested concentraiions are shown below. Different concentrations may also be used, as long as all of the melhod requirements are met. Make sure to clearly label each digestion lube. Calibration standards must be prepared fresh each day. Add 5 ml of DI water lo each standard before digestion. The final concentration of Hg is calculated in the final digestate.

Ml of 10 ppb Hg solution	ml of 100 ppb Hg solution	Total ug of Hg	ug/L of Hg
0.000	0.000	0.000	0.000
2.00	0.000	0.020	0.20
5.00	0.000	0.050	0.50
0.00	1.00	0.100	1.00
0.00	2.50	0.250	2.50
0.00	5.00	0.500	5.00

10.2 Samples. For each sample, homogenize the sample well and weigh out a 0.5 to 0.6 g aliquot of the sample into one labeled digestion tube. A solid lab control should be prepared in the same manner.

10.3 Make up additional quality control samples as shown below. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the method.) Make sure to clearly label each digestion tube. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve and al a different level lhan the CCV or the calibration standards. A low check standard is also required. This 0.20 ug/l check can be made up as outiined for the standard curve.

Sample ID	ml of 100 ppb Hg solution	ml of DIwater	µg/l of Hg
CCV Check(s)	2.5	7.5	2.5
MB	0.0	10.0	0.0
MS	2.0	0.0	2.0
MSD	2.0	0.0	2.0
Duplicate*	0.0	0.0	0.0
ICV	3.0	7.0	3.0

*Per project specification.

10.4 To all samples, QC, and standards add 5 ml of DI water and 5 ml of aqua regia and then heat for 2 minutes in a digestion block at 95 ± 3 °C. These reagents can be added with a bottle pipeltor that is accurale lo within 90 to 110%.

10.5 Cool the samples and then add 25 ml of DI water and 15 ml of potassium permanganate solution to each sample and mix thoroughly. Allow Ihe samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

10.5.1 These reagents can be added with a bottle pipettor that is accurate to wilhin 90 lo 110%.

10.5.2 For samples containing a mixture of solvent and water, take a sample aliquot of approximately 20 g (lower for higher solvent samples) of sample and add the reagents listed above. Pour the sample in a beaker and heat on a hot plate at 95 ± 3 °C until no solvent layer is visible. Then transfer the digestate to a digestion tube and proceed as outiined below. A method blank and spike blank must also be taken through tihs entire procedure.

10.6 Cap the samples and place them in the graphite digestion block for 30 minutes al 95 ± 3 °C. Record the temperalure and time for each digestion batch on ihe analysis sheet. Remove and cool.

10.7 Enter the prep dala into the LIMS system, double checking all weights and spike amounts. After the prep data is checked, it can be approved and is available for use In the final calculation.

11.0 MERCURY ANALYSIS PROCEDURE HYDRA AA

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outiined below. Additional instructions are available in the instmment operaiors manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure thai it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottie. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow il to warm up.

11.1.3.1 In the software, go to the Runner section and select the control tab. Click on the Hg lamp and the pump. The gas will turn on automatically when the pump is turned off. If can also be turned on separately if necessary. The pump rates and gas pressure are set in the protocol. Refer to the instrument maintenance manual for more informalion on setting up a new protocol. If the

Hg lamp needs to be optimized, it can be done using the lab adjust on this page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.5 In the software, go to the Utility tab and pick the gas controi test option. Tbe output should be approximately 7 psi and the input should be between 60 lo 90 psi. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.6 Start a batch lo save your data.

11.1.6.1 Go to the sample runner lab and click on start new batch. The batch name is limited to 8 characters. The batch should normally be named H1 or H2 followed by the month and date, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument 2 for 3/24/03 would be named H20324w1. The realtime print option can also be turned on from this tab.

11.1.7 Set up autosampler racks containing the samples that are going to be run.

11.1.7.1 Go lo main tab and click on the rack editor button. Enter your samples and the appropriate QC. CCV and CCB checks can be entered in the macro column. This tab may also be reached by clicking on the autosampler icon at the top of the page.

11.1.8 Set up the calibration.

11.1.8.1 Enter or verify the standard values. From the runner menu click on the standard lab. Click the buttons lo the left of the standards that are to be run. Also click on the number of replicates lo be run for each standard. Normally one replicate is run per standard. The standard concentrations are defined under the database menu under the line info lab. The check standard concentrations and acceptance ranges are also defined under this line info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Finish the preparation of the samples and standards as outlined below.

11.2.1 For samples that were digested in the water bath or the graphite digestion block, add 6 mi of hydoxylamine hydrochloride or hydroxylamine hydrosulfale to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

11.2.1.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

11.3 Measure out aliquots of the digested standards arid samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

11.4.1 Turn on the real time report by checking the real time printing option on the runner menu either under main or under sample. Then go to the runner menu and the standard tab. Push the standard auto button. The calibration curve will be run by the autosampler. When the curve is complete, go to the database menu and click the calibration curve tab. Check to make sure that all acceptance criteria are met and then accept the curve. See section 13.3 for calibration curve criteria. Make sure that the curve is printed as soon as it is accepted.

11.5 After the calibration has been accepted, start to run the samples.

11.5.1 Go to the mnner menu and the sample tab. Pick the autosampler rack that is to be run and type in the start cup and the end cup. Then push the button for run auto.

11.5.2 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see 8.1.2) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.6 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

11.6.1 Go to the data base menu and pick the report tab. Make sure that the correct report specification has been chosen (normally Accutest). Pick the batch that is to be printed and then push the generate report button. Generate both the electronic reports (prn file) and printed reports (report) from this menu.

11.7 The calculations are done in the LIMS as described beiow. . For soils, the calculation shown below is used. A final volume of 100 ntl is used for calculation purposes. (The final volume is factored but since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

11.8 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.9 Shut down the instruments.

11.9.1 To shut down the Hydra AA instrument, move the stannous chloride line from the stannous chloride bottle to the rinse container. Let the system rinse with 10% nitric for several minutes. Then switch the bath to DI water and let rinse for several more

minutes. Then empty the rinse bath and let the pump and gas run until the lines are completely dry. Go to Taskmaster and select the standby mode option. Release the tension on all of the pump clamps.

12.0 MERCURY ANALYSIS PROCEDURE HYDRA AA II

12.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators manual.

12.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

12.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

12.1.3 Turn on the analyzer and allow it to warm up.

12.1.3.1 Open the Envoy software. Go tp Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

12.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

12.1.5 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

12.1.6 Start a batch to save your data.

12.1.6.1 Create a new chapter (Data File) by clicking Analysis. The batch should normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch ori instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

12.1.7 Set up autosampler racks containing the samples that are going to be mn.

12.1.7.1 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

12.1.8 Set up the calibration.

12.1.8.1 For the Hydra AA II, go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

12.2 Finish the preparation of the samples and standards as outlined below.

12.2.1 For samples that were digested in the water bath or the graphite digestion block, add 6 ml of hydoxylamine hydrochloride or hydroxylamine hydrosulfate to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

12.2.1.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

12.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

12.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

12.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (i.e. IGV) and click start from here.

12.5.2 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see 8.1.2) and reanalyzed. it is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

12.6 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

12.6.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

12.7 The calculations are done in the LIMS as described below. For soils, the calculation shown below is used. A final volume of 100 ml is used for calculation purposes. (The final volume is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

12.8 Review the data in the LIMS, adding comments and accepting results as appropriate.

12.9 Shut down the instruments.

12.9.1 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

13.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

13.1 Instrument Detection Limits (IDLs). The instrument detection limits are determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of 7 consecutive replicates of a standard solution at a concentration from 3 to 5 times the estimated detection limit. IDLs must be done quarterly (every 3 months) for each Instrument.

13.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

13.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards must be digested using the same procedure as the samples. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met.

13.3.1 A linear calibration using the equation $y = mx + b$ is applied where m is the slope and b is the intercept. The calibration is not forced through zero.

13.3.2 The correlation coefficient is calculated using the following equation:

$$Correl(X,Y) = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

where x is the measured absorbance and y is the standard concentration.

13.3.3 If the calibration curve does not meet criteria, and is redigestion, then any samples digested along with that calibration curve must aiso be redigested.

13.4 Initial Calibration Verification Standard (ICV)). During each analysis, a standard from a different source than the calibration standard should be analyzed. Normally this is analyzed at the beginning of the run. For this method, the ICV shoutd be within 10 percent of the true value. When the measurements exceed these controt limits, the analysis shall be terminated, and the problem corrected before proceeding. All reported results must be bracketed by compliant QC. The exception is, if the ICV is biased high (110 to 150 % recovery) and no mercury is found in the samples, then the sampte results may be reported for mercury.

13.5 Continuing Catibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 20 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.)

13.6 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not tess than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

13.7 CRA (Low) Check or LLQC (Lower Limit of Quantitation Check). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A criterion of 50 to 150% recovery is apptied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

13.7.1 A number of clients have specific program requirements for frequency and recovery ranges on CRA checks. Check with the metals supervisor for additional information on these programs.

13.7.2 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

13.8 Method Blank. The laboratory must digest and analyze a method blank with each batch of 20 samples. A minimum of one method blank is required for every 20 samples. A sample batch is defined as a maximum of 20 field samples In a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required

every 20 samples. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 limes the melhod blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

13.9 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample or spike blank wilh each set of samples. A minimum of one lab control or spike blank is required for every 20 samples. Note: For soils, if a lab conlrol is not available, a spike blank can be used. For a running batch, a new lab conlrol sample ls required for each different digestion day. The laboratory should assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120%. In house lab conlrol limits may aiso be generated to support these default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. ff the lab control is outside of the control limits for a given element, all samples must be redigested and reanalyzed for lhat element. The exception is if the lab control recpvery is high and the results of the samples to be reported are less than the reporting limit. In lhat case, the sample results can be reported wilh no flag.

13.10 Matrix Spike. The laboratory must add a known amouni of each analyle lo a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The laboratory should assess the matrix spike recovery against control limits of 80 to 120. (In house control limits are generated annually for information purposes only.). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the conlrol limits and should be footnoted lo lhal effecl. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

13.11 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sartiple for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the original sample should be assessed. The rpds are calculated as shown below and should be assessed against a limit of 20% RPD. (In house conlrol limits are generated annually for information purposes only.). If a matrix spike duplicate or a duplicate is out of control, then the results should be flagged with the appropriate footnote. if the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: Bolh the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is beated as zero.

$$\frac{(\text{Sample Result - Duplicate Result}) \times 100}{(\text{Sample Result + Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|MS\ Result - MSD\ Result|) \times 100}{(MS\ Result + MSD\ Result)/2} = MSD\ RPD$$

14.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

14.1 Sample Worksheets. Digestion data sheets for the Hg soil samples must show all digestion information including the sample ID's, sample weights, bottle numbers, type of heating used, start times, end times, and pressure or temperature, as appropriate for all digestions. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the comments sections. Make sure also that all dilutions are clearly documented.

14.2 Make sure to record thermometer ID, correction factor, and corrected and uncorrected temperatures for all temperature measurements.

14.3 Standards and Reagents. All stocks and reagents must be recorded in the reagent log book. All standards should be recorded on the digestion log with the samples.

14.4 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

14.5 Annual bottle calibration verifications must be documented in the Mercury Bottle calibration log.

15.0 DATA REVIEW AND REPORTING

15.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

15.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

15.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP.

All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in seciion 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes.

16.2.3 Chlorinated organic solvents.

16.2.4 Non-chlorinated organic solvents.

16.2.5 Hazardous solid wastes.

16.2.6 Non hazardous aqueous wastes.

17.0 ADDITIONAL REFERENCES

17.1 Leeman Hydra AA instrument manual.

17.2 Leeman Hydra AA II instrument manual.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager Nancy Cole

QA Manager Greg Gordonich for Phil Worley

Effective Date: 9/12/11

TITLE: DIGESTION OF NON-POTABLE WATERS FOR ICP OR ICP-MS ANALYSIS.

REFERENCES: SW846 3010A

Revised Sections: 8.5, 10.3.5

1.0 SCOPE & APPLICATION

1.1 This method is applicable for the digestion of aqueous samples, TCLP extracts, and wastes that contain small amounts of suspended solids. After digestion, the samples can be analyzed by ICP or by ICP-MS. This digestion method is based on SW846 3010A.

2.0 SUMMARY

2.1 Samples for metals analysis are digested on a hot plate or in a digestion block at 90 to 95° C to solubilize the metals before analysis. Nitric and hydrochloric acids are used for digestion.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. See determinative method.

3.2 Method Detection Limit. MDLs must be established using a solution spiked at approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of three replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs must be determined approximately once per year for frequently analyzed parameters.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a batch. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specifled in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: ff control limits are not specified In the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyle to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike dala is available lo generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sampie cannot be assessed against the control limits and must be footnoted to lhat effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Inlralaboratory split samples spiked with identical concentrations of target analyle(s). The spiking occurs prior to sample preparation and analysis. They are used lo documeni the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Resull})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new melhod blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent lo the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the melhod blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is wheri the samples to be reported contain greater than 10 times the method blank level. In addition, if ali the samples are less lhan a ciient required limit and the method blank is also less than lhat limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confldence lhat the analyte concentration is greater lhan zero and is determined from analysis of a sample in a given matrix conlaining the analyte. MDLs are determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank lhat has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination Introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the melhod blank.) Either a reagent blank or a melhod blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over

the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. All digestions must be done in a hood. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Expose to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of date handling sheets must be made available to all personnel involved in these analyses.

6.0 COLLECTION, PRESERVATION, & HOLDING TIMES

6.1 All samples must be preserved with nitric acid at the time of collection to a pH of < 2.

6.1.1 Samples received without preservation must be preserved following the specifications in the Accutest QSM.

6.2 All samples must be digested and analyzed within 6 months of the time of collection.

7.0 APPARATUS AND MATERIALS

7.1 The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses may be used in place of the digestion block and digestion tubes.

7.2 Digestion block. Temperature adjustable and designed to hold sample digestion tubes and capable of maintaining temperatures from 90 to 95°C.

7.3 Thermometers, calibrated with NIST traceable thermometers. To be used to monitor digestion temperatures.

7.4 Sample digestion tubes and ribbed watch glasses.

7.4.1 If sample digestion tubes are used to measure initial and final volumes, then they must be calibrated following the procedure outlined in EMP203, the digestion tube calibration SOP.

7.5 Automatic pipeter bottles.

7.6 50 ml volumetric flasks or 50 ml TD volumetric cylinders (Class A).

7.6.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with distilled, deionized water.

7.7 Glass funnels.

7.8 Whatman #41 filter paper or equivalent.

7.9 Volumetric pipets, class A.

7.10 pH paper.

8.0 STANDARDS & REAGENTS

8.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required.

8.2 Hydrochloric acid. Baker instra-analyzed or equivalent.

8.3 Nitric Acid. Baker instra-analyzed or equivalent.

8.4 Metals Spiking Solutions. All metals spiking solutions must be made up in a solution of 2 % nitric acid following the procedures outlined in the metals standards preparation SOP.

8.5 Hydrogen Peroxide, 30%. (Used only if sulfur is an analyte of interest).

9.0 INTERFERENCES

9.1 Organics in a matrix may cause interferences if the sample is not digested rigorously enough. In addition, high levels of acids in the final digestate may cause interferences in the analysis. Both of these interferences can be avoided by choosing the appropriate digestion method and by bringing the sample to an appropriate final volume. For a discussion of other interferences, refer to specific analytical methods.

10.0 PROCEDURE

10.1 Below is the procedure to be followed for the digestion of aqueous samples prior to ICP or ICP-MS analysis.

10.2 Before starting the analysis, check the initial pH of the sample with pH paper and verify that it is < 2. If it is < 2, then enter a Y in the pH check column on the metals prep logs. If the sample is not < 2, then adjust it to < 2 with nitric acid and record both the initial and final pH on the digestion log.

10.2.1 For highly basic or buffered samples, where more than a few drops of acid are required, adjust an aliquot of the sample rather than the whole amount and record the amount of acid used for the adjustment.

10.2.2 Samples for TCLP matrix or leachate spikes will be received unpreserved from the TCLP leaching area. These must be aliquoted, spiked, and preserved on receipt in the metals prep area.

10.2.3 For some clients, additional documentation of the pH adjustment is necessary. For all samples from Ohio, the pH adjustment must be noted in the case narrative or conformance summary for the samples.

10.3 Measure out 50 ml of each sample into a labeled digestion tube or into a beaker. The sample may be measured by using a graduated cylinder or by using a calibrated digestion tube. Make sure that the sample identification is accurately recorded with the digestion tube/beaker numbers on the sample digestion log. In addition to the samples, a Spike Blank or a Lab Control and a Method Blank must be set up with each batch of 20 samples or less. A Matrix Spike and a Matrix Spike Duplicate (or Matrix Duplicate) must be set up with each batch of 20 samples. Matrix Spike Duplicates are normally used unless otherwise specified by client requirements. Check with the metals supervisor for spiking levels to use for the matrix spikes and the spike blank or lab control.

10.3.1 For the method blank, add 50 ml of deionized water to the digestion tube.

10.3.2 For the lab control, add 50 ml of lab control solution to the digestion tube. Refer to the metals spiking solution SOP, EMP202, for information on the preparation of the lab control solution.

10.3.3 For the matrix spike and matrix spike duplicates, add the spiking solution directly to the 50 ml of sample in the designated tubes. Refer to the metals spiking solution SOP, EMP202, for information on the preparation and amounts of spiking solution required.

10.3.4 TCLP blank spikes must be prepared using 50 ml of the appropriate TCLPE extraction fluid.

10.3.5 If the sample is going to be analyzed for sulfur by method 6010, then add 5 ml of peroxide at room temperature to the sample and QC and let them sit for 30 minutes before proceeding. The purpose of this step is to oxidize any sulfide that is present before the digestion.

10.4 Add 1.5 ml of concentrated nitric acid to all quality control and samples.

10.5 Place the labeled tubes into a digestion block and cover with watch glasses. (If using beakers, cover the beakers with watch glasses and place them on a hot plate.) Heat the samples at 90 to 95°C until they come to a gentle reflux and then continue to heat the samples until they are evaporated to near dryness, for example 10 ml or less. After the heating is complete, allow the samples to cool.

10.5.1 Watch glasses may be removed if necessary to allow for faster volume reduction, but should be left on for the maximum time possible to limit contamination.

10.6 Add an additional 1.5 ml of concentrated nitric acid to all quality control and samples. Continue heating the samples at a gentle reflux until the sample is completely digested. (More acid may be added as necessary to complete the digestion.)

10.6.1 Signs of a complete digestion are if the digestate is light in color and/or if the appearance of the sample does not change with continued refluxing.

10.7 Add 5 ml of 1:1 HCl to each sample and reflux for an additional 15 minutes.

10.8 Wash down the beaker walls and watch glass with Dt water. Bring the sample to a final volume of 50 ml with deionized water. The sample is now ready for analysis by ICP.

10.8.1 If the sample contains particulate, it can be filtered through Whatman # 41 filter paper (or equivalent) before analysis. If any samples in a batch are filtered, then all of the associated quality control must also be filtered in the same manner.

10.8.2 For ICP-MS analysis, the digestate is normally further diluted at the instiument before analysis (at least by a factor of 2) and the dilution factor must be added to the instrument file.

11.0 QUALITY ASSURANCE

11.1 A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required every 20 samples.

11.2 For each digestion batch of 20 samples or less, a lab control (and a spike blank) and a method blank is prepared. Besides a lab control, a spike blank is also digested when analyzing the odd elements, such as B, Si, Sr, Sn and Pd.

11.3 For every 20 samples, digest a matrix spike/matrix spike duplicate pair instead of a matrix spike/ duplicate pair unless otherwise requested by a client.

11.4 Refer to the analytical methods SOPs for additional information on method quality control.

12.0 DOCUMENTATION

12.1 All digestion information must be entered on a digestion log. The information required includes the sample identification, the initial sample volume, the final sampie volume, the initial sample pH, the acids used (including both amount and lot number), the spikes used, and the digestion times and temperatures, and the thermometer identification. Both the corrected and uncorrected temperatures must be recorded. If filtration is done, the filter type and lot must also be recorded.

12.2 The analyst must write additional information such as unusual sample characteristics In the Commenis section. All spiking solution information must be entered in the metats spiking solution notebook.

13.0 DATA REVIEW & REPORTING

13.1 The prep analyst is responsible for updating the samples to SCH status in the LIMS system and for entering the prep information into the LIMS. This may be done manually or electronically. When the prep information is in the LIMS, the completed paperwork must be turned into the metals supervisor for review.

13.2 The supervisor or a metals analyst reviews the preparation information and approves the data in the LIMS system.

13.3 The original papenvork is submitted to the report generation department for filing.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform alt procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards,

reagents, and solvents must be limited to the amounts specified in this SOP. Ali safety practices designed lo limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in seciion 14.2.

14.2 Waste Management. Individuals performing this melhod must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes.

14.2.3 Chlorinated organic solvents.

14.2.4 Non-chlorinated organic solvents.

14.2.5 Hazardous solid wastes.

14.2.6 Non-hazardous solid wastes.

15.0 ADDITIONAL REFERENCES

15.1 Refer to the ICP and ICPMS analytical SOP's, the spiking procedure SOP (EMP202), and the digestion tube calibration SOP (EMP203).

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:_____

QA Manager:_____

Effective Date: _____

TEST NAME: DIGESTION OF SOILS FOR ICP AND ICP-MS ANALYSIS

REFERENCE: SW846 3050B (Revision 2, December 1996)

Revised Sections, 10.2.3, 10.2.4, 12.1

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the digestion of sediments, soils, sludges, solid wastes, and wipes. After digestion, the samples can be analyzed by ICAP or by ICP-MS (or by graphite furnace AA for antimony). This digestion method is based upon SW846 method 3050B, Revision 2, 12/96.

2.0 SUMMARY

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Then hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals, this digestate is filtered and the filter paper and residues are rinsed, first with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.2 In method 3050B, the final HCl addition is not included for ICP-MS digestates as chloride is an interference for a number of elements on ICP-MS. However, the HCl is necessary for good solubility of many elements. HCl interferences at the ICP-MS can normally be addressed with corrections at the ICP-MS. Therefore it is recommended that HCl be added for ICP-MS digestions by this method unless otherwise directed by the lab supervisor or manager.

2.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 See determinative method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every **20** samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. if the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than **10** times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with **99%** confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK. The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of **20** samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than **10** times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE. Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and mustd be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe

handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Non-aqueous samples should be refrigerated at the time of receipt.

6.2 All samples should be digested and analyzed within 6 months of the time of collection.

7.0 INTERFERENCES

7.1 Sludge and soil samples can contain diverse matrix types, which may contain a variety of interferences. Spiked samples can be used to determine if these interferences are adequately treated in the digestion process. For a discussion of other interferences, refer to specific analytical methods.

8.0 APPARATUS

8.1 The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses might be used in place of the digestion block and digestion tubes.

8.2 Digestion block. Temperature adjustable and designed to hold sample digestion tubes and capable of maintaining temperatures from 90 to 95°C.

8.3 Thermometers, calibrated with NIST traceable thermometers. To be used to monitor digestion temperatures.

8.4 Sample digestion tubes and ribbed watch glasses.

8.5 Automatic pipeter bottles.

8.6 100 ml volumetric flasks.

8.7 Glass funnels.

8.8 Whatman #41 filter paper.

8.9 Top loader balance.

8.10 Volumetric Pipets, class A.

8.11 Disposable Wood Spatulas

8.12 Ceramic Mixing Bowl.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required.

9.2 Hydrochloric acid. Baker instra-analyzed or equivalent.

9.3 Nitric Acid. Baker instra-analyzed or equivalent.

9.4 Hydrogen Peroxide, 30 %.

9.5 Metals Spiking Solutions. All metals spiking solutions should be made up in a solution of 2 % nitric acid as described in Table 1. Use volumetric glassware and pipets or autopipets. Check with the metals supervisor for additional information. Different levels of spiking solutions may be used as specified by the area supervisor.

9.5.1 The expiration date for the spiking solution is defined as the eariiest date of any element or compound in that solution.

9.6 Tefion Chips

10.0 PROCEDURE

10.1 Weigh out an amount of wet sample equivalent to 1 g of dry sampie into a numbered digestion tube. The sample should be weighed out using a top loader balance and the weights should be recorded to two places past the decimal. Make sure that the sample identification is accurately recorded with the digestion tube numbers on the sample digestion log.

10.1.1 Make sure that the sample has been thoroughly mixed before weighing out the representative sample. Discard rocks, sticks, etc. from the sample. (Refer to the SOP EQA042 for proper sample aliquoting procedures). All homogenization and sample handling should be done with wooden spatulas and ceramic (or other non-metal) bowls.

10.1.2 If the sample has a low percent solids, a larger sample size may be used to obtain a weight approximately equivalent to 1 g of dry sample. Check with the metals supervisor for additional direction with sampled with low percent solids or unusual matrices.

10.1.3 If the sample is a wipe, weighing is not necessary. Transfer the entire wipe into the labeled digestion tube and proceed with the digestion following steps 10.2 through 10.10. Extra wipes must be supplied by the client for the matrix spike or duplicate.

10.2 In addition to the samples, a spike blank or a lab control and a method blank must be set up with each batch of 20 samples or less. A matrix spike, a matrix spike duplicate or a duplicate should be set up with each batch of 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. Refer to Table 1 for spiking levels to use for each MS and Spike Blank.

10.2.1 For the method blank and spike blank, instead of weighing out soil add approximately 1 g of Teflong chips to the digestion tube. Add the spiking solution to the blank spike after the chips are in the tube.

10.2.2 For some clients, a solid lab control is required rather than a blank spike. In that case, the solid lab control must be weighed out in the same manner as a sample.

10.2.3 For the matrix spike and matrix spike duplicate, refer to the metals spiking SOP, EMP202, for information on the preparation and amount of spiking solution require to be added to the sample in the digestion tube.

10.2.4 For the matrix spike and matrix spike duplicate, refer to the metals spiking SOP, EMP 202, for information on the preparation and amount of "odd metals spike" is to be added to the sample in the digest tube when necessary.

10.2.5 For additional details on spiking solutions and preparation, refer to the metals spiking sop, EMP202.

10.3 Add 10 ml of 1:1 nitric acid to all Quality Control and samples.

10.4 Place the numbered tubes into a digestion block and cover with watch glasses. (If using beakers, cover the beakers with watch glasses and place them on a hot plate.) Heat the samples at 90 to 95°C until they come to a gentie reflux and then continue to heat the samples for an additional 10 to 15 minutes. Do not allow the samples to boil. After the heating is complete, allow the samples to cool.

10.5 Add an additional 5ml of concentrated nitric acid to all quality control and samples. Heat the samples at a gentie reflux for an additional 30 minutes. Do not allow the volume to be reduced to below 5 ml. Cool.

10.5.1 If brown fumes are generated during this digestion, add an additional 5ml aliquot of concentrated nitric acid and heat for 30 more minutes. Repeat this process until no more brown fumes are generated.

10.6 Continue the digestion at 90 to 95°C until the volume is reduced to 5 ml or for a period of 2 hours. Do not let the samples boil at any point during the digestion process.

10.7 Add 2 ml of water and 3 ml of 30 % hydrogen peroxide to each sample and reflux until the effervescence subsides. Cool.

10.7.1 The 30% hydrogen peroxide may be added in smaller or larger initial aliquots depending on the sample characteristics. If sample effervescence is suspected to be a problem, smaller aliquots should be used.

10.8 Continue to add 30 % hydrogen peroxide in 1ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. NOTE: Do not add more than a total of 10 ml of 30 % hydrogen peroxide. Continue the digestion at 90 to 95°C until the volume is reduced to 5 ml or for a period of 2 hours.

10.9 Add 10 ml of concentrated HCl and reflux for an additional 15 minutes.

10.9.1 HCl may be omitted for some ICP-MS digestions for limited elements (As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, and Tl) at the discretion of the area supervisor or manager. However, in normal circumstances it should be added. Refer to section 2.2.

10.10 Filter the digestate through Whatman #41 filter paper (or equivalent) into 100 ml volumetric flasks. Make sure to rinse the digestion tubes and the filter paper well with deionized water. Dilute to volume with deionized water. The sample is now ready for analysis.

10.10.1 For ICP-MS analysis, the digestate should be further diluted at the instrument before analysis (normally at least by a factor of 2 to 5) and the dilution factor should be added to the instmment file.

11.0 QUALITY ASSURANCE

11.1 For each digestion batch of 20 samples or less, a lab control or a spike blank and a method blank should be prepared. Besides a lab control, a spike blank is also digested when analyzing the odd elements, such as B, Si, Sr, Sn and Pd.

11.1.1 Solid lab controls are required for some clients. Check with the metals supervisor for additional information.

11.2 For every 20 samples, a matrix spike, a matrix spike duplicate or a duplicate should be prepared. Matrix spike duplicates are normally used unless otherwise specified by the client requirements.

11.3 If a batch is a running batch, samples can be added to the batch (along with a method blank and spike blank or lab control) up to a maximum of 2 weeks.

11.3.1 Running batches are not allowed for all clients. Check with the metals supervisor for additional information.

11.4 Refer to the analytical methods SOPs for additional information on method quality control.

12.0 DOCUMENTATION

12.1 All digestion information should be entered on a digestion log. The information required includes the sample identification, the initial sample weight, the final sample volume, the acids used (including both amount and lot number), the spikes used, and the digestion times, temperatures, and the thermometer identification. Both the corrected and uncorrected temperature must be recorded.

12.2 The analyst should write additional information such as unusual sample characteristics in the Comments section. All spiking solution information should be entered in the metals spiking solution notebook.

12.3 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.4 Certificates of analysis for all primary stocks must be kept on file. If a certificate is received in the lab, give the original to the area supervisor for submission for filing with the QA department.

13.0 DATA REVIEW & REPORTING

13.1 The prep analyst is responsible for updating the samples to SCH status in the LIMS system and for entering the prep information into the LIMS. This may be done manually or electronically. When the prep information is in the LIMS, the completed paperwork should be turned into the metals supervisor for review.

13.2 The supervisor or a metals analyst reviews the preparation information and approves the data in the LIMS system.

13.3 The original paperwork is submitted to the report generation department for filing.

13.4 Supervisory (or peer) personnel will review and sign all reagent documentation a minimum of once per month.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.2 Non hazardous aqueous wastes.

14.2.3 Hazardous aqueous wastes.

14.2.4 Chlorinated organic solvents.

14.2.5 Non-chlorinated organic solvents.

14.2.6 Hazardous solid wastes.

14.2.7 Non-hazardous solid wastes.

15.0 ADDITIONAL REFERENCES

15.1 Refer to the ICP and ICPMS analytical SOP's and the spiking procedure SOP (EMP202).

TABLE 1: SOIL SPIKING SOLUTION FOR 6010B (1.0 g sample)

Spiking Solution	Element	Stock Conc. in mg/l	Vol. of Stock in ml	Final Vol. of Spiking Solution in ml	Spiking Solution Conc. in mg/l	Amt of spike added in ml	Final Digestate Vol. in ml	Final Conc. at the instrument in mg/l
Mixed ICP Metals	Al	200.00	NA	NA	200.00	2.00	100.00	4.00 +
	Sb	50.00			50.00			1.00
	As	200.00			200.00			4.00
	Ba	200.00			200.00			4.00
	Be	5.00			5.00			0.10
	Cd	5.00			5.00			0.10
	Cr	20.00			20.00			0.40
	Co	50.00			50.00			1.00
	Cu	25.00			25.00			0.50
	Fe	100.00			100.00			2.00 +
	Pb	50.00			50.00			1.00
	Mn	50.00			50.00			1.00
	Ni	50.00			50.00			1.00
	Se	200.00			200.00			4.00
	Ag	5.00			5.00			0.10
	Tl	200.00			200.00			4.00
	V	50.00			50.00			1.00
	Zn	50.00			50.00			1.00
Soil Mineral Mix	Al	10000.00	50.00	200.00	2500.00	2.00	100.00	50.00 +
	Fe	10000.00	50.00	200.00	2500.00			50.00 +
	Ca	10000.00	12.50	200.00	625.00			12.50
	Mg	10000.00	12.50	200.00	625.00			12.50
	K	10000.00	12.50	200.00	625.00			12.50
	Na	10000.00	12.50	200.00	625.00			12.50
Odd Melals	B	1000.00	20.00	200.00	100.00	1.00	100.00	1.00
	Mo	1000.00	20.00	200.00	100.00			1.00
	Sn	1000.00	20.00	200.00	100.00			1.00
	Sr	1000.00	20.00	200.00	100.00			1.00
	Ti	1000.00	20.00	200.00	100.00			1.00
	Pd	1000.00	20.00	200.00	100.00			1.00
	Si	1000.00	40.00	200.00	200.00			2.00
	W	1000.00						

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:_____

QA Manager:_____

Effecttve Date: _____

TITLE: TOTAL ORGANIC CARBON IN SOILS SAMPLES

METHOD REFERENCES: "Procedures for Handling and Chemical Analysis of Sediment and Water Samples" prepared for the US EPA Corps of Engineers, May 1981, modified, and SW846 Method 9060, September 1986, modified, and EPA Region 2 Lloyd Kahn Method, July 1988.

Revised Sections: 8.1, 10.2 *(all)*, 4.0 Definition of MDL

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine total organic carbon in any solid matrix. It may also be used for liquid matrices containing a high level of total organic carbon. Samples that are primarily aqueous may also be analyzed using this method, but sample sizes should be limited to $\leq$ 0.10 g.

1.2 The product code for total organic carbon is TOC for the Corp. of Engineers methods and for the modified SW846 9060 method. The product code is TOCLK for total organic carbon run by the Lloyd Kahn EPA Region 2 method.

2.0 SUMMARY OF METHOD

2.1 Total organic carbon is determined by combusting an acidified sample and quantitating the carbon dioxide released using infrared analysis. The quantitation is done by comparison to a linear calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 The normal reporting limit for TOC in soils is 1000 mg/kg. This is based on a 0.1 g sample size. A minimum reporting limit of 100 mg/kg can be obtained by using a 1.0 g sample size. A reporting limit of 100 mg/kg is required for samples being analyzed for Lloyd Kahn TOC. A low level calibration standard is run at the level of this reporting limit.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria. Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier or limits defined in the SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK SAMPLE. Digest and analyze a high and a low standard with each batch of samples. These standards must have a recovery of 90 to 110 %. If the spike blank is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

LAB CONTROL SAMPLE. A solid lab control sample from an external source may be distilled with a batch, depending on individual client requirements. The solid lab control is evaluated using manufacturer's limits. If the lab control is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance agaihst the control limits that are specifled in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in controi. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. If a matrix spike is out of control, then the results should be fiagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMIT (MDL) The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if alt the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The furnace operates at high temperature and the furnace should be allowed to cool down before doing any system maintenance or troubleshooting. If there are any signs of a system blockage, open the sample introduction port and turn off the furnace to prevent build up of back pressure.

5.3 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Soil samples should be kept under refrigeration at 4^0 C until they are analyzed.

6.2 No holding time is outlined in the Corp. of Engineers method for TOC. SW846 9060 specifies a holding time of 28 days for aqueous samples. Unless otherwise specified, this 28-day holding time will also be applied to solid samples analyzed using this SOP.

6.3 A 14 day holding time should be followed when analyzing TOC soils following the EPA Region II Lloyd Kahn method.

7.0 INTERFERENCES

7.1 High results may be obtained if the inorganic carbon is not completely removed from the sample before analysis. To ensure that all of the inorganic carbon is removed, heat an acidified sample at least 10 minutes at 75°C before starting the analysis. Some volatile organics may be lost in this heating step, resulting in a low bias in the TOC result.

8.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

8.1 Shimadzu 5000 TOC analyzer or TOC-V analyzer with soil analysis module or equivalent.

8.1.1 Each day of analysis, the humidifier should be checked to ensure that the water level is within 1 inch of the top of the humidifier.

8.1.2 Each day of analysis, the baseline should be checked to make sure that it is stable and near zero.

8.1.3 Whenever calibration check recoveries or blanks are out of compliance, the flow and the condition of the catalyst should be checked. If the catalyst appears bad (contains many small fines), it should be cleaned and replaced. Refer to the instrument manuals for additional information on system maintenance.

8.2 Syringes, 0.100 ml size.

8.3 Analytical balance, capable or weighing to 0.1 mg. The calibration of the analytical balance should be verified each day before use.

8.4 Volumetric glassware, class A, for standards preparation.

8.5 Ceramic boats.

8.6 Drying oven, capable of being set to 75°C

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water taken from the DI tap with the carbon filter should be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent logbook.

9.1 Sucrose Stock Solution, 200000 mgC/l (20% C from sucrose): Dry sucrose in dissector. Weigh out 47.5 grams into a 100 ml volumetric flask containing approximately 80 ml of DI water. Add concentrated hydrochloric acid to bring the pH to less than 2. Mix well and bring to a final volume of 100 ml. Note: This stock should be replaced whenever crystallization of the sucrose is apparent. It can be held for a maximum of 3 months. Refrigeration is not required.

9.2 Sucrose Standard Solutions: Dilute the above stock solution (200000 mC/l) as shown below to make the suggested calibration standards. Add concentrated hydrochloric acid to bring the pH to less than 2 before diluting each standard to the final volume.

9.2.1 Different standards may be used, but a minimum of 5 standards and a blank are required for the initial calibration. The top standards shown below are close to the top of the linear range of the instrument and sometimes will not work at these levels.

9.2.2 Two suggested curve levels are shown below. These standards must be held for no longer than one month.

9.2.3 High curve. Either the 50000 mgC/l or the 40000 mgC/l may be used as the highest standard. Both are not required.

Standard Level	ml of stock	Final volume (ml)
50000 mgC/l	25.0	100
40000 mgC/l	20.0	100
25000 mgC/l	12.5	100
10000 mgC/l	10.0	200

5000 mgC/l	5.00	200
1000 mgC/l	1.00	200
Blank	0.000	100

9.2.4 Lower curve.

Standard Level	ml of stock	Final volume (ml)
25000 mgC/l	12.5	100
20000 mgC/l	10.0	100
10000 mgC/l	10.0	200
5000 mgC/l	5.00	200
1000 mgC/l	1.00	200
Blank	0.000	100

9.3 Glucose Stock solution, 50000 mgC/l (5% C from glucose): Dry glucose in dessicator. Weigh out 12.5 grams into a 100 ml volumetric flask containing approximately 80 ml of DI water. Add concentrated hydrochloric acid to bring the pH to less than 2. Mix well and bring to a final volume of 100 ml. Note: This stock should be replaced whenever crystallization of the glucose is apparent. It can be held for a maximum of 1 month. Refrigeration is not required.

9.4 Glucose Check Solution, 25000 mgC/l (2.5% C from glucose): Dilute 50.00 ml of the glucose stock solution (50000 mC/l) to approximately 80 ml with DI water. Add concentrated hydrochloric acid to bring the pH to less than 2 and then dilute to a final volume of 100 ml with DI water. This solution should be made up monthly.

9.4.1 A different concentration of this check solution will be needed if a lower curve is run.

9.4.2 This is from a separate source than the calibration curve and can be used as the ICV check.

9.5 Nitric Acid, reagent grade. Used for acidifying samples to remove inorganic carbon.

9.5.1 Dohrman Instruments recommends that phosphoric acid not be used for this purpose. Dohrman found that the phosphoric acid tended to coat both the boat and the catalyst in the furnace with a layer of polyphosphoric acid and that, possibly as a consequence of this, the release of inorganic carbon as carbon dioxide was slower than with nitric acid and possibly incomplete.

9.6 Oxygen Gas, high purity.

9.7 Pre-baked cat litter or silica sand.

10.0 PROCEDURE

10.1 Below is the procedure to be followed for the analysis of soil samples for total organic carbon using the Shimadzu TOC soil analyzer. For the procedure with the newer Shimadzu TOC-V soil analyzer, refer to step 10.2. (More details for use of the software can be found in the TOC-V CPH/CPN users manual.)

10.1.1 Turn on the oxygen. The pressure in the soil module should be set at 2 and the carrier gas should be set as marked on the dial (0.5 l/min). The oxygen pressure at the tank must be at least 60 psi to maintain sufficient pressure at the instrument. Check to make sure that the humidifier contains sufficient water. It should be filled to within approximately 1 inch of the top of the humidifier. (The humidifier is located under the magnetic plate on the right side of the instrument.)

10.1.2 If the power is off, then turn on the power at the side of the soil and water modules and for the computer.

10.1.3 Go into the TOC software on the TOC. Select measure and then connect. Wait for the software to connect with the TOC analyzer. Proceed to options and then instrument conditions. Under TOC, there should be no check next to Furnace on. Under ASI, there should be no check next to ASI used. Under SSM, the TOC furnace should be turned on.

10.1.4 Go to view and click on the background monitor. A graph will appear on screen showing the position of the baseline and the status of the furnace temperature. Wait for the baseline to stabilize and for the furnace temperature to indicate that it is OK. Make sure that the hatch on the boat sampler is tightiy closed and that there are no leaks in the system. If the baseline is not within ± 10 of zero, then the zero of the instrument may need to be adjusted. Check with the lab supervisor or manager for further instructions.

10.1.5 If the instrument has not been calibrated within the last month, then it is recommended that it be calibrated at this point. (A new calibration is required at least once per quarter.)

10.1.5.1 Select a new file and insert standards. A minimum of 2 injections must be used for each standard. Five standards and a blank are required for the calibration. The lowest standard should be at 1000 mgC/l or lower. A 100 ul injection size should be used for all standards.

10.1.5.2 After the standard file is created and inserted into the run file, then save the run file using the save as command. The file should be named with the instrument ID (A or B), the last digit of the year, the month, the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on instrument A from 3/28/01 would be named A10328s1.

10.1.5.3 Press start in the software and follow the prompts. Place a clean boat filled with a small tuft of glass wool in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch and push the boat all the way fonward. Enter OK at the software.

10.1.5.4 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.1.5.5 Select the option to repeat the injection and repeat the steps outiined above.

10.1.5.6 When all of the standards have been completed, then review the curve using the view, calibration option.

10.1.5.6.1 If a correlation coefficient of greater than 0.995 is obtained, then save the curve using the file, save option. Check to make sure that the intercept, calculated using a weight of 1.0 g for Lloyd Kahn or using a weight of 0.1 g for other TOC analyses, is less than the reporting limit for each method (100 mg/kg for Lloyd Kahn or 1000 mg/kg for other TOC soils.)

10.1.5.6.2 If either the correlation coefficient or the intercept does not meet the above criteria, than recalibrate before proceeding with the samples.

10.1.5.7 If a previous calibration is being used, then it must be verified with a low and a high standard and a blank before proceeding on each analysis day. The low standard must be within 30 percent of the true value. All other check standards must be within 10 percent of the true value. The blank must contain less than the reporting limit for TOC. Make sure to use duplicate injections for all analyses. Note: The method blank may be used as the calibration blank check.

10.2 Below is the procedure to be followed for the analysis of soil samples for total organic carbon using the Shimadzu TOC-V soil analyzer.

10.2.1 Turn on the oxygen. The pressure in the water module should be set at 200 Kpa and the carrier gas should be set as marked on the dial (150 ml/min). The oxygen pressure at the tank must be at least 60 psi to maintain sufficient pressure at the instrument. Check to make sure that the humidifier contains sufficient water. It should be filled to within the two white lines on the side of the humidifier. (The humidifier is located inside the water analyzer at the right side of the instrument.)

10.2.2 If the power is off, then turn on the power at the side of the soil modules and at the bottom right of the front panel of the water moldule and for the computer.

10.2.3 Go into the TOC software on the TOC. In the TOC-Control V main window, double click on the sample table editor and click OK on the user name box.

10.2.4 Before starting the run, open the background monitor to make sure that the baseline is stable and the furnace is up to temperature. If there are problems at this point, check with the lab supervisor or manager for further instructions.

10.2.5 Click File, New, and choose Calibration Curve and click OK. Follow the directions on each screen. For the system, pick TOC-V with SSM. Click on the calibration points. Then enter the file name. The file should be named with the instrument identifier (A or B or C), year (1 digit), the month (2 digits), the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on

instrument C from 3/12/07 would be named A70312s1. Enter the file name and then go to the volume. Enter the concentration and number of points. Edit the points to correct the concentrations. Enter next until the last screen is reached and then click on finish.

10.2.5.1 If using a previously generated calibration, then this step can be omitted. A new calibration is required at least once per quarter, but it is recommended that this be run once per month.

10.2.6 Go back to the TOC-Control V main window and double click the sample table editor. Click File and New to open the sample run icon. Click the system tab and select the TOC-SSM system. Click on the new file and follow the prompts on the screen. Name the file using the convention as described above.

10.2.7 Connect to the instrument using the connect toolbar button or from the instrument menu. Insert the calibration file created above into the sample table. You must load the new curve into the method before running the samples.

10.2.8 To start running the calibration, press start in the software and follow the prompts. Place a clean boat filled with a small tuft of glass wool in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch. Enter 100 ul into the volume prompt and then hit start. Wait for the prompt and then push the boat forward.

10.2.9 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.2.10 When all of the standards have been completed, then review the curve using the view, calibration option. If a correlation coefficient of greater than 0.995 is obtained and the intercept is less than the RDL, then save the curve and put it into the method(s) that you are running. Then you can proceed to add samples.

10.6 After the calibration or calibration checks are completed, then analyze the external check standard made from glucose. This standard must agree within 10 percent of the true value. If it is not within this range, determine the source of the problem before proceeding. Note: The spike blank may be used as the external calibration check, but then the results must be within 10 percent of the true value.

10.7 After every 10 samples, a continuing calibration check (CCV) sample must be analyzed. The continuing calibration check should be a standard near the mid-range of the curve. The continuing calibration check should agree within 10 percent of the true value. If the CCV is not within 10% of the true value, then no samples can be reported in the area bracketed by this CCV unless the CCV is biased high (110 to 150%) and the sample results to be reported are less than the reporting limit.

10.8 For some clients, a continuing calibration blank (CCB) may be required. This is not required as part of the normal TOC protocol. If it is required, than it should be run after each CCV check. The results of the CCB must be less than the reporting limit for TOC. If the CCB is

not less than the reporting limit, then no samples can be reported in the area bracketed by this CCB unless the samples results to be reported are less than the reporting limit.

10.9 Begin analyzing the samples following the procedure outlined below.

10.10.1 Weigh out from 100 to 1000 mg of sample (wet weight) into a ceramic boat using a 4-place analytical balance. For samples that contain high levels of TOC smaller sample sizes may be needed. For unknown samples, start with a sample size of 100 mg. (All method blanks and spike blanks should be calculated assuming a 100 mg sample size and should be set up using silica sand or pre-baked cat litter.) Samples that contain non-homogeneous particulates should be homogenized with a mortar and pestle before weighing out the sample aliquot.

10.10.1.1 If a client is requiring a detection limit lower than 1000 mg/kg, then larger sample sizes are required. A detection limit of 100 mg/kg requires a weight of 1 gram. A smaller sample size may be used only to bring the sample to within the range of the calibration curve.

10.10.1.2 If less than 50 mg is used for a sample to bring it within linear range, then 4 replicates must be analyzed at that weight.

10.10.2 Add nitric acid dropwise to the sample until no additional effervescence is observed and the surface of the sample is covered with the acid. Heat the acidifled sample in an oven at 75°C for a minimum of 10 minutes.

10.10.3 If the duplicate sample injections have a coefficient of variation (CV) of greater than15 percent or an RPD of greater than 20%, then repeat the analysis with 2 additional duplicate injections. If, on the repeated analysis, a high CV or RPD is still obtained, then the sample results should be reported with a flag due to possible sample non-homogeneity. This 15% CV or 20% RPD criteria does not apply if the sample results are low and the results are within plus or minus the reporting limit of each other.

$$CV = (\text{Std Dev}_{n-1} / \text{mean}) \times 100$$

$$RPD = (\text{Result1} - \text{Result 2})) \times 100/\text{mean}$$

10.10.4 With each batch of 20 samples or less, a matrix spike and a duplicate should be analyzed. On each analysis day, a method blank and spike blank must be analyzed. All of these quality control points must be analyzed in duplicate.

10.10.4.1 Prepare the method blank by treating a small amount (approximately 100 mg) of pre-baked cat litter or silica sand with nitric acid and heating at 75 ° C for a minimum of 10 minutes.

10.10.4.2 Prepare the spike blank in the same manner as the method blank, but spike it with 100 ul of a 20000 mgC/l standard or external solution before adding the acid. Note: The spike blank can be used in place of the external check, but then must be prepared from the external source and must meet the 10 % check criterion.

10.10.4.3 Prepare the duplicate in the same manner as a sample.

10.10.4.4 Prepare the matrix spike by adding 100 ul of a 20000 mgC/l standard or external solution to a sample aliquot before adding the acid and heating the sample.

10.10.5 At the end of the analysis, a continuing calibration check must be analyzed. If the calibration check is not within 10 percent of the true value then all samples bracketed by the out of compliance CCV must be reanalyzed. (If the CCV is within 110 to 150%, then samples with results <RDL may be reported.)

10.10.6 If required, a CCB should be analyzed after the final CCV check of the analysis. Refer to Section 10.9.

10.11 The final sample results are calculated using the equation shown below. The calculation is done automatically in the Shimadzu TOC software except for the percent solids correction. The percent solids correction is added when the data is transferred in the LIMS system. See area supervisor or manager for further details.

Organic Carbon, Total (mg/kg) =

$$\frac{\text{Conc. from curve (ug)}}{\text{sample weight in g x \%sol/100}}$$

11.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.1 Method Detection Limits (MDLs). MDLs should be established using a blank sample spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year.

11.2 Calibration Curve. The instrument must be calibrated a minimum of once per quarter. It is recommended that the instrument be calibrated at least once per month. The calibration curve must have a correlation coefficient of at least 0.995 and the intercept must be less than the reporting limit. If the instrument is not calibrated on a given day, then the curve must be verified using a low and a high standard and a blank before proceeding on each analysis day. The low standard must be within 30 percent of the true value. All other check standards must be within 10 percent of the true value. The blank must contain less than the reporting limit for TOC.

11.3 Method Blank. The laboratory must prepare and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different analysis day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that

limit, the samples must reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.4 Spike Blank. The laboratory must prepare and analyze a spike blank with each set of 20 or less samples. For a running batch, a new spike blank is required for each different analysis day. The laboratory should assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. (If the spike blank is used in place of the external, then it must be within recovery limits of 90 to 110 percent.) If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. In all other situations, all samples associated with a spike blank outside of recovery limits must be reanalyzed.

11.5 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. (Note: For Florida samples, spikes should be prepared for 1 in 10 samples.)

11.5.1 The spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

11.5.2 The matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.6 Matrix Duplicate. The laboratory must prepare and analyze a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. Matrix spike duplicates may be used in place of matrix duplicates. The duplicate rpd is calculated as shown below.

11.6.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

11.6.2 This duplicate fills the requirement for quadruplicate injections for one sample in 20 for the TOCLK method.

11.6.3 The duplicate RPD should be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \text{\% RPD}$$

11.7 Quality Control Sample (also referred to as Initial Calibration Verification Standard, (ICV)). A standard from a separate source than the calibration should be run at the beginning of

each run. This ICV should be within 10 percent of the true value. If it is not, the problem must be resolved before any samples can be analyzed. Note: The spike blank may be used in place of the ICV as long as a separate source standard is used and the 10 percent criterion is met.

11.8 Continuing Calibration Verification (CCV). Analyze the continuing calibration verification solution after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high (111 to 150%) and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

11.9 Continuing Calibration Blank (CCB). For some clients, a continuing calibration blank (CCB) may be required. This is not required as part of the normal TOC protocol. If it is required, than it should be run after each CCV check. The results of the CCB must be less than the reporting limit for TOC. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by this CCB unless the sample results to be reported are less than the reporting limit.

12.0 DOCUMENTATION REQUIREMENTS

12.1 Each analyst should review all data and assemble a data package consisting of the following information. This data package should be turned into the supervisor for review after the analysts complete their LIMS review (see 12.3 below).

- Results report, showing dilutions, replicate injection results, and CV or RPD results.
- Preparation/mn log showing weights taken at the balance for each injection.
- Standards prep sheet.
- Reagent information sheet.
- QC Summary sheet with calculations

12.2 In addition, all reagent information such as lot numbers should also be recorded in the reagent log book. Any unusual characteristics of the samples should be noted on the raw data or on the preparation log. Make sure that all sample ID's and dilutions are labeled on the data.

12.3 An ASCI format file should be generated and copied over to the LIMS. The analyst is responsible for reviewing the data in the LIMS and adding appropriate spike amounts and true values before sending the data for supervisor approval.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This

document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 ADDITIONAL REFERENCES

14.1 Shimadzu Instrument Manual

ACCUTEST LABS
STANDARD OPERATING PROCEDURE

Lab Manager_____

QA Manager_____

Effective Date:_____

SOP Titte: GRAIN SIZE AND SIEVE TESTING

METHOD REFERENCE: ASTM D422-63

Revised Sections: 14.2, 14.3, 5.1, 5.2, 15.2

1.0 SCOPE AND APPLICATION

1.1 This method is used as a quantitative determination of the distribution of particle size in soils. The distribution of particle sizes larger than 75pm (retained on the number 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75pm is determined by a sedimentation process, using a hydrometer.

2.0 SUMMARY OF METHOD

2.1 An air-dried sample is divided into two portions; one portion is retained on a number 10 sieve and the second portion contains only particles that pass the number 10 sieve. The portion retained on the number 10 is separated into a series of fractions using as many sieves as needed depending on the sample. The portion passing the number 10 sieve is soaked in a dispersing agent for 16 hours, vigorously stirred, transferred to a sedimentation cylinder, and allowed to settle for a period of up to 24 hours with hydrometer readings taken at specific intervals.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit is not application for this method. Results are reported as a percent of the total sample weight.

3.2 Method Detection Limit. Method Detection limits studies are not required for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is analyzed at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is

available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. if the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outiined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All samples should be kept under refrigeration at 4^0 C until they are analyzed.

6.2 No specific holding time is listed in this method.

7.0 INTERFERENCES

7.1 No interferences are specified in this method.

8.0 APPARATUS

The following items are needed for the analysis of samples following the method outiined below:

8.1 Sieves, a series of sieves, of square-mesh woven wire cloth giving uniform spacing of data points for graph. The series of sieves listed below is recommended. An alternate series of sieves is also allowed in the method.

Sieve Name	Particle size
3 in	75.0 mm
1.5 in	37.5 mm
¾ in	19.0 mm
3/8 inch	9.5 mm
No. 4	4.75 mm
No. 8	2.36 mm
No. 10	2.00 mm
No. 16	1.18 mm
No. 30	0.600 mm
No. 50	0.300 mm
No. 100	0.150 mm
No. 200	0.075 mm

8.2 Four decimal place analytical balance. The balance must have its calibration verified with Class S weights

8.3 Stirring apparatus. A mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10000 rom without a load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber. Humboldt model 936 stirrer or equivalent should be used in the lab.

8.4 Dispersion cup equipped with baffle rods. Humboldt model H-2465 or equivalent should be used in the lab.

8.5 Hydrometer, 152H, meeting ASTM specifications. (Hydrometer 151H may also be used as described in the method, but this SOP describes the use of hydrometer 152H.)

8.6 Sedimentation cylinder marked for a volume of 1000 ml and an inside diameter such that the 1000-ml mark is 36 ± 2 cm from the bottom on the inside.

8.7 Thermometer accurate to 1°F (0.5°C)

8.8 Timing device, watch or clock with a second hand

8.9 Beakers, at least 250-ml capacity

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent log book. All chemicals must be low in silica.

9.2 Dispersing Agent, dissolve 40 gm of sodium metaphosphate (sometimes called sodium hexametaphosphate) in DI water with stirring and dilute to 1 liter. **NOTE:** If acidic, solutions of this salt will slowly hydrolyze back to the orthophosphate form with a decrease in dispersive action. New solutions should be made at least once a month or be adjusted to pH of 8 or 9 by means of sodium carbonate.

10.0 SAMPLE PREPARATION PROCEDURE AND SIEVE ANALYSIS
(Note – refer to Figure 1 for a summary of the steps in Sections 10 and 11.)

10.1 Weigh out a sample aliquot of approximately 100 to 200 g. Enough dried sample must be obtained to have 65 g of clay or silt or 115 g of sand that passes through the number 10 sieve. Spread the sample aliquot out evenly on a piece of aluminum foil or other clean surface. Let the sample air dry until dry in appearance. If the sample forms a crust during the drying processing, use a spatula to break up the crust and prevent water from being trapped below the crust. Mix the dried sample well.

10.2 Place an aliquot of the dried sample in the mortar and break it into small pieces with a rubber covered pestle. All clay clumps, etc. should be broken apart. Weigh out enough sample to have approximately 65 g of clay or silt sample passing through the Number 10 sieve or 115 g of sandy sample passing through the Number 10 sieve. Record the final weight.

10.3 Sieve the sample through the number 10 sieve. Shake the sieve stack laterally and vertically, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments of the sample through the sieve by hand. Continue shaking until not more than 1% of the mass remaining on the sieve passes that sieve during 1 minute of shaking. **NOTE**: Do not overload the sieve to the extent that the soil that would normally be retained on that sieve interferes with the soil that would normally pass through the sieve).

10.4 Pour the sample remaining on the top of the Number 10 sieve back into the mortar and use the pestle to again break up any clumps of clay or dirt.

10.5 Pour this sampie back into the number 10 sieve and repeat the sieving process outlined in step 10.3.

10.6 Combine all sample going through the number 10 sieve into a separate container and save for additional sieve testing, moisture testing, and hydrometer testing as outlined below.

10.7 Take the sample remaining on the number 10 sieve and wash it with a small amount of water to remove any dust, etc. still adhering to the particulate. If insignificant dust remains on the sample, then this step may be omitted. Air dry the sample and record the final weight.

10.8 Separate the sample portion retained on the number 10 sieve into a series of fractions using as many sieves as needed depending on the sample or upon the specifications for the material being tested. The normal series of sieves used include the 3 inch sieve, the 1.5 inch

sieve, the ¾ inch sieve, the 3/8 inch sieve, the number 4 sieve, and the number 8 sieve. Follow the following protocol for each sieve.

10.8.1 Shake the sieve stack laterally and vertically, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments of the sample through the sieve by hand. Continue shaking until not more than 1% of the mass remaining on the sieve passes that sieve during 1 minute of shaking.

10.8.2 When the step 10.8.1 is complete for a given sieve, then weigh the portion of sample remaining on the sieve and record the weight.

10.9 Weigh out an aliquot of approximately 10 g of the sample portion passing through the number 10 sieve (from section 10.6) and record the weight. Dry the aliquot to constant mass at 110 ± 5°C. Constant mass is defined as a change of less than 0.01 in the hygroscopic moisture correction factor. Calculate the hygroscopic moisture correction factor by dividing the mass of the oven dried sample by the mass of the air dried sample. (This correction factor will be used to correct the remaining test material mass to determine an accurate dry mass for the sample in the hydrometer testing).

10.10 Perform the hydrometer testing as outiined in Section 11 using the air dried sample that passed through the number 10 sieve. After the hydrometer testing is complete, pour the suspended sample through a number 200 sieve and wash well with DI water. Then dry the sample in an oven at 110 ± 5°C until completely dry.

10.11 Separate the oven-dried aliquot into a series ef fractions using as many sieves as needed depending on the samples or upon the specifications for the material being tested. The normal series of sieves used include the number 16 sieve, the number 30 sieve, the number 50 sieve, the number 100 sieve, and the number 200 sieve. Follow the steps outlined above in 10.8.1 and 10.8.2 for the sieving process.

10.11.1 If hydrometer testing is not performed, then oven dry the whole aliquot of sample to be used for the sieves smaller than number 10.

10.12 Calculate the percentage of sample passing through each sieve. This can be done using the calculation template or it can be calculated by hand.

10.12.1 The equation to be used to calculate the percentage of the sample passing through the number 10 or larger sieve is shown below.

% of sample passing through the sieve (number 10 and larger) =

$$\frac{100 \times (\text{tot. sample wt} - (\text{wt retained on sieve of interest} + \text{wt retained on all larger sieves}))}{\text{tot. sample wt}}$$

10.12.2 The equations to be used to calculate the percentage of the sample passing through a sieve smaller than number 10 are shown below. These calculations include a correction factor to take into account the size of the aliquot used. Note that the weight of the aliquot is the weight of sample put into the hydrometer when

hydrometer testing is done as the sample is poured through the number 200 sieve when it is first removed from the hydrometer.

A = (wt retained on sieve of interest + wt retained on ali larger sieves under 10)

$$\text{Fraction of aliquot} = \frac{(\text{wt. of aliquot} - A)}{\text{wt. of aliquot}}$$

$$\%\ \text{passing through sieve} = \text{Fraction of aliquot} \times \frac{\text{air dry weight passing through 10}}{\text{total air dry weight sieved}}$$

10.13 Calculate the percentage in the sample of gravel, sand, and silt, clay, and colloids. Gravel is defined as the sample passing through the 3 inch sieve and retained on the No. 4 sieve. Sand is defined as the sample passing through the No. 4 sieve and retained on the No. 200 sieve. Silt, clay, and colloids are defined as sample passing through the No. 200 sieve.

11.0 HYDROMETER ANALYSIS PROCEDURE

11.1 Determine hygroscopic moisture correction factor as described in section 10.9 above.

11.2 Determine the Composite Correction for Hydrometer – In a sedimentation cylinder, add 125 ml of the dispersing agent and dilute with DI water to 1000 ml (control sample).

11.2.1 Adjust the temperature of the control sample to 20 deg. C.(or to the lowest temperature expected during the measuring process.) Place the thermometer and the hydrometer into the control sample. Record the hydrometer and thermometer readings. Record the composite correction faction which is the difference between the hydrometer reading and zero.

11.2.1.1 The hydrometer should be read at the top of the meniscus formed on the stem.

11.2.2 Adjust the temperature of the control sample to 24 deg. C.(or to the highest temperature expected during the measuring process.) Place the thermometer and the hydrometer into the control sample. Record the hydrometer and thermometer readings. Record the composite correction faction which is the difference between the hydrometer reading and zero.

11.2.3 Use the known composite correction factors and temperatures to determine composite correction factors at different temperatures in the range tested.

11.3 When the soil is mostly clay and silt sizes, weigh out approximately 50 g of air-dried soil. When the soil is mostly sand, weigh out approximately 100 g. Record the weight used. Place the sample aliquot into a beaker and cover with 125 ml of the sodium metaphosphate solution (5.1). Stir until the soil is thoroughly wetted. Allow it to soak for at least 16 hours.

11.4 After soaking, pour the sample into the dispersion cup, making sure to wash any sediment remaining in the original sample container into the dispersion cup with deionized water. Add deionized water so that the cup is more than half full and stirr for a period of 1

minute. Immediately after dispersion, transfer the slurry to the sedimentation cylinder, making sure all of the sample is removed from the beaker by using a wash bottle. Dilute to the 1000-ml mark on the cylinder with DI water.

11.5 Using Parafilm and the palm of the hand over the open end of the cylinder (or a robber stopper), turn the cylinder upside down and back for a period of 1 minute to complete the agitation of the slurry. Any soil remaining at the bottom of the cylinder during the first few turns, should be loosened by vigorous shaking while the cylinder is in the inverted position. The number of turns should be about 30, counting the turn upside down and back as one turn.

11.6 Set the sample cylinder next to the control cylinder and take hydrometer readings for the sample and the control at the following time intervals: 2, 5, 15, 30, 60, 250 (4 hours and 10 minutes), and 1440 minutes (24 hours).

11.6.1 When it is time to take a reading, record the temperature and the uncorrected hydrometer reading of the control sample on the data sheet. Then insert the hydrometer into the soil sample cylinder at the approximate depth it will have when the reading is taken (insert hydrometer 20 to 25 seconds before scheduled reading time). Record the uncorrected hydrometer reading for the sample on data sheet. The hydrometer should be read at the top of the meniscus formed on the stem

11.6.2 Clean the hydrometer after each reading in deionized water and store in deionized water between readings. They hydrometer should not be left in the sample after the reading.

11.7 Calculate the final particle sizes and percent smaller than a given diameter using the following equations. These calculations may be done manually or may be done in a spreadsheet.

11.7.1 Percentage of soil in suspension (percent smaller than a given diameter of soil) = (R x a)/W

where R = hydrometer reading with composite correction applied
a = correction factor from Table 1
W = 100 x (air dried mass used for hydrometer x hygroscopic moisture correction factor)/% passing through No. 10 sieve)

Note: Specific gravity of the soil is needed for Table 1. If the specific gravity is not listed on the table, extrapolate to an appropriate correction factor.

11.7.2 Diameter of soil particles = $K (L/T)^{1/2}$

Where K = constant taken from Table 3
L = effective depth taken from Table 2
T = time interval in minutes

Note: Specific gravity of the soil is needed for Table 3. If the specific gravity is not listed on the table, extrapolate to an appropriate K value.

11.7.3 Plot the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. Read back the percentage of particles smaller than 0.075 mm, 0.005 mm, and 0.001 mm from the graph and record on the data sheet for entry into the LIMS. Note: depending on the conditions of the experiment, there may not be data for the percentage of particles at 0.001. In that case, report the percentage of particles at the lowest diameter available and footnote the result with the actual diameter.

12.0 QC REQUIREMENTS

12.1 A summary of the main quality control requirements are given below. Other requirements specific to a given client or matrix may also be required. Check with the supervisor or manager to determine if there are additional quality control requirements.

12.2 A hydrometer control should be analyzed periodically or whenever a new hydrometer is used.

12.3 A duplicate should be analyzed with each batch of 20 samples or less. Control limits are compiled by Accutest annually and should be used to determine if matrix problems are present. If the duplicate is outside of the control limits, and all other quality control is within limits, then no reanalysis is necessary, but the QC results must be footnoted to indicate possible sample non-homogeneity or matrix interferences. Until control limits can be generated, default control limits of 20% rpd should be applied.

13.0 DOCUMENTATION REQUIREMENTS

13.1 The analyst should document all relevant information, including all sample weights, all sample and control analysis results, and any relevant comments.

13.2 All reagent identification numbers should be recorded on the sample worksheets. In addition, all reagent information such as lot numbers should also be recorded in the reagent log book.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to QC batches in the LIMS system. The analyst should calculate all sample results and all duplicate RPD's. They should verify that all calculations are complete and that all reagents are documented and traceable.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The supervisor is also responsible for making sure that the QC calculations are done correctly and responsible for reviewing the data entry into the LIMS. No LIMS entry review is necessary when the data is electronically transferred.

14.3 After the supervisor or designated reviewer completes their review, the data is released for client access in the LIMS. The raw data is submitted to the area manager. The department manager does an additional periodic review on the sample data as appropriate. The raw data is then filed electronically in the report generation department.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

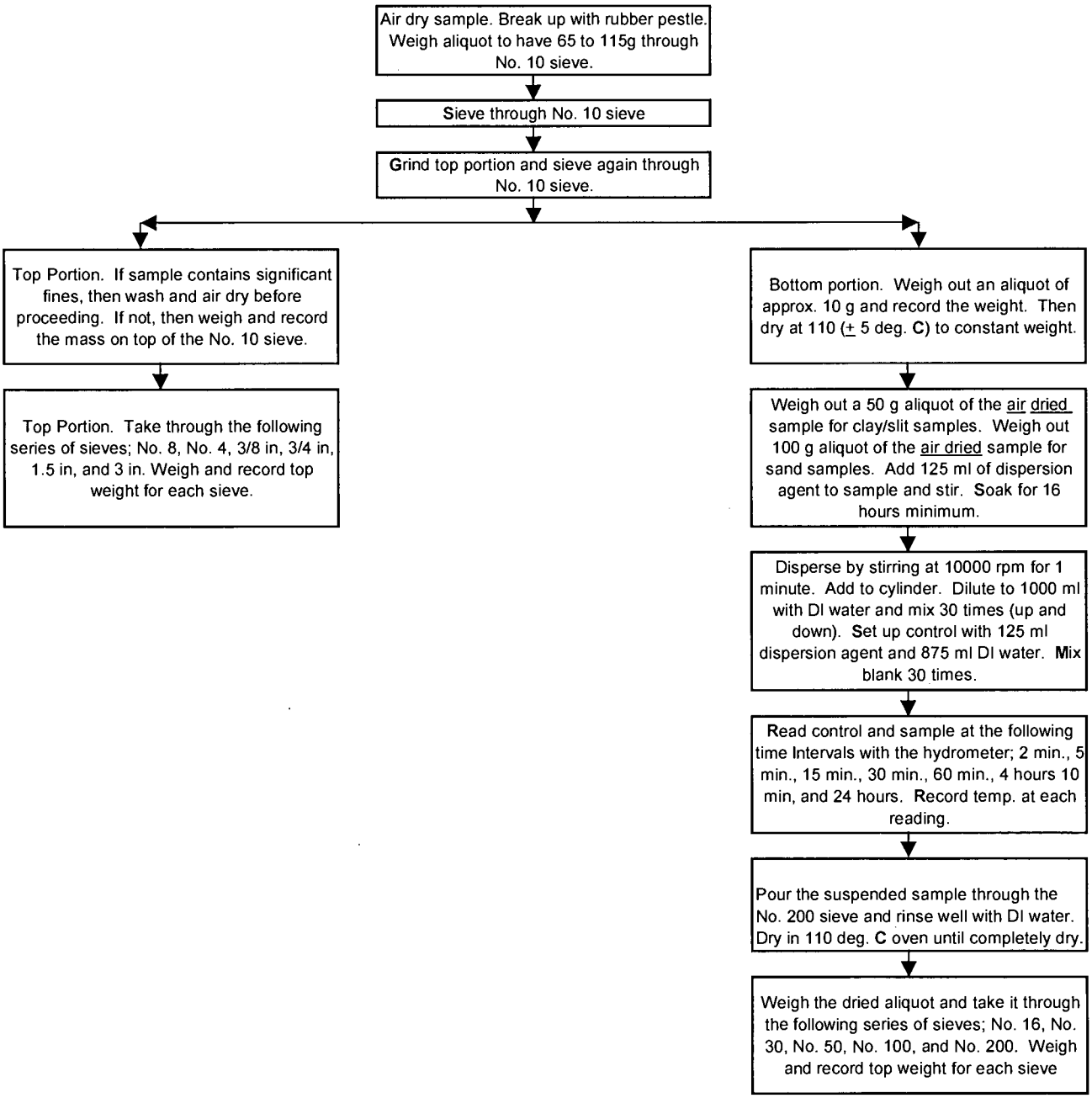
16.0 ADDITIONAL REFERENCES

16.1 Refer also to ASTM D421-85 for additional details on preparation of the soil samples.

16.2 Refer to ASTM D422-63 for Tables 1, 2, and 3

16.3 Refer to SOP EGN247 for the process to use to determine soil specific gravities.

FIGURE 1: SIEVE AND HYDROMETER PROCESS FLOW CHART



Inductively Coupled Plasma - Mass Spectrometry

References: Method 6020A, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Draft Update IVA, May 1998.

Method 6020, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update II, September 1994

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Name: John Kowalski Position: Metals Department Manager

Signature: _____ Date: 7/6/2011

Authorized By:

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Signature: Joseph Watkins Date: 7/11/11

ISSUE AMENDMENTS

Changes since last issue:

Edited signatories.

Inductively Coupled Plasma - Mass Spectrometry

References: Method 6020A, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Draft Update IVA, May 1998.

Method 6020, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update II, September 1994

1. Scope and Application

Matrtces: Inductively coupled plasma-mass spectroscopy (ICP-MS) is applicable tp the determination of multi-element trace metals in water and other aqueous samples (surface and saline waters, groundwaters, domestic and industrial wastes), toxicity characteristic leaching procedure (TCLP) extracts, acid-volatile sulfide – simultaneously extractabie metals (AVS-SEM)) and solid samples (soils, sediments, sludges, and tissues).

Deffnittons: Refer to Alpha Analytical Quality Manual.

Inductively coupled plasma-mass spectroscopy (ICP-MS) determines traee metal concentrations in solution. The method is applicable to all of the metals and matrices listed below. This method is approved for use in compliance monitoring programs such as the Clean Water Act (NPDES). All matrices, with the exception of dissolved metals samples, require extraction and/or digestion prior to analysis. The metals listed in the tables of Section 16 can accurately be determined in the range of 0.2 pg/L to 50,000 pg/L for aqueous samples, and tn the range of 0.02 to 5000 mg/Kg for solid samples, for samples that do not require dilution.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of lhe modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the ICPMS and in the interpretation of ICPMS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarteriy laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

Parameter	CAS	Parameter	CAS	Parameter	CAS
Aluminum (Al)	7440-36-0	Copper (Cu)	7440-50-8	Strontium (Sr)	7440-24-6
Antimony (Sb)	7440-36-0	Iron (Fe)	7439-89-6	Silver (Ag)	7440-22-4
Arsenic (As)	7440-38-2	Lead (Pb)	7439-92-1	Sodium (Na)	7440-23-5
Barium (Ba)	7440-39-3	Magnesium (Mg)	7439-95-4	Thallium (Tl)	7440-28-0
Beryllium (Be)	7440-41-7	Manganese (Mn)	7439-96-5	Tin (Sn)	7440-31-5
Boron (B)	7440-42-8	Molybdenum (Mo)	7439-98-7	Titanium (Ti)	7440-32-6
Cadmium (Cd)	7440-43-9	Nickel (Ni)	7440-02-0	Vanadium (V)	7440-62-2
Calcium (Ca)	7440-70-2	Potassium (K)	9/7/7440	Zinc (Zn)	7440-66-6
Chromium (Cr)	7440-43-9	Selenium (Se)	7782-49-2		
Cobalt (Co)	7440-48-4	Silicon (Si)	7440-21-3		

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2. Summary of Method

An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately measured or weighed for sample preparation. Prior to analysis, all samples, with the exception of samples requiring dissolved metal analysis, must be "solubilized" or digested in acid using the appropriate sample preparation methods as noted in above. Dissolved metals do not require acid digestion if the samples are filtered and acid preserved prior to analysis. Once the samples have been digested, they are ready for analysis by ICP-MS.

This analytical method entails the simultaneous multi-elemental determination of sub-pg/L concentrations of many trace metals by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Samples are nebulized and the resulting aerosol is transported to the plasma torch by argon gas. The ions produced by a radio-frequency inductively coupled plasma are then introduced into a quadrapole mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

2.1 Method Modifications from Reference

The calibration blank is used as a reference to monitor changes in internal standard recoveries in QC samples and client samples. This deviates from the refererice method which suggests the use of the initial calibration standard. The instrument software can not be changed to perform this analysis. There is no apparent impact to the quality of the data as indicated by successful analysis of PT samples over the period of operation of the instrument.

3. Reporting Limits

Reporting Limits are listed in Table 1.

4. Interferences

4.1 Isobaric elemental interferences occur when an isotope of one element is at the same nominal mass-to-charge ratio (m/z) as an isotope of another element (*i.e.*, Mo 98 and Ru 98). Corrections for isobaric interferences may be made by measuring the intensity due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Most commonly used corrections for isobaric interferences are already present as default interference equations in the ELAN NT software. A list of the corrections used is given in the listing of the isotopes monitored in the 6020A method in Table 3 of this SOP.

Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample. Extreme caution should be exercised when reporting metal concentrations where the "apparent concentration" from an interfering element accounts for 90% of the measured concentration. This can be estimated by closely monitoring the concentrations of the non-spiked metal concentrations in the daily analysis of the ICSA solution.

4.2 Isobaric molecular and doubly-charged ion interferences are caused by ions consisting of more than one atom or charge. Common molecular interferences include ArCl, ClO, nitrogen dimer, oxygen dimer, and oxide species. Most isobaric interferences have been identified in the literature. Isobaric molecular interferences can often be corrected for in the same manner as isobaric elemental interferences, i.e., measuring the intensity present at

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another isotope and using isotope ratios to calculate the amount of the interfering species. For example, corrections for interferences of $Ar^{40}Cl^{35}$ on As at mass 75 may be made by measuring the intensity of ArCl present at mass 77 ($Ar^{40}Cl^{37}$) and converting to the apparent intensity of ArCl at mass 75 by using the isotopic ratio of Cl^{37} to Cl^{35}. A list of the corrections used is given in the listing of the isotopes monitored in the ELAN 6020 method in Table 3 of this SOP.

It may be possible to eliminate or minimize isobaric interferences by using the DRC ICP /MS equipped with a reaction cell. See Section 11.9.

Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample. Extreme caution should be exercised when reporting metal concentrations where the "apparent concentration" from an interfering element accounts for 90% of the measured concentration. This can be estimated by closely monitoring the concentrations of the non-spiked metal concentrations in the daily analysis of the ICSA solution

4.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Differences in solution volatility can also cause inaccuracies when organic solvents are involved. if physical interferences are present, they must be reduced by diluting the sample. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The argon flow rate is controlled with a mass flow controller. Changing the nebulizer and removing salt buildup at the tip of the torch sample injector is used as an additional measure to control salt buildup when there is an obvious decrease in instrument sensitivity. An internal standard can also be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similariy affected by matrix changes. When the intensity level of an internal standard is outside of the 70% - 120% range for Method 6020A then the sample must be reanalyzed at a 5 X dilution.

4.4 Memory interference results when analytes in a previous sample contribute to the signals measured in a new sample. Sample deposition and buildup on the sampler and skimmer cones can be minimized by flushing the system with rinse blanks between samples. A normal rinse time of 60 seconds can be increased if memory interference is suspected. Any sample suspected of having memory interference must be reanalyzed.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. Alt Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and

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before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept AlphaNet.

5.2 Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at all times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting devise and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

5.3 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely defined; however, each chemical compound shall be treated as a potential health hazard. From this viewpoint, exposure to chemicals must be reduced to the lowest possible level by whatever means available. All standards and reagents shall be prepared in a hood while using the proper PPE.

5.4 Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Section Head Supervisor immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Section Head Supervisor immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

5.5 Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintain an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

5.6 Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

5.7 Care must be taken when handling all liquid samples, digestates, and standards since they are preserved to a pH <2.

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6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Aqueous Samples for total metal analysis: The volume of sample required is dependent on the analyses requested. Typically, a 500 mL of sample is collected in plastic or glass containers. Samples of this volume should be preserved with 2 mL of 1:1 nitric acid per liter of sample (pH ≤ 2) at time of collection.

Solid samples: A minimum of 10.0 grams of sample must be collected in a glass jar.

6.2 Sample Preservation

Aqueous Samples for total metal analysis: Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions should be acidified with nitric acid to a pH ≤ 2 upon receipt at the laboratory. Following acidification, the sample must be held for a minimum 16 hours before pouring an aliquot for sample digestion. If conditions do not permit field preservation, this must be noted on the COC and in the laboratory case narrative.

Aqueous samples for dissolved metal analysis: Samples may be fietd filtered and preserved. If the laboratory is required to filter the samples, the sample must be filtered through a 0.45-pm membrane filter. Glass or plastic filtering apparatus must be acid rinsed to avoid possible contamination. A plastic apparatus must be used when determination of boron or silica is critical. Use a portion of the filtered sample to rinse the filter fiask, discard this portion and collect the required volume of filtrate. Immediately following filtration acidify the filtrate with nitric acid to a pH ≤ 2.

6.3 Sample Shipping

None.

6.4 Sample Handling

Aqueous Samples for total metal analysis: The samples can be stored at room temperature or can be refrigerated and maintained at 4°±2°C until digestion and analysis. All aqueous samples must be analyzed within 6 months from date of collection

Solid samples: The samples must be refrigerated and maintained at 4°±2°C until digestion and analysis. All solid samples must be analyzed within 6 months from the date of collection. The hold time for samples that require AVS/SEM analysis is 21 days.

Note: Although mercury is not typically analyzed by ICP-MS, the hold time for samples that require mercury analysis is 28 days.

7. Equipment and Supplies

7.1 Perkin-Elmer ELAN 6100 or ELAN DRCe inductively coupled argon plasma – mass spectrometer (ICP-MS): Capable of providing resolution better than or equal to 1 amu at 10% peak height. The system has a mass range from 6-240 amu with a data system that allows for correction for interferences and the application of the internal standard technique.

7.1.1 ELAN 6100 and DRCe computer system

7.1.2 ELAN software

7.1.3 Printer

7.1.4 Mixing block manifold for on-line addition of internal standards

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7.1.5 Autosampler
7.1.6 Peristaltic pump tubing

7.1.6.1 Sample Introduction; Black/Black - 0.76 mm (0.030") i.d

7.1.6.2 Internal Standard Introduction; Green/Orange - 0.38 mm (0.015") i.d.
7.1.6.3 Drain; Black/White – 3.18 mm (0.125") i.d

7.1.6.4 Rinse; Red/Red - 1.14 mm (0.045") i.d

7.1.6.5 Making Connections; Blue/Blue - 1.65 mm i.d

7.1.6.6 Making Connections; Purple/Purple -2.06 mm i.d

7.2 Liquid Argon - 99.999% purity and regulator.

7.3 Oxygen: High purity gas and regulator

7.4 Ammonia: High purity gas and regulator

7.5 Glassware - Assorted Class-A volumetric flasks, beakers, graduated cylinders and pipettes of appropriate sizes for preparing reagents, standards, and measuring sample volumes

7.6 Air Displacement pipetters: Eppendorf brand or equivalent digital pipettes capable of delivering volumes ranging from 0.1 to 5000 pL with an assortment of high quality disposable pipette tips

7.7 Autosampler tubes: t5-mL plastic AS-91 and/or S10

7.8 Digestion tubes: 50-mL plastic with caps

7.9 Analytical balance: Capable of accurate measurement to the nearest 0.01 g

8. Reagents and Standards

Deionized (DI) water is ASTM Type II laboratory reagent grade water or better (*i.e.*, Type I). The Barnstead NANO-pure system provides Type I water used in the preparation of samples and standards. ACS Trace Metal grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration is less than the RL then the reagent is acceptable.

Solutions below expire six months from preparation unless noted. All stock and working calibration standards expiration dates are based on manufacturer expiration date or one year from date received. All solutions are stored at room temperature

8.1 Nitric acid (HNO_3), concentrated. Trace metal grade or ultra-pure from sub-boiling distillation is preferred. Suggested suppliers include: Seastar ™- Sub-boiling distilled grade, Sidney, BC; J. T. Baker - ULTREX® Grade; and Fisher - Optima Grade. Lots should be checked for purity prior to use and the results stored in a reagent check log book.

8.2 Hydrochloric acid (HCL), concentrated. Trace metal grade or ultra-pure from sub-boiling distillation is preferred. Suggested suppliers include: Seastar™ - Sub-boiling distilled grade, Sidney, BC; J. T. Baker - ULTREX® Grade; and Fisher - Optima Grade. Lots should be checked for purity prior to use and the results stored in a reagent check log book.

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8.3 2% (vol/vol) Nitric acid. Prepare by adding 40 mL of concentrated nitric acid to 2000 mL reagent water in a clean glass bottle or 180 mL of concentrated nitric acid to 9000 mL reagent water in a clean carboy. This acid minimizes the damage to the interface and also minimizes isobaric molecular-ion interferences.

8.4 10% (vol/vol) Nitric acid. Prepare by adding 200 mL of concentrated nitric acid to 2000 mL reagent water in a clean glass bottle or 900 mL of concentrated nitric acid to 9000 mL reagent water in a clean carboy. This acid is the maximum concentration used for calibration standards, samples and rinse acid as recommended by the instrument manufacturer.

8.5 0.1% (vol/vol) Sub-boiling distilled Nitric acid. Prepare by adding 1.0 mL of concentrated sub-boiling distilled nitric acid to 1000 mL reagent water in a clean polyethylene bottle.

8.6 5% (vol/vol) Nitric acid. Prepare by adding 50 ml of concentrated nitric acid to 950 mL reagent water in a clean polyethylene bottle.

8.7 Single element stock solutions for the following elements are typically maintained in the laboratory. These are normally purchased as 1000 mg/L standards from Fisher Scientific or equivalent. The ICP MS is capable of determining concentrations of **73** elements in the Periodic Table. Other calibration standards, not present in Table 4, may be purchased as necessary for non-routine analyses.

8.7.1 Arsenic

8.7.2 Beryllium

8.7.3 Selenium

8.7.4 Strontium

8.7.5 Tin

8.7.6 Zinc

8.8 Tuning Solution Stock standards consist of 1000 mg/L beryllium (Be), cobalt (Co), indium (In), thallium (Tl), and uranium (U).

8.8.1 100 mg/L Tuning Solution Intermediate Standard . Prepare 1:10 dilutions by pipetting 100 µL of each 1000 mg/L single element stock solutions of Co, In, Tl, and U into a 1 mL autosampler cup containing 900 µL 2% nitric acid.

8.8.2 Tuning solution: 150 µg/L Be and 10 µg/L Co, In, Tl, and U. Prepare by pipetting 100 µL of 100 mg/L tuning solution standard in 10.8.1 and 150 µL of 1000 mg/L Be into a 1 liter volumetric flask filled with 200 mL of reagent water and 20 mL of concentrated nitric acid. Dilute to a final volume of 1 liter with reagent water and mix well.

Can also order Perkin Elmer part # N812-2014 for the tuning solution.

8.9 The Internal Standard Solution is prepared from single element standards consisting of 100 mg/L Germanium (Ge), 100 mg/L indium (In), 100 mg/L lithium (Li^6), 100 mg/L scandium (Sc) and 100, mg/L terbium (Tb).

8.9.1 Add 10 mL of concentrated nitric acid to a 500 ml volumetric flask containing 250 ml of DI water.

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8.9.2 Add 5 ml of 100 mg/L Li^6. Li^6 is used routinely when analyzing beryllium and boron or other elements as needed. If these elements are not being analyzed then it is not necessary to add this internal standard.

8.9.3 Add 1.0 mL of a stock solution containing 100 mg/L of Sc.

8.9.4 Add 0.5 mL of 100 mg/L of In, Ge and Tb stock solutions

Note: All solutions including calibration blanks, calibration standards, samples, quality control standards, and quality control samples must be spiked with the same level of the internal standard spiking solution. Use the above solution in conjunction with the on-line mixing block for addition of internal standards to calibration standards and samples. Internal standard intensities should be between 100,000 cps and 1500,000 cps. The internal standard solution as made here should be diluted 1:2 for the DRCe ICP MS instrument due to the greater sensitivity of the instrument.

Note: Other internal standards are suggested for use such as Y, Ho, Lu and Bi and may be used if poor performance is observed from the above standards

8.10 Calibration Stock Standard and Intermediate Working Standard Solutions

Intermediate Working Standard solutions are prepared from certified vendor Stock Standard solutions and include those analytes listed below. Vendor sources are subject to change and equivalent solutions may be used.

Mixed calibration standard solutions must contain the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. The acid matrix for all standards is 0.1% HNO_3 (10.5), 2% HNO_3 (10.3), 5% HNO_3 (10.6) and 10% HNO_3 (10.4). These concentrations do not damage to the ICP-MS interface and also minimizes isobaric molecular-ion interferences with the analytes. A diluent of the acid matrix preparation is described in 10.3 and 10.4. *Note: Silver and antimony may precipitate out of solution at higher concentrations between 50-500 pg/L. Higher silver concentrations (>500 pg/L) require additional HCl. Caution: Many metal salts are extremely toxic if inhaled or swallowed. The Health and Safety precautions noted in Section 5 must be followed.* All standards are stored in the metals instrument laboratory at room temperature. The expiration dates are monitored from vendor supplied dates. The element or mix of elements that expires first in a solution dictates the expiration date for the entire solution. Standard and spike solutions are labeled using an alpha-numeric system based on the date prepared. All standards or spikes that are prepared are recorded in the metals laboratory logbooks. It is suggested that standards with a final concentration of less than 1 mg/L be prepared daily

8.10.1 CPI-19: *Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Tl, Ti, V and Zn* from CPI containing all of the listed elements at 100 mg/L.

8.10.1.1 (Date)-C1: Intermediate working standard is prepared by adding 1 mL of CPI-19 (10.9.1) to 9 ml of 0.1% Acid (10.5). This standard is prepared approximately every two weeks and is used to prepare the daily calibration standards

8.10.2 CPI-7: *K* at 1000 mg/L, Si at 50 pg/ml, and *Al, Ba, B, Ag and Na* at 100 mg/L from CPI at the concentrations noted.

8.10.2.1 (Date)-C2: Intermediate working standard is prepared by adding 1 mL of CPI-7 (10.9.2) to 9 ml of 0.1% Acid (8.5). This standard is prepared

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approximately every two weeks and is used to prepare daily calibration standards.

8.10.3 AT-3: *Al, Ca, Fe, Mg, K,* and *Na* a custom mix from Inorganic Ventures at 500 mg/L for each element.

8.10.3.1 Date)-C3: Intermediate working standard is prepared by adding **1** mL of AT-3 (8.9.3) to 9 ml of 0.1% Acid (8.5). This standard is prepared approximately every two weeks and is used to prepare daily calibration standards.

8.10.3.2 (Date)-C4: This standard is prepared by pouring AT-3 (8.9.3) into a satellite container for use in preparing daily calibrations standards.

8.10.4 IQC-026: *Sb, Ag, Al, As, B, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Na, Ni, Se, Tl, Ti, V* and *Zn* at 100 mg/L, *Si* at 50 mg/L and *K* at 1000 mg/L from Ultra Scientific.

8.10.4.1 (Date)-t1: Intermediate working standard is prepared by adding 1 mL of IQC-026 (8.9.4) to 9 ml of 0.1% Acid (8.5). This standard is prepared approximately every two weeks and is used to prepare daily calibration standards.

8.10.5 XAQU-15: *Fe, Al, Mg, Na, Ca* and *K* a custom mix from SPEX at 500 mg/L for each element listed.

8.10.5.1 (Date)-I2: Intermediate working standard is prepared by pouring XAQU-15 (8.9.5) into a satellite container for use in preparing daily calibrations standards.

8.11 Daily Calibration Standards

An Initial Calibration Curve is prepared for each level and is described below. Every element is not in each level of the calibration curve. At minimum, a high level, a low level that confirms the reporting limit (**STD1**), and a calibration blank (**STD0**), is used. See Table 4 for a list of the initial calibration concentrations. Standards are prepared in either 0.1% (8.5), 2% (8.3), 5% (8.6) or 10% (8.4) nitric acid to matrix match standards to samples depending on the how samples and sample digests are diluted for analysis. Standards used to analyze undiluted Dissolved Aqueous samples are prepared in 0.1% nitric acid. Standards used to analyze undiluted Total Aqueous samples prepared by hot plate (MP-004) are prepared in 5% nitric acid. Soil/Sediment samples prepared by Hot Plate Method 3050 (MP-001) and Tissue samples prepared by microwave oven (MP-003) and diluted 1:2 are prepared in 10% nitric acid. Standards used to analyze Total Aqueous samples (11.4) prepared by hot plate (MP-004), diluted 1:5, and Soil/Sediment samples prepared by Hot Plate Method 3050 (MP-001), diluted 1:5, are prepared in 2% nitric acid.

8.11.1 **STD0 (Calibration Blank):** Calibration Blank: A solution containing the same acid matrix as samples and standards

8.11.2 **STD1 (Reporttng Ltmtt Standard):** Prepared from the ICV Standard (8.12). Add 100 µL of ICV standard to 50 ml digestion tube and bring to volume with diluent acid. The final concentration of each element is: *Sb, Ag,, As, B, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo Ni, Se, Tl, Ti, V* and *Zn* at 0.1 µg/L, *Al, Ca, Fe, Mg,* at 10.1 µg/L, *Si* at 0.05 µg/L and *K* at 11 µg/L.

8.11.3 STD2: Add 50 pL of (Date)-C1 (10.9.1.1) and 100 µL of (Date)-C3 (8.9.3.1) to a 50mL digestion tube and bring to 50mL with the diluent acid. The final concentration of each element is: *As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se , Ti, Tl, V* and *Zn* at 10 pg/L; *Al, Ca, Fe,* and *Mg* at 110 pg/L; *K* and *Na* at 100 pg/L; and *Si* at 5 pg/L. Note: only 16 of the 19 elements in this mix are evaluated at this concentration level.

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8.11.4 STD3: Add 100 pL of (Date)-C1 (10.9.1.1) and 100 µL of (Date)-C4 (8.9.3.2) to a 50mL digestion tube and bring to 50mL with the diluent acid. The final concentration of each element is: *As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V and Zn* at 20 pg/L; *Al, Ca, Fe, and Mg* at 1020 pg/L; *K and Na* at 1000 pg/L; *Hg* at 5 pg/L, and *Si* at 10 pg/L. Note: only 16 of the 19 elements in this mix are evaluated at this concentration level.

8.11.5 STD4: Add 500 pL of (Date)-C1 (8.9.1.1) and 1000 µL of (Date)-C4 (8.9.3.2) to a 50mL digestion tube and bring to 50mL with the diluent acid. The final concentration of each element is: *As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V and Zn* at 100 pg/L; *Al, Ca, Fe, and Mg* at 10100 pg/L; *K and Na* at 10000 pg/L; and *Si* at 50 pg/L. Note: only 16 of the 19 elements in this mix are evaluated at this concentration level.

8.11.6 STD5: Add 500 pL of (Date)-C2 (8.9.2.1) to a 50mL digestion tube and bring to 50mL with the diluent acid. The final concentration of each element is: *Ag, B and Ba* at 100 pg/L; *Si* at 50 pg/L. Note: These three metals are only performed with a 3 point calibration rather (including the blank).

8.12 Initial calibration verification (ICV) and continuing calibration verification (CCV)

The ICV and CCV standards are prepared from sources separate from the initial calibration curve and are used to verify the initial calibration curve throughout the analytical sequence. See Table 4 for a list of the ICV/CCV concentrations. To prepare this solution add 0.25mL of (Date)-I t (8.9.4.1) and 0.5mL of (Date)-I2 (8.9.5.1) to a 50mL digestion tube and bring to 50mL with the diluent acid. The final concentration of each element is: *As, Ag, Sb, B, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Si, Ti, Tl, V and Zn* at 50 pg/L; *Al, Ca, Fe, and Mg* at 5050 pg/L; *K* at 5500 pg/L; and *Si* at 25 pg/L.

8.13 Calibration blank (STD0),

initial and continuing calibration blanks (ICB and CCB) are the analysis of the matrix diluent and are analyzed prior to the initial calibration curve and after the ICV and CCVs, respectively.

8.14 Contract Required Detection Limit – CRDL

The detection limit of an analysis is determined through method detection limit studies and supported by a calibration standard which is at or below the reporting limit (STD1 – 8.10.2). A contract required detection limit (CRDL) can also be verified by determining the analyte recovery from a CRI check standard. The analyte concentrations of this standard and acceptance ranges for recoveries may be established by project specifications. This check standard can be analyzed separately following the initial calibration and/or at the end of the analytical sequence.

8.15 Interference Check Solutions – ICS

Twp Interference Check Solutions (ICSA and ICSAB) are prepared to contain known concentrations of interfering elements and analytes that will provide an adequate test of correction factors. Concentrations of the interfering analytes correspond to concentrations in Table 1 of USEPA, "Method 6020A - Inductively Coupled Plasma-Mass Spectrometry," in Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Revision 1, September 1998.

The sensitivity if the ICP MS to most analytes allows sample digests from the preparations in 2.2 – 2.5 to be diluted prior to analysis and still meet required reporting. Dilution can reduce isobaric and physical interferences as well as instrument exposure to strong acids used in sample preparation. If sample digests are diluted prior to analysis, then the concentrations of the interferent analytes in the ICS solution are reduced proportionately during preparation of the ICSA and ICSAB standards.

Digests of water samples may be analyzed without dilution, at 1:5 dilution or higher to bring analyte concentrations within the linear dynamic range of the instrument. Digests of soil/sediment samples and tissue samples must be diluted 1:2 in DI water, at a minimum, to

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reduce the high acid concentraiion used in the preparation. The instrument manufacturer suggests a maximum acid concentraiion of 10% be used during analysis

Three solutions are used to prepare the interference check solutions ICSA and ICSAB.

8.15.1 6020ICS-9A: Supplied by Inorganic Ventures with concentrations of 20,000 ppm Cl^-; 3000 ppm Ca; 2500 ppm Fe and Na;1000 ppm Al, Mg, P, K, and S; 2000 ppm C; 20 ppm Mo and Ti

8.15.2 (Date)-C1: See 8.10.9.1.1

8.15.3 (Date)-C2: See 8.10.2.1

8.15.4 Interferent concentrations based on sample dilution are given in the following table.

Interferent	No Ditution (mg/L)	1:2 Ditution (mg/L)	1:5 Dilutioin (mg/L)
Cl^-	2000	1000	400
Ca	300	150	60
Fe, Na	250	125	50
Al, Mg, P, K, S	100	50	20
C	200	100	40
Mo, Ti	2	1	0.4

8.15.5 The ICSA Solution is prepared in a 50 ml screw cap digestion tube by adding 5 ml (no dilution), 2.5 ml (1:2 dilution) or 1 ml (1:5 dilution) of 6020ICS-9A (10.14.1) to 0.1% nitric acid (8.5), 2% nitric acid (8.3), 5% nitric (8.6) or 10% nitric acid (8.4) depending on the acid being used for analysis (see section 8.10). This solution can be used for multiple analyses and can be stored until the expiration date of the standard.

8.15.6 The ICSAB Sotution is prepared as a 10 ml aliquot according to the following tabte and must be prepared daily as some analytes are not stable in solution. The final concentrations of analytes in (Date)-C1 are 100 µg/L and 50µg/L for (Date)-C2 with the exception of *Mo* and *Tl* which are present as interferenis.

Note: Method 6020A suggests a concentraiion of 200 µg/L for Cr, Co, Cu, Mn, Ni and V. The reduced concentrations prepared for this standard represeni a more rigorous test of isobaric corrections.

Sotution	No Ditution (mL)	1:2 Ditution (mL)	1:5 Ditution (mL)
6020ICS-9A (8.4.1)	1	0.5	0.2
(Date)-C1	0.1	0.1	.1
(Date)-C2	.05	.05	.05
Acid (8.3, 8.4, 8.5, 8.6)	8.85	9.35	9.65

8.16 Laboratory Control Sample (LCS) or Laboratory Fortified Blank (LFB) for aqueous samples is prepared from a source other than the calibration standard sources.

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It is prepared and stored for use in the metals preparation laboratory. The LCS for solid samples is either a liquid LCS/LFB or a solid LCS purchased from ERA at known and certified values. See the metals preparation SOPs for LCS preparation details.

8.17 Matrix Spike (MS) solution for aqueous and solid samples is the same solution as the aqueous LCS/LFB in 10.15. It is prepared and stored for use in the metals preparation laboratory. See the metals preparation SOPs for MS preparation details.

8.18 Daily Performance Standard: Prepare by adding 0.1 ml of a 1:10 dilution of 1000 mg/L stock Ba, Ce, Mg, Pb, In, U and Rh standards to 1 L volumetric flask containing 100 ml of Di water with 20 ml of concentrated HNO_3. Mix and bring to volume with DI water.

8.19 Dual Detector Calibration Solution: Add 0.15 ml of CPi-19 stock (or equivalent), 0.15 ml of CPI-7 stock (or equivalent), 0.15 ml of 500 ml/L Al, Ca, Fe, K, Mg and Na stock and 0.1 ml each of 1000 mg/L As, Be, and Zn and 0.2 ml of 1000 mg/L Se stock to 100 ml volumetric flask containing 2% HNO_3. Bring to volume with 2% HNO_3. This solution is required for optimization of the pulse and analog state detectors. Other analytes may be added to this solution as needed.

9. Quality Control

The laboratory must maintain records to documerit the quality of data that is generated. Ongoing data quality checks are compared with established performanee criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank

9.1.1 A method blank must be analyzed once per every 20 samples or per metals digestion batch, whichever is more frequent.

9.1.2 Metal concentrations must not be detectable in the method blank at values greater than the reporting limit.

9.1.3 Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. Digestion of the method blank and all associated samples must be performed until the method blank for the out ef control metal is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Section Head if the samples associated with an out of control method blank are below the reporting limit for the affected metal or if the concentrations of the affected metal are greater than t0x the blank level in the samples. In such cases, the sample results are accepted without corrective action for the high method blank result. The client must be notified in the project narrative associated with the sample results.

9.2 Laboratory Control Sample (LCS) / Laboratory Fortified Blank (LFB)

9.2.1 The LCS/LFB is from a second source to verify the accuracy of the digestion and analytical procedures. The LCS/LFB is digested along with the samples. An LCS/LFB must be digested and analyzed once per every 20 samples or per metals digestion batch, whichever is more frequent.

9.2.2 The acceptable recovery QC limits are 80%-120% (Method 6020A) for an aqueous LCS/LFB and 75%-125% (or within manufacturer's control limits) for the solid LCS.

9.2.3 Corrective Action: May repeat analysis once to see if an analytical error has occurred. If the LCS/LFB recovery is still out of control, re-digest and re-analyze

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the LCS/LFB and all associated samples. Samples cannot be analyzed until an acceptable LCS/LFB is obtained. Exceptions may be made with approval of the Section Head if the samples associated with the out of control LCS/LFB are also associated with a matrix spike that is in control. This is an acceptable measure of accuracy of the digestion and analytical procedures. An explanation of this out of control LCS recovery must be included in the project narrative to the client and the sample data reported with the acceptable MS results as batch QC.

9.3 Initial Calibration Verification (ICV)

9.3.1 Initial Calibration

9.3.1.1 A three-point calibration curve must be performed if the CRI standard is not analyzed.

9.3.1.2 The correlation coefficient must be r $\geq$0.995.

9.3.1.3 Corrective Action: Re-calibrate until criteria are met.

9.3.2 Initial Calibration Verification (ICV) Check Standard

9.3.2.1 The initial calibration verification check standard is from a second source to verify the accuracy of the standard curve. The concentration of the ICV is at approximately the mid-level of the calibration curve.

9.3.2.2 The acceptable recovery QC limits for the ICV is 90-110%. In addition, the relative standard deviation between three replicate readings must be less than 5% RSD.

9.3.2.3 Corrective Action: May repeat analysis once to see if an analytical error occurred. If the ICV still exceeds the control limits, re-calibrate the instrument.

9.3.3 Initial Calibration Blank (ICB)

9.3.3.1 An ICB must be analyzed immediately following the ICV.

9.3.3.2 The acceptance limit for the ICB is ± 3 times the Instrument Detection Limit (IDL).

9.3.3.3 Corrective Action: May repeat analysis once to determine if analytical error has occurred. Results may be reported from the analysis if the ICB concentration is less than the reporting limit. If the ICB still exceeds the reporting limits, re-calibrate the instrument and re-analyze a fresh blank.

9.4 Continuing Calibration Verification (CCV)

9.4.1 Continuing Calibration Verification (CCV) Check Standard

9.4.1.1 A CCV must be analyzed at a minimum of every 10 samples and at the close of an analytical sequence. The concentration of the CCV is at approximately the mid-level of the calibration curve. This standard monitors instrument performance throughout the duration of the analytical sequence.

9.4.1.2 The acceptable recovery QC limits for the CCV is 90-110%. In addition, the relative standard deviation between three replicate readings must be less than 5% RSD.

9.4.1.3 Corrective Action: May repeat analysis once to see if an analytical error occurred. If the CCV still exceeds the control limits, re-calibrate and re-analyze all samples since the last acceptable CCV.

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9.4.2 Continuing Catibration Btank (CCB)

9.4.2.1 A CCB must be analyzed immediately after every CCV

9.4.2.2 The acceptance limit for the CCB is ± 3 times the IDL.

9.4.2.3 Corrective Action: Results may be reported from the analysis if the CCB concentration is less than the reporting limit. If not, repeat analysis once to see if an analytical error occurred. if the CCB still exceeds the reporting limit, re-calibrate the instrument and re-analyze a fresh blank. All samples associated with the out of control metals in the CCB must be re-analyzed (since the last acceptable CCB). Exceptions may be made with approval of the Section Head if the samples associated with the out of control method blank are non-detect for the affected metals or if sample concentrations for the affected metals are greater than t0x the blank levels. In such cases, the sample results are accepted without corrective action for the high CCB and the client is notified in a project narrative associated with the sample results.

9.5 Matrix Spike

9.5.1 A matrix spike must be performed once per 20 samples (5% frequency) and is from a second source to verify the accuracy of the digestion and analytical procedures. The matrix spike recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{MS_{recovery} - Rt}{MS_{true\ value}} \times 100$$

When project specifications dictate, a Matrix Spike Duplicate (MSD) may also need to be performed at the same frequency as the MS.

9.5.2 The acceptable recpvery QC limits for a MS/MSD is 75%-125% for both the solid and aqueous MS/MSD pair. Calculate the %RPD as in 12.3.2 above when analyzing a MS/MSD pair. The acceptable %RPD is ≤ 20%.

9.5.3 Corrective Action: May repeat analysis once to see if an analytical error has occurred. If the % recovery or %RPD still exceeds the control limits and the LCS is compliant; include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy or precision of the affected metals results as evidenced by matrix spike recovery or %RPD outside of QC limits.

9.6 Laboratory Duplicate

9.6.t Duplicate analyses (matrix duplicate) must be performed once per 20 samples (5% frequency).

9.6.2 Acceptable relative percent difference (RPD) for duplicate analysis is ≤ 20 % for both aqueous and solid matrices. Acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate RPD as follows:

$$RPD = \frac{Rt - R2}{\frac{[Rt + R2]}{2}} \times 100$$

9.6.3 Corrective Action: May repeat analysis once to see if an analytical error has occurred. If the % RPD still exceeds the control limits; include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the affected metals results as evidenced by the matrix duplicate RPD exceedence

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9.7 Method-specific Quality Control Samples

9.7.1 Tuning Sotution, Mass Catibration, and Resotution Checks

9.7.1.1 The tuning solution, mass calibration, and resolution checks are required prior to sample analysis. The tuning solution must be analyzed 4 times prior to instrument set up at the beginning of the day.

9.7.1.2 The analytes in the tuning solution must meet ≤5 percent relative standard deviation. The mass calibration must not differ by more than 0.1 amu from the true value. The resolution must be less than 0.0 amu full width at 10 percent peak height.

9.7.1.3 Corrective Action: Adjust the mass calibration to the correet value or correct the problem until criteria are met.

9.7.2 CRI Standard Check Sampte (Reporting Limit Standard)

This solution is used to verify instrument sensitivity at the reporting limit. This standard is routinely analyzed as the lowest standard in the initial calibration curve, or STD1, see Section 8.13. When included in the initial calibration curve, the curve must meet the criteria for linearity (r = 0.995). When project specifications dictate, the CRI can be analyzed separately from the iriitial calibration. The concentration of the CRI, when analyzed as a separate cheek from the initial calibration curve, is equivalent to the reporting limit for each element in STD1, see Table 1, or at higher levels representing project specific reporting limits. See Section 8.8.2 for preparation details. This check standard, when analyzed, follows the ICV and ICB.

9.7.2.1 The CRI Check sample, when analyzed per client specifications, must be analyzed at the beginning of an analytical run or twice during every 8-hour work shift, whichever is more frequent. These solutions verify the accuracy at the low end of the calibration curve.

9.7.2.2 Results for all metals in the CRI solution must be within the 50-150% recovery criteria. When performing work for the Departmeni of Defense (DoD, Army Corps of Engineers or the US Navy) the CRI acceptable recovery criteria is 80-120%.

9.7.2.3 Corrective Action: May repeat analysis once to see if an analytical error pccurred. If the CRI solutions still exceed the control limits, re-calibrate and/or re-analyze a fresh CRI solution. All samples associated with the out of control metals in the CRI must be re-analyzed (since the last acceptable CRI check sample).

9.7.3 Interference Check Samptes (ICSA and ICSAB) Solutions

9.7.3.1 The ICSA and ICSAB solutions must be analyzed at the beginning of an analytical run or every 12-hour work shift, whichever is more frequent. These solutions verify the isobaric corrections.

9.7.3.2 Results for all spiked non-interference metals in the ICSAB solution must be within 80-120% recovery criteria. Il may be necessary to correct concentrations measured in the ICSAB solution with background concentrations measured in the ICSA solution. Results for aluminum, calcium, iron, sodium, potassium, and magnesium in the ICSA solution should be within 80-120% recovery, however, depending on the sample dilution used, concentrations of the these elements may be close to or exceed the linear range of the instrument which can cause the channel to saturate.

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9.7.3.3 Corrective Action: May repeat analysis once to see if an analytical error occurred. If the ICSA or ICSAB solutions still exceed the control limits, re-calibrate and/or re-analyze a fresh ICSA or ICSAB. If the sample results are accepted without corrective action for the ICSA or ICSAB exceedence(s), the client must be notified in a project narrative associated with the sample results.

Note: If an interference is suspected, use of computerized compensation or comparison with an alternate method such as graphite furnace is recommended.

9.7.4 Internal Standard Recovery

9.7.4.1 Internal standard intensities must be monitored in all solutions.

9.7.4.2 Intensities of internal standards in all subsequent analyses of instrument QC samples (including ICV, ICB, CCV and CCB) solutions must be within 70% -120% of the levels in the original calibration blank. Intensities of internal standards in samples must be within the same limits as the QC samples.

9.7.4.3 Corrective Action: If the instrument QC sample does not meet criteria, may reanalyze once to determine if analytical error has occurred. If QC sample still does not meet criteria, terminate the analysis for analytes associated with the internal standard, correct the problem, re-calibrate, and reanalyze all affected samples since the last in-control CCV/CCB. If a sample does not meet criteria, may reanalyze the sample and/or dilute the sample five-fold and reanalyze. This procedure is followed for the sample until the internal standard intensities fall within the prescribed window.

9.7.5 Serial Dilution Analysis

9.7.5.1 Serial dilution analysis must be performed once per 20 samples (5% frequency).

9.7.5.2 Analysis of a 1:5 dilution must agree within 10% of the original determination, if the metal concentration is sufficiently high (minimally, a factor of 50 above the method detection limit) in the original undiluted analysis.

9.7.5.3 Corrective Action: Analysis may be repeated once to see if an analytical error has occurred. If the %D still exceeds the control limits; include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy of the affected metals results as evidenced by the serial dilution %D exceedence.

9.7.6 Post Digestion Spike (PDS)

9.7.6.1 Post digestion spike analysis may be performed if the MS or MSD does not meet recovery criteria. A known spike amount is added to a portion of a prepared sample, or its dilution. The spike addition should produce a minimum level of 10 times, and a maximum of 100 times, the method detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

9.7.6.2 The post digestion spike recovery is 75%-125% of the known value.

9.7.6.3 Corrective Action: If the post digestion spike exceeds the control limits; include a project narrative with the results to client noting that there may

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be potential matrix effects on the accuracy of the affected metals results as evidenced by the post digestion spike exceedence.

9.8 Method Sequence

Initial calibration curve (Total of 6 standards, 2-3 levels for each element)
ICV
ICB
CRI – If required
ISCA
ICSAB
Method Blank
LCS
Sample analysis (samples 1-6)
CCV
CCB
Sample analysis (7-16)
CCV
CCB
Sample analysis (17-26)
CCV
CCB

10. Procedure

10.1 Equipment Set-up

10.1.1 Prior to using the Perkin-Elmer ELAN 6100 and DRCe ICP/MS, the operator must read and become familiar with the operating procedure guidelines specified in the operating manual. The analyst must be trained and familiarized with the instrument software provided by the manufacturer. The instrument must be set up with the proper operating parameters and conditions described in the Perkin-Elmer ELAN 6100 and DRCe ICP/MS operating manual. The criteria for the background correction points, analytical dynamic ranges, method and instrument detection limits and isobaric molecular-ion correction equations must be established and documented prior to initial calibration.

10.1.2 The plasma torch must be aligned before ignition and is done with an alignment tool supplied with the instrument. The procedure centers the torch within the load coil and adjusts the distance of the torch to the sampler cone surface. This is outlined in the Elan 6100 Hardware Guide. This is not required on a routine basis, only initially upon instrument set up and following any changes, such as removal and cleaning of the plasma torch. The instrument must become thermally stable (usually 30-60 minutes) before beginning operation.

10.1.3 Isobaric corrections must be put into the equations page of any method used to generate quantitative analytical data. The correction equations can be found in Table 3. These corrections are based on natural isotopic abundance's and cannot be altered.

10.1.4 A linear dynamic range (LDR) study must be conducted annually. The LDR is determined by analyzing increasingly higher standard concentrations of each element until the observed concentrations are no more than ± 10% of the true value of the standard. Sample analyte concentrations that are above the linear dynamic range must be diluted and re-analyzed. The linear dynamic range must be established for each analytical run by analysis of a high level standard or Linear Range Verification (LRV) standard. Results greater than the daily calibration range but within the linear calibration can be reported provided that analyte recovery from the LRV is within 10% of the true value. If the

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recovery from the LRV is outside of the 10% acceptance limit then samples may be diluted below the concentration of the highest calibration standard or reanalyzed. The linear dynamic range must be checked and verified annually. See Table 5 for the current linear range.

10.2 Initial Calibration

10.2.1 Prior to daily calibration, inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt or debris that could constrict flow and affect instrument performance. Clean the system when needed following the manufacturer's instructions.

10.2.2 A series of calibration standards are prepared for the initial calibration curve as described in Section 8.0. The preparation date of these standards, the initials of the analyst, the lot number of the source material, stock concentrations, volumes used, final volumes, final concentrations and manufacturer must be recorded in the metals standard preparation logbook. All standards are traceable to NIST via internal and external calibration checks. Certificates of Analysis accompany the receipt of standard solutions and are kept on file in the laboratory. The Perkin-Elmer ELAN 6100 and DRCe are calibrated using a multi-point calibration curve consisting of a blank and a two to three standards per analyte. The standards are named, for example, "C" for calibration, plus "Date" for the date prepared, followed by the letter M and a number 1, 2, 3 etc. for first, second or third set of standards prepared that day. "I" is used to determine the ICV standard. Standard "I040402M1" is the first ICV standard for the ICP MS made on 04/04/02. Standard "I040202M2" is the second ICV standard for the ICP MS made on 04/02/02. This nomenclature is for traceability and to distinguish calibration standards from independent check standards and field samples.

10.2.3 A Linear Through Zero curve type is be selected for all analytes.

10.3 Equipment Operation and Sample Processing

Samples are prioritized by the Section Head for analysis based on hold time and client due date. Section 11 outlines the steps for data reporting that will contain the sample analysis final results.

10.3.1 Preliminary treatment or sample preparation of most matrices is necessary because of the complexity and variability of sample matrices. Aqueous dissolved samples that have been pre-filtered and acidified do not require acid digestion as long as the samptes and standards are matrtx matched. See the sample preparation SOPs.

10.3.2 Ensure that the instrument configuration and operating procedures established in Section 10.1 are selected.

10.3.3 Affix clips to the peristalic pump windings and open the Device window, click on Connect and click on the right pointing arrow (counterclockwise). Check that the fiuid is flowing through all tubing and that waste is flowing out of the spray chamber. Initiate the plasma and allow a warm-up of 30-60 minutes.

10.3.4 Conduct mass calibration and resolution check.

Note: Tuning and optimization procedures are performed without the Internal Standard mixing block in-line for The ELAN 6100.

10.3.4.1 Open the Tuning workspace. Aspirate the Tuning Solution (10.7) solution containing Be, Co, In, Tl and U. Click on Tune Mass Spec. The measured mass difference must be less than 0.1 amu from the actual value. The resolution must be less than 0.9 amu full width at a 10% peak height (the instrument default setting is 0.65 amu). If the resolution is not achieved for an element, the

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Resolution Digital to Analog Conversion (Res. DAC) value is changed for that element (increasing the DAC value by **30** units will decrease the peak width by **0.1** amu). If the Measured Mass values are not within **0.1** amu of the exact value then the Mass DAC values must be changed. Increasing the Mass DAC increases the measured mass value. This is done daily before sample analysis. Print the calibration and store with the daily performance check.

Note: Extreme care must be taken when adjusting DAC values. Instrument performance can be severely degraded if tuning parameters are not correct.

10.3.4.2 Open the Daily Performance workspace

10.3.4.2.1 Aspirate the Daily Performance Solution (**10.17**).

10.3.4.2.2 Click on "Analyze Sample" in the manual sample window.

10.3.4.2.3 Monitor daily performance measures as recommended by Perkin Elmer for Ba, Ce, Mg, Rh, Pb, In and U sensitivity, background, % double charged and % oxide levels.

10.3.4.2.4 See Manufacturer's recommendations for sensitivity. If criteria are not met then follow optimization procedures specified by the manufacturer.

10.3.4.2.5 The background at mass **220** should be < **30** eps.

10.3.4.2.6 The % double charged ions (Ba^{+}/Ba^{++}) should< **3%** and not to exceed **5%**.

10.3.4.2.7 The % oxides (Ce/CeO)should be < **3%** and not to exceed **5%**.

10.3.5 Open the appropriate analytical method. Turn on the autosampler and click on the "Sampling" icon in the Method. Select "Go to Rinse" at which point the sampling probe should go to the rinse station. Click on "OK". It may not be necessary to analyze for all the metals listed in the 6020A method. The analyte list can be edited down for only those metals required. Go to the Timirig Page in the method and highlight the metals to be deleted. Go to the Edit Menu and select "delete rows". Save the method as a different name. For reporting purposes, the Report File Name on the Report Page of the 6020 Method or edited Method is saved under c:\elandata\dataset\dataset**LIMS WG#.** etc. for each analysis on that date.

10.3.6 Open the "Sample" window and click on batch analysis to update with new sample information.

10.3.7 Open the 6020TEMP sample file or a previously used file and edit the table with sample names, autosampler positions and dilutions. Select the Method for analysis and record all standard ID's and acids used in the Description Column of the Batch Analysis page. Save the file as a different name.

10.3.8 Calibrate the instrument using the calibration standards listed in Section **8.0**, Reagents and Standards. The system must be flushed with a rinse blank sample (equivalent to the calibration blank) between each standard to protect against potential carry-over. The average intensity of **3** multiple exposures must be performed for QC samples and field samples to reduce random instrument error. The calibration curve consists of a blank and two to three standards.

10.3.9 The Calibration action for the first sample for which concentration results are desired must be "Analyze Blank, Standards, and Sample".

10.3.10 The calibration action for all other samples is usually "Analyze Sample", unless periodic re-calibration is desired.

10.3.11 Click on the "Dataset" Icon, go to the "File Menu" and click on "New". The dataset name is designated by **LIMS WG#.**

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10.3.12 Select "Analyze Batch"

10.3.13 Flush the system with the rinse blank solution between samples. The rinse blank nitric acid concentration corresponds to the acid concentration in samples and standards (see 10.10). The DRCe, 10% nitric acid is always used in the rinse solution. The same time must be elapsed between CCVs and CCBs as is allowed between samples. Analyze the CCV and the CCB after each 10 samples and at the end of the analytical sequence.

10.3.14 The CRI (if required), ICSA, and ICSAB solutions must be analyzed at the beginning of an analytical run or once every 12 hours, whichever is more frequent.

The CRI analysis is not performed if a calibration standard is prepared at the reporting limit and included in the initial calibration curve and if not specifically requested by the client. The calibration curve must always meet the criteria for linearity (r = 0.995).

10.3.15 Analysis Review

Two forms are used to primary and secondary review the analysis. These are called the "ICP MS Checklist" and the "Blank Reporting Limit Checklist" and are shown below.

10.3.15.1 ICP MS Checktist

This analysis review form is used by the analyst and secondary reviewer to note passing/failing QC standards and to record any other comments as communication for reporting sample results.

10.3.15.2 Btank Reporting Limit Checktist

This analysis review form is used to set the sample reporting limit based on the batch preparation blank and to compare instrument blanks (ICB and CCB's) to instrument detection limits. Instrument blanks are compared to the limit of 3 times the IDL. Instrument blanks, which exceed the IDL limit, are recorded on the form and may require sample reanalysis or reporting limit elevation. This form is generated annually as IDL studies are completed.

10.3.16 Target analytes detected above the calibration range must be diluted and re-analyzed. See Section 9 for all Quality Control frequencies and criteria.

10.4 Continuing Calibration

See Section 9.4.

10.5 Preventive Maintenance

10.5.1 General cleaning tips for ICP-MS

10.5.1.1 Sampling and skimmer cones should be removed and cleaned on a weekly basis or more often under high usage. Remove the cones with the tool provided with the instrument and clean with 10% HCl, and rinse thoroughly with deionized water. Reinstall cones and perform XY alignment procedures after igniting the plasma and the instrument has warmed up for 30 minutes (see 14.4).

10.5.1.2 Peristaltic pump tubing must be inspected regularly for wear and changed if necessary. Sample and internal standard tubing should be changed after 8 hours of use. Rinse and drain tubing less often.

10.5.1.3 The aspiration chamber may be cleaned periodically using the sonication soap solution in the sonication bath for 0.5 hrs and rinsed with 10% HNO_3 and deionized water.

10.5.1.4 To clean the autolens, the vacuum must be turned off, the cover to the vacuum chamber removed and the autolens taken out. Clean with 10% HCl, dry

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thoroughly and return to the chamber. The autolens may also be polished with a wire brush. Replace the cover and evacuate.

10.5.2 Electron multiplier voltages require periodic optimization if Daily Performance Standard criteria in Section 10.3.4.2 are not met (see Operators Manual).

11. Data Evaluation, Calculations and Reporting

11.1 All calculations necessary to convert raw data (ion counts/second) are performed by the ELAN software. The calculated quantities are selected by choosing the desired options in the Report Options screen. The default report option for the ELAN 6020 Method is 6020.rop.

11.2 All calculations performed in the ELAN software are based on the ratio of the analyte intensity (cps) to the internal standard intensity (cps). In all calculations where internal standards are used, the ratio of the analyte intensity to internal standard intensity is taken before any other calculation is performed. Note: *Method 6020 requires the use of internal standards.*

11.3 The metal results are calculated by the following equation:

Aqueous:

$$\text{Metal result in pg/L} = \frac{C \times B}{A} \times DF$$

where:

A = Initial sample volume in mL, typically 25 mL
B = Digestate final volume in mL, typically 25 mL
C = Concentration of sample from instrument read-out in pg/L
DF = Dilution Factor

Solid:

$$\text{Metal result in mg/Kg} = \frac{\frac{C \times B}{A} \times DF \times \frac{100}{DW}}{1000}$$

where:

A = Initial sample weight in grams, typically 1 gram
B = Digestate final volume in mL, typically 50 mL
C = Concentration of sample from instrument read-out in pg/L
DF = Dilution Factor
DW = Dry Weight

11.4 To calculate Hardness:

(Ca result (in mg/L) x 2.5) + (Mg result (in mg/L) x 4.12) = Hardness in mg/L

11.5 All metal results should be reported to three significant figures

11.6 The primary analyst does data entry into the LIMS system. The LIMS is "linked" to the instrument, so the analyst must choose the sample(s) and elements to be reported from that

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analytical sequence. All associated preparation and instrumental QC samples and dilutions are also chosen. The laboratory generates two types of data packages from the LIMS: "Commercial" for routine projects, and "Full Deliverable" or "CLP-like" for fully data validated projects. A Commercial package consists of sample results and the associated method blank and LCS results. A Full Deliverable package includes all sample results, all preparation and instrumental QC results and the associated supporting raw data.

11.7 All solids including soils, sediments, and sludges must be reported on a dry-weight basis. Tissue results may be reported in wet-weight depending upon client request.

11.8 A secondary review is performed on all data.

11.9 If interferences on sample analysis resulting in false positive, false negative or biased results are suspected or have been determined, it may be possible to eliminate or minimize these interferences through use of the DRCe ICP MS equipped with a reaction cell. The reaction cell allows for the introduction of oxygen and ammonia to react with the analyte or the interfering ion.

11.9.1 Arsenic analysis

The ArCl interference (see section 4.2) on As at m/z of 75 can be removed by introducing oxygen into the reaction cell. Oxygen reacts with As to form AsO. This analyte is measured at m/z of 91 and is not affected by the ArCl interference. The internal standard used for this analysis is 300 pg/L In. The following conditions have been found to be suitable for analysis of As in seawater. Seawater is a source of high chloride concentration.

Analyte	Cell Gas	Flow Rate (ml/min)	RP_0	RP_q
As	Oxygen	0.6	0	0.75
In	Oxygen	0.6	0	0.85

Note: These conditions may change to optimize the analysis for a particular sample matrix.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 outlines sample batch QC acceptance criteria. If non-compliant metals results are to be reported, the Department Manager and/or the Laboratory Director must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst or Section Head performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

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13.2 Instrument Detection Limit

The instrument detection limit (IDL) is the smallest signal above the background noise that an instrument can detect. The IDLs can be calculated by multiplying by **3**, the average standard deviations for measurements of a reagent blank analyzed on three analytical runs on three non-consecutive days. Seven consecutive measurements must be taken per day. The IDLs are not required to go through sample digestion. Each measurement must be performed as though it were a separate sample. The current IDLs are available upon request.

13.3 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.3.1 Initiat (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.3.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Mariagement and Disposal SOP

16. Attachments

Table 1: Reporting Limits
Table 2: QC Acceptance Criteria
Table 3: Isotopes Monitored and Equations Used
Table 4: Initial Calibration Levels and ICV/CCV Concentrations
Table 5: ELAN 6100 and DRCe Linear Ranges for Method 6020A

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Table 1 – Reporting Limits

Metal	Aqueous (pg/L)	Solid - Hot Plate (mg/Kg)	Tissue – Microwave (mg/Kg)
Aluminum	100	10	10
Antimony	0.5	0.05	0.05
Arsenic	0.5	0.05	0.1
Barium	0.5	0.05	0.05
Beryllium	0.5	0.02	0.05
Boron	10	0.5	0.5
Cadmium	0.2	0.02	0.02
Calcium	100	50	20
Chromium	0.5	0.2	0.05
Cobalt	0.2	0.02	0.05
Copper	0.5	0.1	0.05
Iron	50	20	10
Lead	1.0	0.05	0.02
Magnesium	50	10	10
Manganese	0.5	0.2	0.1
Molybdenum	0.5	0.05	0.05
Nickel	0.5	0.1	0.05
Polassium	200	10	10
Selenium	1.0	0.05	0.1
Silver	0.2	0.05	0.05
Sodium	100	10	10
Strontium	0.5	0.05	0.05
Thallium	0.2	0.02	0.02
Tin	0.5	5.0	0.10
Titanium	0.5	0.2	
Vanadium	5.0	0.1	0.1
Zinc	10	0.1	0.5

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Tabte 2 – QC Acceptance Criteria

QC Parameter	Acceptance Criteria
Tuning Solution	≤ 5% RSD
Mass Calibration	Must not differ by more than 0.1 amu from true value
Resolution Checks	Less than 0.9 amu at 10% peak height
Initial Calibration Curve	R ≥ 0.995
Method Blank	< reporting limit
Laboratory Control Sample	80-120%R for aqueous and 75-125%R (or Manufacturer's control limits) for solid
Matrix Duplicate	≤ 20%RPD for results >5x reporting limit
Matrix Spike	75-125%R for solid and aqueous
Matrix Spike Duplicate (if requested)	75-125%R for solid and aqueous, and ≤20% RPD
Initial and Continuing Calibration Verification	90-110%R
Initial and Continuing Calibration Blank	± 3X IDL
CRI (Reporting Limit Check)	50-150%R (DoD = 80-120%R)
ICSA and ICSAB Solution	80-120%R for spiked analytes
Internal Standard	70-120%R (Method 6020A) for instrument QC samples and field samples
Serial Dilution Sample	<10% D
Post Digestion Spike	75-125%R

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Table 3 - Isotopes Monitored and Equations Used

1.1.1.1 1.1.1.2 Analyte	Symbol	Isotopes Monitored	1.1.1.3 1.1.1.4 Correction Equations
Aluminum	Al	27	
Antimony	Sb	121,123	Sb 123 = Sb 123 - 0.127189 * Te 125
Arsenic	As	75	As 75 = As 75 - 3.127 * [ArCl 77 - (0.815*Se 82)]
Barium	Ba	135,137	
Beryllium	Be	9	
Cadmium	Cd	106,108,111,114	Cd 111 = Cd 111 - 1.073 * [MoO 108 -(0.712*Pd 106)] Cd 114 = Cd 114 - 0.026826 * Sn 118
Chromium	Cr	52,53	
Calcium	Ca	44	
Cobalt	Co	59	
Copper	Cu	63,65	
Iron	Fe	54	Fe 54 = Fe 54 - 0.028226 * Cr 52
Lead	Pb	206,207,208	Pb 208 = Pb 208 + 1* Pb 206 + 1* Pb 207
Calcium	Ca	44	
Manganese	Mn	55	
Molybdenum	Mo	95,97,98	Mo 98= Mo 98 - 0.110588 * Ru 101
Nickel	Ni	60,62	
Potassium	K	39	
Selenium	Se	77,82	Se 82 = Se 82 - 1.008696 * Kr 83
Silver	Ag	107,109	
Sodium	Na	23	
Thallium	Tl	203,205	
Vanadium	V	51	V 51 = V 51 - 3.127*[ClO 53 - (0.113*Cr 52)]
Zinc	Zn	66,67,68	
1.1.1.4.1 Internal Standards			
Lithium	Li	6	
Scandium	Sc	45	
Germanium	Ge	74	
Yttrium	Y	89	
Rhodium	Rh	103	
Indium	In	115	
Terbium	Tb	159	
Bismuth	Bi	209	

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Table 4 - Initial Calibration Levels and ICV/CCV Concentrations

Analyte	STD1	STD2	STD3	STD4	STD5	ICV,CCV
	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
Ag	0.10				100	50
Al	10.1	110	1020	10050		5050
As	0.10	10	20	100		50
B	0.10	10	20	100		50
Ba	0.10				100	50
Be	0.10	10	20	100		50
Ca	10.1	110	1020	10100		5050
Cd	0.10	10	20	100		50
Co	0.10	10	20	100		50
Cr	0.10	10	20	100		50
Cu	0.10	10	20	100		50
Fe	10.1	110	1020	10100		5050
K	11.0	100	1000	10000		5500
Mg	10.1	110	1020	10100		5050
Mn	0.10	10	20	100		50
Mo	0.10	10	20	100		50
Na	10.1	100	1000	10000		5050
Ni	0.10	10	20	100		50
Pb	0.10	10	20	100		50
Sb	0.10	10	20	100		50
Se	0.10	10	20	100		50
Si	0.05	5	10	50		25
Sn	0.10	10	20	100		50
Sr	0.10	10	20	100		50
Ti	0.10	10	20	100		50
Tl	0.10	10	20	100		50
V	0.10	10	20	100		50
Zn	0.10	10	20	100		50

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Table 5 - ELAN 6100 and DRCe Linear Ranges for Method 6020A.

Analyte	Mass	Linear Range (mg/L)
Ag	107	5
Al	27	50
As	75	5
B	11	5
Ba	138	5
Be	9	5
Ca	44	50
Cd	114	5
Co	59	5
Cr	52	5
Cu	63	5
Fe	57	50
K	39	50
Mg	24	50
Mn	55	5
Mo	98	5
Na	23	50
Ni	60	50
Pb	208	5
Sb	121	5
Se	82	5
Si	28	5
Ti	48	5
Tl	205	5
V	51	5
Zn	66	5

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Microwave Assisted Acid Digestion of Sediments, Soils, and Tissues

References: Method 3051A, *Test Methods for the Evaluation of Solid Wastes*, (USEPA Office of Solid Waste and Emergency Response), SW-846, Method 3051A, Rev. 1, Nov. 1998

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Signature: Joseph Watkins Date: 7/11/2011

ISSUE AMENDMENTS

Changes since last issue:

Edited signatories.

Microwave Assisted Acid Digestion of Sediments, Soils, and Tissues

References: Method 3051A, *Test Methods for the Evaluation of Solid Wastes*, (USEPA Office of Solid Waste and Emergency Response), SW-846, Method 3051A, Rev. 1, Nov. 1998

1. Scope and Application

Matrices: This method is applicable to the microwave-assisted acid extraction/dissolution of sediments, soils and tissue samples.

Definitions: Refer to Alpha Analytical Quality Manual.

This microwave extraction method is designed to mimic extraction using conventional heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl), according to EPA Methods 200.2, 3010, and 3050. Since these methods are not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution[1] of sediments, soils and tissue samples for the elements listed below.

This method is provided as an alternative to EPA Method 3050. This method provides options for improving the performance for certain analytes, such as antimony, iron, aluminum, and silver by the addition of hydrochloric acid, when necessary. It is intended to provide a rapid multi-element acid extraction or dissolution prior to analysis so that decisions can be made about materials and site cleanup levels, the need for TCLP testing of a waste (see EPA Method 1311, Section 1.2, for further details), and whether a BDAT process is providing acceptable performance. Digests produced by the method are suitable for analysis by flame atomic absorption spectrophotometry (FLAA), graphite furnace atomic absorption spectrophotometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). However, the addition of HCl may limit the methods of detection, or increase the difficulties of detection with some techniques.

Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of experienced analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

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Parameter	CAS	Parameter	CAS
Aluminum (Al)	7429-90-5	Magnesium (Mg)	7439-95-4
Antimony (Sb)	7440-36-0	Manganese (Mn)	7439-96-5
Arsenic (As)	7440-38-2	Mercury (Hg)	7439-97-6
Barium (Ba)	7440-39-3	Molybdenum (Mo)	7439-98-7
Beryllium (Be)	7440-41-7	Nickel (Ni)	7440-02-0
Boron (B)	7440-42-8	Potassium (K)	7440-09-7
Cadmium (Cd)	7440-43-9	Selenium (Se)	7782-49-2
Calcium (Ca)	7440-70-2	Silver (Ag)	7440-22-4
Chromium (Cr)	7440-47-3	Sodium (Na)	7440-23-5
Cobalt (Co)	7440-48-4	Strontium (Sr)	7440-24-6
Copper (Cu)	7440-50-8	Thallium (Tl)	7440-28-0
Iron (Fe)	7439-89-6	Vanadium (V)	7440-62-2
Lead (Pb)	7439-92-1	Zinc (Zn)	7440-66-6

2. Summary of Method

For soils, sediments and tissues, a representative sample of 0.5-1.5 g is extracted and/or dissolved in 10mL concentrated nitric acid for 10 minutes using microwave heating with a suitable laboratory microwave unit. The sample and acid(s) are placed in a fluorocarbon polymer (PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate determinative method.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Refer to the appropriate analytical SOP for reporting limit information.

4. Interferenees

4.1 Very reactive samples or volatile materials may create high pressures due to the evolution of gaseous digestion products. This may cause venting of the vessels with potential loss of sample and/or analytes. The complete decomposition of either carbonates, or carbon based samples, may produce enough pressure to vent the vessel if the soil sample size is greater than 0.25 g (depending on the pressure capability of the vessel). Variations of the method to accommodate very reactive materials are specifically addressed in Section 10.3.1.3.

4.2 Many types of samples will be dissolved by this method. A few refractory sample matrix compounds, such as quartz, silicates, titanium dioxide, alumina, and other oxides may not be dissolved and in some cases may sequester target analyte elements. These bound elements are considered non-mobile in the environment and are excluded from most aqueous transport mechanisms of pollution.

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5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 The microwave unit cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation. Never use an Advanced Composite Vessel without a composite sleeve. Prior to use, all vessel components must be dry and free of particulate matter. Drops of liquid or particles will absorb microwave energy that can lead to localized charring which can lead to vessel damage or failure. Never install more than one rupture membrane in an Advanced Composite Vessel.

CAUTION: There are many safety and operational recommendattons specific to the model and manufacturer of the microwave equipment. The analyst is advised to consult the equipment manual (see 1.3), the equipment mahufacturer, and other appropriate literature for proper and safe operation of the microwave equipment arid vessels.

5.2 The method requires essentially microwave transparent and reagent resistant materials such as fluorocarbon polymers (examples are PFA or TFM) or quartz to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The internal volume of the vessel should be at least 45mL, and the vessel must be capable of withstanding pressures of 200psi, arid capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which tiere are many adequate designs by many suppliers. CEM provides t00mL vessels made of Teflon PFA, caps made of Ultem polyetherimide (reinforced), and sleeves of composite glass, Tefion PFA and Ultem.

5.3 *CAUTION:* The reagent combination (9mL nitric acid to 3mL hydrochloric acid) results in greater pressures than those resulting from the use of only nitric acid. Pressures of approximately 12atm have been reached during the heating of the acid mixture alone (no sample in the vessel). Pressures reached during the actual decomposition of a sediment sample (with low organic content) have more than doubled when using the 9mL nitric and 3mL hydrochloric acid mixture. These higher pressures may necessitate the use of vessels having higher pressure capabilities. Matrices having large organic content, such as oils, can produce approximately 25atm of pressure inside the vessel (as described in EPA Method 3052).

5.4 *CAUTION:* Another safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. Some digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only fiuorocarbon (such as PFA or TFM and others) or quartz containers with pressure relief mechanisms or containers with fiuorocarbon or quartz liners and pressure relief mechanisms are considered acceptable.

5.5 *CAUTION:* Laboratories should NOT use domestic (kitchen) type microwave ovens for this method because of significant safety issues. When acids such as nitric and hydrochloric are used to effect sample digestion in microwave units in open vessel(s), or sealed vessel(s),

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there is the potential for any released acid vapors to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.

5.6 Users are therefore advised NOT to use domestic (kitchen) type microwave ovens or sealed containers which are not equipped with controlled pressure relief mechanisms for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of SW-846. Refer to that chapter, as updated, for guidance.

All sample containers must be pre-cleaned by the vendor. Plastic and glass containers are both suitable. For further information, see Chapter Three of SW-846.

6.2 Sample Preservation

No preservatives are used.

6.3 Sample Shipping

No special shipping requirements. Typical shipping procedures may be found in the Alpha's Sample Receipt and Log-In SOP (01-01).

6.4 Sample Handling

Samples should be refrigerated upon receipt (4°C ± 2) or frozen at -20°C ± 10°C.

7. Equipment and Supplies

7.1 Microwave apparatus: Milestone Ethos E 1000 W Microwave Oven with maximum operating temperature of 200°C and maximum operating pressure of 200 PSIG/13.8 Bar.

7.1.1 The temperature performance requirements necessitate the microwave decomposition system to sense the temperature to be within ± 2.5° C and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2.5° C (including the final reaction temperature of the digestion procedure). Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e., different vessel types and microwave oven designs), temperature feedback control is preferred for reproducible microwave heating.

7.1.2 Alternatively, for a specific vessel type, specific set of reagent(s), and sample type, a calibration control mechanism can be developed. Through calibration of the microwave power for a specific number and type of vessels, vessel load, and heat loss characteristics of a specific vessel series, the reaction temperature profile described in Sec. 11.3.5 can be reproduced. The calibration settings are specific for the number and type of vessels and microwave system being used, in addition to the specific reagent combination being used. Therefore, no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of microwave equipment and vessel type. In this circumstance, the microwave system provides programmable power, which can be programmed to within ± 12

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W of the required power. Typical systems provide a nominal 600 W to 1200 W of power. Calibration control provides backward compatibility with older laboratory microwave systems which may not be equipped for temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older vessels with lower pressure capabilities may not be compatible.

7.1.3 A rotating turntable is employed to ensure the homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm. Other types of equipment that are used to assist in achieving uniformity of the microwave field may also be appropriate.

7.1.4 Milestone Fiber Optic Temperature Probe Part # FO00110

7.2 Mechanical Pipette: Class A or appropriate

7.3 Volumetric Graduated Cylinder: Class A or appropriate, 50 or t00mL capaeity or equivalent.

7.4 Filter paper, quatitative or equivalent

7.5 Filter funnel, glass, polypropylene, or other appropriate material

7.6 Balance: Top loading balance capable of reading two decimal places

7.7 Spatulas

7.8 Digestion Tubes: Pre-cleaned, graduated, disposable tubes, 50 mL volume (Environmental Express part # SC475 or equivalent) with Filter Assembly (Environmental Express Part # SC0408 or equivalent). The 50mL volume of each Lot of tubes is verified and documented in a logbook (Form No.: 105-02).

8. Reagents and Standards

All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use withoui decreasing the accuracy of the determination. If the puriiy of a reagent is questionable, the reagent should be analyzed to determine the level of impurities. The reagent blank must be less than the RL in order to be used. The expiration date of all reagents and standards is six months unless otherwise noted. Reagents and standards are stored at room temperature.

8.1 Concentrated nitric acid (HNO_3). Prior to use, the acid is analyzed to determine levels of impurity. If the method blank is less than the RL, the acid can be used. Results of this analysis are kept in a logbook.

8.2 Concentrated hydrochloric acid (HCl). Prior to use, the acid ise analyzed to determine levels of impurity. If the method blank is less than the RL, the acid can be used. Results of this analysis are kept in a logbook.

8.3 Reagent Grade Deionized Water (DI): Reagent water shall be interference free. All references to water in the method refer to reagent grade DI water unless otherwise specified.

8.4 Spiking solutions:

8.4.1 Laboratory Control Sample (LCS) and High Matrix Spiking (MS) solution for 3051: Spike 0.5mL of S1 into the LCS and MS samples. The final concentration in the LCS and MS samples are Be and Cd at 0.5mg/L; Sb, Ba, B, Cr, Cu, Co,

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Mn, Zn, Ni, Pb, V, Tl, As, Se and Mo at 1.0mg/L; Al, Ca, Fe, Mg, K, and Na at 5.0mg/L

8.4.1.1 S1 Sotution: Prepare by adding 5mL of concentrated HNO_3 to a t00mL volumetric flask using a 5mL glass pipette. Then add t0mL of ICUS-624 (Ultra Scientific) solution containing Be and Cd at 500mg/L, for a concentration of 50mg/L, and Sb, Ba, B, Cr, Cu, Co, Mn, and Mo at t000mg/L, for a concentraiion of t00mg/L. Next add t0mL of ICUS-625 (Ultra Scientific) solution containing Zn, Ni, Pb and V at 1000mg/L for a concentration of t00mg/L, and Al, Ca, Fe, Mg, K, and Na at 5000mg/L, for a concentration of 500mg/L. Next add t0mL each of Tl, As and Se (SPEX) at 1,000mg/L for a concentration of t00mg/L. This solution is brought to volume with DI water

8.4.2 Laboratory Controt Sampte (LCS) and Low Matrix Splking (MS) solution for 3051: Spike 0.80mL of S3 into the LCS sample and MS sample.

8.4.2.1 S3 Sotution: Prepare by adding 5mL of concentrated HNO_3 to a t00mL volumetric fiask using a 5mL glass pipette. Then add 2.5mL of IQC-026 (Ultra Scientific) Elements solution containing Ag, Al, As, Ba, Be, B, Ca, Cd, Cr, Cu, Co, Fe, Pb, Mq, Mn, Mo, Ni, Sb, Se, Tl, Ti, V, and Zn at t00mg/L. Si is present at 50 mg/L and K is present at 1000 mg/L for a concentration of 2.5mg/L for all elements except Si (1.25 mg/L) and K (25 mg/L). This solution is brpught to volume with DI water.

8.4.2.2 Hg sotution: Prepare by diluting the 1000 mg/L stock standard 1:50 in 2% HCl. Add 0.1 mL of stock to 100 ml volumetric flask and bring to volume to make a 1.0 mg/L solution. Add 1.25mL of 1.0mg/L Hg to LCS and matrix spike low standards

Note: The mercury spike concentration may be reduced if lower reporting limits are required. The spike volume used for plant tissue is 0.025 mL.

8.5 **Blank Sand:** Catatog #058 from Environmental Resource Associates (ERA)

8.6 **Solid Matrix Sample:** Catalog # 540 from ERA

9 Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characterisiics of the method.

9.1 Blank

A blank must be processed with each analytical batch or every 20 samples whichever is more frequent. A blank is brought through the whole sample preparation and analysis process. All measured analyte concentrations in the preparation blank must be below the reporting limit. Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. The batch should be re-prepared for any analyte whose concentration exceeds the reporting limit. A blank whose analyte concentrations exceed the reporting limit may be deemed acceptable by the Metals Supervisor if analyte concentration in the affected sample are below the reporting limit or greater than ten times the reporting limit.

If required, and a blank solid material of a similar matrix type (Environmental Resource Associates #058 or equivalent) of high enough purity can be obtained to meet required

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reporting limits, a solid material may be used in the Method Blank preparation to matrix match QC samples and field samples.

9.2 Laboratory Control Sample (LCS)

A LCS is processed with each analytical batch or every 20 samples whichever is more frequent. A LCS is a blank spike brought through the whole sample preparation and analysis process. Nominal recovery limits for an LCS are 80% - 120%. Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. The batch should be re-prepared for any analyte whose recovery is outside of these limits. The Metals Supervisor may deem an LCS whose recovery for any analyte is outside of these limits acceptable if acceptable recoveries from a matrix spike and/or SRM prepared with the batch are within control limits.

If required, a solid LCS (Environmental Resources Associates # 544 or equivalent) may be prepared to matrix match QC samples and field samples.

9.3 Initial Calibration Verification (ICV)

Not Applicable

9.4 Continuing Calibration Verification (CCV

Not Applicable

9.5 Matrix Spike

Spiked samples (MS) or standard reference materials should be included with each group of samples processed, or every 20 samples whichever is more frequent. A spiked sample should also be included whenever a new sample matrix is being analyzed. An SRM is used when required by the project.

9.6 Laboratory Duplicate

Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analysis process. A duplicate sample must be processed with each analytical batch or every 20 samples whichever is more frequent. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

9.7 Method-specific Quality Control Samples

9.8 Method Sequence

- Method Blank
- Laboratpry Control Sample
- Laboratory Duplicate
- Matrix Spike
- Samples 1-20

10 Procedure

10.1 Equipment Set-up

10.1.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Method control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within ± 2.5 °C and permit adjustment of the microwave output power within 2 seconds.

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10.1.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with DI water. For normal cleaning, vessels are rinsed with DI water and soaked in DI water overnight. They are then assembled, 10 ml concentrated HNO_3 is added and digested using the method program. They are then rinsed with DI water and dried in a clean environment. When switching between high concentration samples and low concentration samples, all digestion vessels (fluoropolymer or quartz liners) should be thoroughly cleaned using the procedure above, visually inspected, and checked for contamination by the analysis of a preparation blank. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from prior sample digestions in vessels is suspected.

10.2 Initial Calibration

Not applicable

10.3 Equipment Operation and Sample Processing

10.3.1 Sample Digestion

10.3.1.1 For soil, sediment and tissue samples, weigh a well-mixed sample to the nearest 0.01 g into an appropriate vessel equipped with a controlled pressure relief mechanism. For soils, sediments, and tissues use 0.5-1.5 g .If the sample can not be well mixed and homogenized on an as received basis, then air or oven drying at 60°C or less, crushing, sieving, grinding, and mixing should be performed as necessary to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reduction in analytical variability, be aware that in certain unusual circumstances there could be loss of volatile metals (e.g., Hg, organometallics) or irreversible chemical changes (e.g., precipitation of insoluble species, change in valence state). See Chapter Three of SW-846 for more details.

10.3.1.2 For soil, sediment and tissue samples, add 10mL ± 0.1mL concentrated nitric acid to the vessel in a fume hood (or fume exhausted enclosure). The addition of concentrated hydrochloric acid to the nitric acid is appropriate for the stabilization of certain analytes, such as Ag, Ba, and Sb and high concentrations of Fe and Al in solution. The addition of hydrochloric acid may, however, limit the detection techniques or increase the difficulties of analysis for some detection systems such as ICP-MS (Method 6020) or GFAA (Method 7000). Samples are predigested for 10-120 minutes under a hood with the vessels loosely capped to allow gases to escape.

CAUTION: The addition of hydrochloric acid must be in the form of concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of chlorine gas, as well as other gases, will result from a premixed acid solution. These gases may be violently released upon heating. This is avoided by adding the acid in the described manner.

CAUTION: Toxic nitrogen oxide(s) and chlorine fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.

CAUTION: The analyst should wear protective gloves and face protection.

CAUTION: The use of microwave equipment with temperature feedback control is required to control any unfamiliar reactions that may occur during the leaching of samples of unknown composition. The leaching of these samples may require additional vessel requirements such as increased pressure capabilities

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10.3.1.3 The analyst should be aware of the potential for a vigorous reaction, especially with samples containing volatile or easily oxidized organic species. When digesting a matrix of this type, initially use no more than 0.100 g of sample. If a vigorous reaction occurs upon the addition of reagent(s), allow the sample to predigest in the uncapped digestion vessel until the reaction ceases. Heat may be added in this step for safety considerations (for example, the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure. However, if no appreciable reaction occurs, a sample mass of 0.250 g for oils, or 0.10-5 g for soil, sediments or tissues may be used.

10.3.1.4 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.

10.3.1.5 This method is a performance based method, designed to achieve or approach consistent leaching of the sample through achieving specific reaction conditions. For soil, sediment and tissue samples, the temperature of each sample should rise to 175 ± 5 °C in approximately 5 minutes and remain at 175 ± 5°C for the remainder of the 10 minutes digestion period. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of vessels that can be heated by the magnetron of the microwave unit according to the heating profile specified previously in this section. (The number will depend on the power of the unit, the number of vessels, and the heat loss from the vessels). If vessel rupture is observed in soil sample digestion, the temperature may be reduced to 150 °C.

NOTE: The pressure should peak between 5 and 10 minutes for most soil, sediment and tissue samples. If the pressure exceeds the pressure limits of the vessel, the pressure should be safely and controllably reduced by the pressure relief mechanism of the vessel.

10.3.1.5.1 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in 11.3.5. The calibration settings will be specific to the quantity of reagents, the number of vessels, and the heat loss characteristics of the vessels. If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with the same acid mixture to achieve the full complement of vessels. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity. Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed).

10.3.1.6 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. Cooling of the vessels may be accelerated by internal or external cooling devices. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained their seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of sample exceeds 10% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection

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of the disk, in addition to weighing, may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or a physical sign that can indicate whether a vessel has vented is appropriate.

Samples must be weighed before and after digestion on a top loading balance capable of reading to 0.01 g. The combined weights of sample plus reagents should lose no more than 10% of the intial mass. If the weight loss exceeds the 10% limit, the sample digest should be considered compromised and re-prepared. Weight loss records will be maintained in the digestion log book albhg with each sample preparation.

10.3.1.7 Complete the preparation of the sample by carefully uncapping and venting each vessel in a chemical fume hood (or fume exhausted enclosure). Vent the vessels using the procedure recommended by the vessel manufacturer. Quantitatively transfer the sample to a clean vial and bring to 50 mL final volume with DI water. If the digested sample contains particulates that may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be, allowed to settle (11.3.7.1), or filtered (11.3.7.2).

10.3.1.7.1 Settling: If undissolved material, such as SiO_2, TiO_2, or other refractory oxides, remains, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

10.3.1.7.2 Filtering: Samples may be filtered in the 50 mL sample vial using a filter assembly (See Section 7.8). If neeessary, a filtering apparatus may be used after thoroughly cleaning and rinsing with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

10.4 Continuing Calibration

Not applicable.

10.5 Preventive Maintenance

10.5.1 Schedule annual maintenance with instrument a service company.

10.5.2 The aceuracy bf the temperature measurement system should be validated prior to use of a new probe and annually. This can be done using oil and an external calibrated temperature measurement system. The solution should be adequately stirred to ensure a homogeneous temperature, and both the microwave temperature sensor and the external temperature sensor placed into the oil. The temperature between the probe and external temperature measurement system should be compared at several different temperatures from room temperature to approximately 100 °C. If the measured temperatures vary by more than 2.5 °C, the microwave temperature measurement system should be calibrated or the probe should be replaced. Consult the microwave manufacturer's instructions about the specific calibration procedure for the temperature sensor. Results are maintained in the Microwave Probe Temperature Calibration Log.

10.5.3 Visually inspect digestion vessels for signs of wear.

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11 Data Evaluation, Calculations and Reporting

11.1 For soil, sediment and tissue samples, calculate the sample dry-weight fraction as follows:

$$\text{Dry-Wt fraction} = \frac{W_2 - W_3}{W_1 - W_3}$$

Where:

W_1 = Wt for sample + vessel, before drying, g
W_2 = Wt for sample + vessel, after drying, g
W_3 = Wt for empty, dry vessel, g

11.2 Convert the soil, sediment and tissue extract concentrations obtained from the instrument in mg/L to mg/kg dry-weight of sample by

$$\text{Sample concentration} = \frac{(C)(V)(D)}{(W)(S)}$$

Where:

C = Concentration in extract (mg/L)
D = Dilution factor
S = Solid dry-weight fraction for sample, g/g
V = Volume of extract, mL x 0.001
W = Weight of undried sample extracted, g x 0.001

12 Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 and the appropriate analytical SOPs outline sample batch QC acceptance criteria. If non-compliant inorganic element results are to be reported, the Metals Section Head and/or the Laboratory Director, and the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The instrument analyst or Section Head performing the secondary analytical review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

13 Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

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13.2.1 Initiat (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14 Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15 Referenced Documents

Chemical Hygiene Plan

SOP/01-01 Sample Receipt & Log-In

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

16 Attachments

None.

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Acid Digestion of Aqueous Samples for Metals Analysis

References: Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, USEPA, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, July 1992 (Revision 1) as promulgated in the Final Update, December 1996.

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Authorized by:

Name: John Kowalski Position: Metals Department Manager

Signature: _____ Date: 8/17/11

Name: Joseph Watkins Position: Laboratory/Technical Director

Signature: Joseph Watkins Date: 8/17/11

ISSUE AMENDMENTS

Changes since last issue:

Sections 6.3, 6.4 and 10.1: Removed references to outdated SOP, G-005

Section 10.1: Corrected section reference.

Corrected document footer.

Acid Digestion of Aqueous Samples for Metals Analysis

References: Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, USEPA, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, July 1992 (Revision 1) as promulgated in the Final Update, December 1996.

1. Scope and Application

Matrices: The method is applicable to groundwater, wastewater and surface water.

Definitions: Refer to Alpha Analytical Quality Manual.

Method 3020A

This acid digestion procedure is used to prepare aqueous samples for analysis by GFAA or ICP-MS. Samples prepared by this method may be analyzed by GFAA or ICP-MS for all the metals listed below:

Element	CASRN	Element	CASRN	Element	CASRN
Aluminum (Al)	7429-90-5	Cobalt (Co)	7440-48-4	Potassium (K)	7440-09-7
Antimony (Sb)	7440-36-0	Copper (Cu)	7440-50-8	Silver (Ag)	7440-22-4
Arsenic (As)	7440-38-2	Iron (Fe)	7439-89-6	Selenium (Se)	7782-49-2
Barium (Ba)	7440-39-3	Lead (Pb)	7439-92-1	Sodium (Na)	7440-23-5
Beryllium (Be)	7440-41-7	Magnesium (Mg)	7439-95-4	Thallium (Tl)	7440-28-0
Cadmium (Cd)	7440-43-9	Manganese (Mn)	7439-96-5	Tin (Sn)	7440-31-5
Calcium (Ca)	7440-70-2	Molybdenum (Mo)	7439-98-7	Titanium (Ti)	7440-32-6
Chromium (Cr)	7440-47-3	Nickel (Ni)	7440-02-0	Vanadium (V)	7440-62-2
				Zinc (Zn)	7440-66-6

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

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2. Summary of Method

- Method 3020A

0.75mL of concentrated nitric acid is added to 25mL of aqueous sample measured into a disposable digestion tube. The sample is heated in a block at 90-100°C and evaporated to approximately 5mL. 0.75mL of additional concentrated nitric acid is added, and the sample is refluxed for approximately 15 minutes, then evaporated to approximately 5 – 10 mL. After cooling, the sample is diluted back to 25mL, the initial sample volume, with deionized water.

If the sample should go to dryness, the sample must be re-prepared.

Some samples may require filtration due to insoluble silicates and the formation of precipitates during digestion. If this is the case, a filter blank must be added to the sample batch.

Samples received for dissolved metals (filtered through 0.45 µm filter) do not require digestion and are analyzed as-received. If filtration is performed in the laboratory, this is documented in the *Metals Filtration Logbook*, and a filter blank is prepared and analyzed with the sample batch.

2.1 Method Modifications from Reference

Method 3020A: The final volume has been reduced from 100mL to 25mL and reagent volumes have been proportionately reduced. Elements have been added to the analyte list as compared to the reference method.

3. Reporting Limits

Refer to the appropriate analytical SOP for reporting limit information.

4. Interferences

All re-usable glassware or plastic must be acid cleaned prior to use to remove residual trace elements.

Based on historical information, or by sample observation, it may be noted that some samples will require filtration after digestion, and prior to analysis, due to insoluble silicates and the formation of precipitates. If this is the case, a filter blank must be prepared for the batch. If the formation of precipitates is noted after sample digestion, and no filter blank was initiated, the associated method blank and laboratory control sample must be filtered.

5. Health and Safety

5.1 The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

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5.2 All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.3 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept in the office area.

5.4 Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at *all* times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting device and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

5.5 All standards and reagents shall be prepared in a hood while using the proper PPE.

5.6 Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Section Head Supervisor immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Section Head Supervisor immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

5.7 Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

5.8 Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

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5.9 Caution should be used when handling all aqueous samples, as they are generally preserved to a pH < 2, and pose a potential acid burn hazard.

5.10 All additional company safety practices shall be followed at all times as written in the *Chemical Hygiene Plan*.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

A sample size of 125mL to 500mL sample must be collected in a HDPE container with a Tefion lined screw cap or equivalent. Samples must be acidified to pH <2 with HNO_3, preferably at the time of collection.

6.2 Sample Preservation

Samples must be acidified to pH <2 with HNO_3, preferably at the time of collection.
NOTE: Samples for dissolved metals are filtered prior to acidification.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Preparation of samples must not begin until 18 hours after sample acidification.

If samples are acidified and/or filtered in the laboratory, this must be documented in the *Metals Filtration Logbook*. Samples for dissolved metals are filtered prior to acidification.

Samples and sample filtrates are stored at room temperature or may refrigerated at 4 ± 2°C and analyzed within 6 months.

7. Equipment and Supplies

7.1 Glassware for Digestion: 50mL disposable digestion tubes, watch covers, glass or plastic filter funnels.

7.2 Electric Hot Plate/Block: Adjustable and capable of maintaining a temperature of 90-95°C equipped with graphite carbon blocks that each have 36 positions to hold the sample tubes.

NOTE: Hotplate/Block temperatures are monitored and recorded regulariy using NIST calibrated and traceable thermometers. If any thermometer is suspected to not be reading the temperatures correctly, see the QA Department for a certified replacement thermometer.

7.3 Other: Adjustable Eppendorf pipettes and replacement tips, pre-cleaned Filter Mate from Environmental Express (2.0urn filter paper and plunger), t0mL glass pipettes, 100mL and 200mL Class-A volumetric fiasks.

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8. Reagents and Standards

ACS Trace Metal grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

The solutions below expire 6 months from preparation, or expire based on the manufacturer's expiration date, whichever comes first. Standards are stored out of direct light at ambient temperature. Reagents are stored at ambient temperature, under a hood if necessary. Acids are kept in a storage crate under a hood. Once opened, initialed and dated, they are kept in a hood. Acid expiration dates are generally provided by the manufacturer and printed on the label.

8.1 Deionized (DI) water: ASTM Type II laboratory reagent grade water or better (*i.e.*, Type I). The Barnstead NANO-pure system provides Type I water used in the preparation of samples and standards.

8.2 Nitric acid, concentrated (HNO_3): ACS reagent grade, Fisher #A509-212, or equivalent.

8.2.1 Nitric Acid (1:1 HNO_3): Add 500mL concentrated HNO_3 to 400mL DI water and dilute to 1L.

8.3 Spiking solutions:

8.3.1 Laboratory Control Sample (LCS Low) for 3020A/200.2T. The final concentration in the LCS samples are Ag, As, Be, Ca, Cd, Cr, Cu, Co, Fe, Pb, Mg, Mn, Mo, Ni, Sb, Se, Tl, Ti, V, and Zn at 0.04mg/L.

Spike 0.40mL of S3 Solution (Section 8.3.1.1) into the LCS sample.

8.3.1.1 S3 Solution: Adding 5mL of concentrated HNO_3 to a 100mL volumetric flask using a 5mL glass pipette. Then add 2.5mL of IQC-026 Elements Solution (Section 8.3.1.1.1). This solution is brought to 100mL volume with DI water. The final concentration of this solution is 2.5mg/L for Ag, As, Al, B, Ba, Be, Ca, Cd, Cr, Cu, Co, Fe, Pb, Mg, Mn, Mo, Na, Ni, Sb, Se, Tl, Ti, V, and Zn. A final concentration of 1.25mg/L for K and 25mg/L for Si.

8.3.1.1.1 IQC-026 Elements Solution: From ULTRA; contains Ag, Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Co, Fe, Pb, Mg, Mn, Mo, Na, Ni, Sb, Se, Tl, Ti, V, and Zn at 100mg/L. Si at 50mg/L and K at 1000mg/L.

8.3.2 Laboratory Control Sample (LCS High) for 3020A/200.2T

8.3.2.1 S1 Solution: Prepare by adding 5mL of concentrated HNO3 to a 100mL volumetric flask using a 5mL glass pipette. Then add 10 mL of ICUS-624 (Ultra Scientific) solution containing Be and Cd at 500mg/L, for a concentration of 50mg/L, and Sb, Ba, B, Cr, Cu, Co, Mn, and Mo at 1000mg/L, for a concentration of 100mg/L. Next add 10mL of ICUS-625 (Ultra Scientific) solution containing Zn, Ni, Pb and V at 1000mg/L for a concentration of 100mg/L, and Al, Ca, Fe, Mg, K, and Na at 5000mg/L for a concentration of 500mg/L. Next add 10 mL each of Tl, As and Se (Ultra, Absolute or equivalent) at 1,000mg/L for a concentration of 100mg/L. This solution is brought to volume with DI water.

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8.3.2.2 High Spike: Spike 0.25 mL of S1 Solution into the LCS High. See Section 8.3.2.1 for the preparation of the S1 Solution. The final concentrations of metals in the High LCS are: Be and Cd at 0.5mg/L; Ag, Sb, Ba, B, Cr, Cu, Co, Mn, Zn, Ni, Pb, V, Tl, As, Se and Mo at 1mg/L; Al, Ca, Fe, Mg, K and Na at 5mg/L.

8.3.3 Matrix Spiking (MS) sotution for 3020A/200:2T:

8.3.3.1 High Spike: Spike 0.25mL of S1 Solution into the MS high sample. See 8.3.2.1 for the preparation of the S1 solution. The final concentration in high MS samples are Be and Cd at 0.5mg/L; Ag, Sb, Ba, B, Cr, Cu, Co, Mn, Zn, Ni, Pb, V, Tl, As, Se and Mo at 1mg/L; and Al, Ca, Fe, Mg, K, and Na at 5mg/L.

8.3.3.2 Low Spike: Spike 0.40mL of S3 into the MS low sample. See Section 8.3.1.1 for preparation of the S3 solution. The final concentration in low MS samples are Ag, As, Be, Ca, Cd, Cr, Cu, Co, Fe, Pb, Mg, Mn, Mo, Ni, Sb, Se, Tl, Ti, V, and Zn at 0.04mg/L.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A method blank must be prepared in deionized water once per every 20 samples or per digestion batch, whichever is more frequent.

Metals elements of interest must not be detectable in the method blank at a concentration greater than the reporting limit.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. Digestion of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboraiory Director or QAO, if the samples associated with the out of control method blank are non-detect for the elements of interest, or if sample concentrations are greater than t0x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

9.2 Laboratory Control Sample (LCS)

Laboratory control sample (LCS) must be prepared once per every 20 samples or per digestion batch, whichever is more frequent, in deionized water and spiked with a solution prepared from a second source or lot number, other than the source used to verify the accuracy of the standard curve for the determinative analytical method. The LCS contains all target elements of interest, and is digested along with the samples as verification of the accuracy of the entire digestion procedure. (Refer to Seciion 8.4.1)

The acceptable recovery QC limits are documented in the applicable analytical SOPs. The aqueous recovery limits are continuously monitored and documented in-house through control charts. The Control Limit Generation SOP (08-07) provides details explaining how control charts are generated and used for quality control.

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Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the LCS recovery is still out of control, re-prepare and re-analyze the LCS and all associated samples. Samples cannot be reported until an acceptable LCS is obtained. Exceptions may be made with approval of the Metals Departmeni Manager, Laboraiory Director or QAO, if the samples associated with the out of control LCS are also associated with a matrix spike that is in control. This is an acceptable measure of accuracy of the digestion and analytical procedures. An explanation of the out of control LCS recovery must be included in the project narrative to the client and the sample data reported noting the acceptable MS results as batch QC.

9.3 Initial Calibration Verification (ICV)

Not applicable to this method.

9.4 Continuing Calibration Verification (CCV)

Not applicable to this method.

9.5 Matrix Spike

A matrix spike (MS) sample must be performed once per 20 samples (5% frequency), or per digestion batch, whichever is more frequent. The MS contains all target elements of interest. (Refer to Section 8.4.1).

The acceptable % recovery QC limits are documented in the applicable analytical SOPs. The aqueous % recovery QC limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The Control Limit Generation SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the % recovery still exceeds the control limits and the LCS is compliant, include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy of the reported results as evidenced by MS recovery outside of QC limits.

9.6 Laboratpry Duplicate

Duplicate analyses (matrix or sample duplicate) must be performed once per 20 samples (5% frequency), or per digestion batch, whichever is more frequent.

Acceptable relative percent differences (RPD) of duplicates are documented in the applicable analytical SOPs. Acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate the RPD as follows:

$$RPD = \frac{Rt - R2}{\frac{[R1 + R21}{2}} \times 100$$

where:
Rt = sample Replicate #1
R2 = sample Replicate #2

The RPD limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The SOP Control Limit Generation (08-07) provides details explaining how control charts are generated and used for quality control.

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Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the % RPD still exceeds the control limits, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the reported metals results as evidenced by the matrix duplicate %RPD exceedance.

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- Method Blank
- LCS
- Samples 1-20
- Matrix Duplicate
- Matrix Spike

10. Procedure

10.1 Equipment Set-up

Samples are prioritized by the Metals Department Manager or Preparation Group Leader for digestion based on hold time and client due date. Gather all samples for digestion from the Sample Custodian. Batch the samples that are being digested in the LIMS. Include the method blank, LCS, MS and Duplicate samples. If samples appear as if they will need filtration, add a filter blank to the batch as per Section 10.3.2. Note: The sample size and proportional volume of reagents used for the digestions have been reduced from the volumes cited in the reference methods.

10.2 Initial Calibration

Not applicable to this method.

10.3 Equipment Operation and Sample Processing

10.3.1 Sample Digestion according to Method 3020A/200:2T

10.3.1.1 Turn on the electric hotplate/hotblock and monitor the temperature to 90-100°C. It takes approximately 120 minutes to reach the proper temperature. Measure 25mL of each sample to the 25mL mark on the disposable digestion tubes. Use 25mL of DI water for the method blank and LCS. Label each tube with the sample batch ID.

10.3.1.2 Add 0.75mL of concentrated nitric acid to each sample. Spike the LCS and MS sample using the solutions prepared in Section 8.4.1, and 8.4.2. All sample spiking must be "spike witnessed".

10.3.1.3 Place the tubes into the block. Cover the samples with a watch cover. Evaporate the samples to approximately 5 – 10 mL, using caution not to let the samples boil, or go to dryness.

10.3.1.4 Remove the samples from the block. When cool, add another 0.75mL of concentrated nitric acid to each sample. Cover the samples with a watch

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cover, and place them back into the block. Refiux the samples for 15 minutes, until the digestion is complete (the digestate does not change appearance with continued refluxing). After cooling, bring to 25 mL mark on the digestion tube with DI water.

10.3.2 Sampte tittration after digestion:

10.3.2.1 If samples appear to require filtration prior to digestion, a filtration blank may be added to the batch at the beginning of the digestion.

10.3.2.2 The correct initial volume of DI water (25mL for 3020A) and Ihe reagents used in the digestion, are added to a digestion tube, and labeled as the filter blank.

10.3.2.3 After digestion, the filter blank, and any samples that need to be filtered, are filtered through a pre-cleaned filter paper that is part of the Filter Mate and plunger system. The filter is pushed, using the plunger, to the bottom of the original digestion tube, where all of the precipitates are held. Note on the sample preparation batch sheet, which samples were filtered.

10.3.2.4 If after digestion, some samples in the batch need to be filtered, but no filter blank was added to the batch prior te digestion, filter the samples that require filtration and filter the associated method blank and LCS for QC purposes, as in Seciion 10.3.2.3. Note on the sample preparation batch sheet, which samples were filtered.

10.3.2.5 If a filter blank was prepared at the beginning of the digestion as part of the sample batch, but after digestion, no samples required filtration, the filter blank may be discarded.

10.3.2.6 If, during the filtration steps above, the digestion tube inadvertently cracks, have a clean new tube near by. Quickly transfer the remaining sample digestate (minimum of 5mL) to the new tube. If less than 5mL of digestate remains, the sample must be re-digested. *Under no circumstances should any foreign object be placed into the sample tube to retrieve or re-set the filter plunger, as this may cause sample contamination.*

10.4 Continuing Calibration

Not applicable to this method.

10.5 Preventive Maintenance

The Hot Block thermometers are calibrated on an annual basis by an instrument service company. Certificates are kept on file.

11. Data Evaluation, Calculations and Reporting

Procedures for data and record management for organic extraction must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the Document Control SOP (G-016). All records must be stored in such a manner as to be safe and accessible for at least 10 years.

See the appropriate analytical SOPs for details on sample analysis, data evaluation, calculations and data reporting.

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All results for the metals elements of interests are reportable without qualification if digestion and analytical holding times are met, preservation (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is not suspected during digestion or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

QC Parameter	Acceptance Criteria
Method Blank	< reporting limit
Laboratory Control Sample	See the applicable analytical SOP for acceptance criteria
Matrix Duplicate	See the applicable analytical SOP for acceptance criteria
Matrix Spike	See the applicable analytical SOP for acceptance criteria
Matrix Spike Duplicate (if needed)	See the applicable analytical SOP for acceptance criteria

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 outlines sample batch QC acceptance criteria. If non-compliant inorganic element results are to be reported, the Metals Department Manager, the Laboratory Director, and/or the QAO must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The instrument analyst or Department Manager performing the secondary analytical review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

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14. Pollution Prevention and Waste Management

The *Hazardous Waste* and *Sample Disposal* SOP (G-006), must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

Once sample batches have completed digestion, the sample containers are stored in lhe metals lab and held for 30 days. If there is no sample remaining in the sample collection bottle, it may be rinsed and thrown away. It must be noted in the *Internal* COC that there is no sample remaining in the bottle, and the bottle was discarded.

Once the samples have been held for 30 days, any aqueous sample remaining must be disposed in a 55-gallon drum labeled "Corrosive Liquid".

Once satisfactory inorganic element results have been generated, the digestates are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled "Corrosive Liquid".

All reagent waste generated during digestion must be stored in satellite containers in the metals preparation laboratory.

Once the reagent waste satellite containers are full, they must be emptied into 55-gallon drums marked "Corrosive Liquid".

Refer to the Chemical Hygiene Plan and the SOP for Hazardous Waste and Disposal (G-006) for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL Generation

SOP/08-12 IDC Generation

SOP/ 01-01 Sample Receipt and Log-In

SOP/08-07 Control Limit Generation

SOP/ 08-01 Document Control

Hazardous Waste and Disposal (G-006)

16. Attachments

None.

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ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:_____

QA Manager:_____

Effective Date: _____

TITLE: pH AND CORROSIVITY FOR SOILS AND SOLID WASTES

METHOD REFERENCE: SW846 9045C and 9045D, SW846 Chapter 7

Revised Sections: Method reference, 4.1, 4.2,

1.0 SCOPE AND APPLICATION

1.1 This method is used to measure the pH and corrosivity of soils and solid wastes. For solid wastes, if an aqueous phase is present, it must be less than 20% of the total volume of the waste. If greater than 20% of the volume is aqueous, then method SW846 9040B should be used.

2.0 SUMMARY

2.1 The sample is mixed with reagent water and then the pH is determined electrometrically using a combination electrode or a separate pH and reference electrode. The pH meter is calibrated before analysis using a series of standard buffer solutions.

3.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit (see Section 3.4.1 for field samples and Section 4.4.3 for laboratory samples). For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits

(usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit

for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

4.0 HEALTH & SAFETY

4.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

4.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.0 PRESERVATION AND HOLDING TIME

5.1 The sample must be stored at 4^0 C. No preservatives should be added to samples to be analyzed for pH.

5.2 There is no regulatory holding time for soil pH analysis. However, it is recommended that all analyses be done within 28 days of sample collection, at the longest.

6.0 APPARATUS

The items needed for the analysis of pH are listed below.

6.1 pH meter with means for temperature compensation.

6.2 pH and reference electrode. Either a combination electrode or separate electrodes may be used. Normally, a combination electrode is employed.

6.3 Magnetic stir plate and stirring bars.

6.4 Graduated plastic or glass beakers.

6.5 Balance, capable of reading to one place past the decimal. The calibration on the balance must be checked each day before use.

7.0 REAGENTS

7.1 pH buffer solutions at pH 4, 7, and 10. Buffer solutions are commercially available and can be purchased from a number of different vendors.

7.2 pH buffer solutions at pH 2 and 12. These buffers should be used when the samples are < 4 or > 10. These buffer solutions are also commercially available.

8.0 INTERFERENCES

8.1 High levels of sodium can cause interferences when pH levels are > 10. The sodium error can be reduced by using a low-sodium-error electrode. Strong acid solutions, with a true pH of < 1, may give incorrectiy high pH measurements.

8.2 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing. An additional treatment with 1:10 hydrochloric acid may be necessary to remove any remaining film.

8.3 Temperature can also effect the final pH readings. The pH meter should have temperature compensation which account for changes in the electrode output at various temperatures. However, temperature changes can also occur due to changes in the sample as the temperature changes. This error cannot be controlled.

9.0 PROCEDURE

9.1 Below is the procedure to be followed for the analysis of soil and solid waste samples for pH.

9.2 Weigh out 50.0 g of each sample and add 50 mL of deionized water. If the sample is hygroscopic (i.e. absorbs water), then add water until the sample can be stirred and record the total volume of water added.

9.2.1 Smaller weights can be used if necessary, but the larger weight and volume is recommended for better sample reproducibility.

9.3 Stir the sample on a stirring plate continuously for 5 minutes and then let the sample stand until the solids have settied to the bottom of the beaker (approximately 15 minutes to 1 hour). If the solids do not settle out, then the sample may be filtered or centrifuge before analysis. While the samples are settling, the pH meter should be calibrated.

9.3.1 If the supernatant is contains oil and water, then decant off the oily phase and measure the pH of the aqueous phase.

9.4 Calibration of the pH Meter.

9.4.1 Turn on the pH meter and allow it to warm up. Gather all standards and allow them to come to 23 to 27 deg. C. Set the temperature compensation to 25 deg. C.

9.4.1.1 For samples with an alkaline pH of 11 or greater, the temperature of the sample must be within the range of 24 to 26 deg. C.

9.4.2 Following the manufacturers instructions, calibrate the meter using the 2 different buffer solutions that bracket the expected pH of the samples. Normally pH 4 and pH 7 buffer solutions are used.

9.4.3 After the calibration is completed, read back the buffer solutions. Record the results of each analysis on the pH worksheet. If the buffers are not within 0.05 pH units, then recalibrate the meter. If results above 7 or below 4 are expected, then read back the appropriate buffer solutions for the expected range(s).

9.4.4 After the meter is calibrated, analyze the samples by placing the pH electrode in each sample and recording the pH value of the solution. Make sure to rinse the electrode well with DI water between samples. At a minimum, read a bracketing buffer solution after every 10 samples. The results for the buffer should be within 0.2 pH units of the true value

9.4.4.1 If the check is outside of the 0.20 pH unit criteria, check the probe for problems. If the problems are unrelated to the sample matrix, then resolve the problems and reanalyze the samples and the check standards.

9.4.4.2 If the 0.20 pH unit criteria cannot be met due to difficulties with the probe caused by the sample matrix, see the area manager or supervisor. Sample results may be reported with a footnote noting the recovery obtained on the check standard.

9.4.5 Record both the pH value and the temperature for all buffer and sample measurements. Make sure to record the pH to 2 places past the dectmal.

9.4.6 If corrosivity is requested, then the sample should be reported as non-corrosive in the range from greater than 2 to less than 12.5. If the pH is less than or equal to 2 or greater than or equal to 12.5, then the sample should be reported as corrosive. Note:

A buffer check at 2 is required for acidic corrosivity checks and a buffer check at 12 is required for basic corrosivity checks if the samples are outside of the range of 4 to 10.

9.4.7 For corrosivity characterization, the sample must be measured at 24 to 26°C if the pH of the sample is above 12.0.

10.0 QUALITY ASSURANCE

10.1 At least 2 pH buffer solutions bracketing the range of the samples and a minimum of approximately 3 pH units apart must be analyzed each time the meter is calibrated, or at a minimum of once per day each day that the meter is used. These buffer solutions should be within 0.05 pH units of the true value.

10.2 A bracketing buffer check should be analyzed, at a minimum, after every 10 samples. This buffer should be within 0.2 pH units of the true value of the solution. Refer to section 9.4.4 for corrective action if the buffer is outside of this range.

10.2.1 A buffer check at 2 is required for acidic corrosivity checks and a buffer check at 12 is required for basic corrosivity checks if the samples are outside of the range of 4 to 10.

10.3 One duplicate should be analyzed for every 20 samples, or one per batch, whichever is more frequent. This quality control point should be evaluated using Accutest's in house quality control limits. If no quality control limits are available, default limits of ± 5 percent should be applied

11.0 DOCUMENTATION REQUIREMENTS

11.1 All analytical work should be documented on worksheets such as the one attached. All reagent preparation information should be written in the reagent preparation log. Lot numbers of purchased reagents should be recorded on the analytical worksheet. The analyst should sign and date the worksheet.

11.2 All calibration information must also be recorded in the pH calibration logs provided by each pH meter.

11.3 The temperature of the samples and buffers must be recorded for each pH measurement.

11.4 All pH measurements should be recorded to 2 places past the decimal.

12.0 POLLUTION PREVENTION & WASTE MANAGEMENT

12.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment

must be followed. All method users must be familiar with the waste management practices described in section 12.2.

12.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

12.2.1 Non hazardous aqueous wastes.

12.2.2 Hazardous aqueous wastes

12.2.3 Chlorinated organic solvents

12.2.4 Non-chlorinated organic solvents

12.2.5 Hazardous solid wastes

12.2.6 Non-hazardous solid wastes

13.0 ADDITIONAL REFERENCES

13.1 Refer to manufacturers manuals for all meters in use.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:_____

QA Manager:_____

Effective Date:_____

TEST NAME: HEXAVALENT CHROMIUM (SOILS)

METHOD REFERENCE: SW846 3060A, Revision 1, Dec. 1996 for digestion
SW846 7196A, Revision 1, July 1992, for analysis.

Revision Sections: 3.1.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium in soils, sludges, brick, concrete, and other solid matrices. The solid sample is digested in an alkaline digestion solution to solubilize both water soluble and water insoluble hexavalent chromium compounds. Magnesium chloride in a phosphate buffer is added to suppress oxidation of Cr(III). The hexavalent chromium is determined in the digestate by reaction with diphenylcarbazide in acid solution. The diphenylcarbazide complex produces a characteristic pink color which can be measured spectrophotometrically at 540 nm.

2.0 SUMMARY

2.1 This method uses an alkaline digestion to solubilize both water-insoluble (with the exception of partial solubility of barium chromate in some soil matrices, and water soluble Cr(VI) compounds in solid waste samples. The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate redigestion of the samples.

2.2 The sample is digested using 0.28M Na2CO3 /0.5M NaOH solution and heating at 90- 95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

2.3 The Cr(VI) reaction with diphenylcarbazide is the most common and reliable method for analysis of Cr(VI) solubilized in the alkaline digestate. The use of diphenylcarbazide has been well established in the colorimetric procedure, in rapid-test field kits, and in the ion chromatographic method for Cr(VI). It is highly selective for Cr(VI) and few interferences are encountered when it is used on alkaline digestates.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at 0.40 mg/kg for soils, based on the low standard of 0.010 mg/l x 100 ml volume volume with a sample weight of 2.5 g.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. Il is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specifled in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequentiy analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: hexavalent chromium.

6.0 PRESERVATION & HOLDING TIME

6.1 Soil samples should be kept under refrigeration at 4^0 C until time of digestion.

6.2 All samples that are analyzed following this method must be analyzed within 30 days of sample collection. The alkaline digestate is stable for up to 168 hours after extraction from soil.

7.0 INTERFERENCES

7.1 Waste material suspected of containing soluble Cr(III) concentrations greater than 4 times the laboratory Cr(VI) reporting limit may have Cr(VI) results that are biased high due to method induced oxidation. The addition of Mg (II) salts, in a phosphate buffer, is added to suppress this oxidation.

7.2 During the analysis of the alkaline digest for hexavalent chromium using diphenylcarbazide, high concentrations of molybdenum and mercury (> 200 mg/l) can interfere. Concentrations of vanadium greater than 10 times the level of hexavalent chromium may also cause interferences.

8.0 APPARATUS

8.1 Volumetric flasks and pipets and graduated cylinders, class A. All glassware should be washed with soap and tap water and then well rinsed with deionized water.

8.2 50 and 250 ml glass beakers with watch glasses. All glassware should be washed with soap and tap water and then well rinsed with deionized water.

8.3 Filter paper, 0.45 um. Acceptable filter papers include the following: MSI cellulostic white grid filters, 0.45 um, 47 mm (catalog number E04WG047S1).

8.4 Filter pump and vacuum filtration apparatus.

8.5 pH meter.

8.6 Hot plate, capable of maintaining the digestion solutions at 90 to 95 C, with constant stirring ability.

8.7 Four place analytical balance.

8.8 Thermometer, calibrated to an NIST certified thermometer a minimum of once per year.

8.9 Graduated plastic beakers.

8.10 One or two place balance.

8.11 Spectrophotometer capable of measurement at 540 nm, providing a light path of 1 cm or longer. The spectrophotometer should be connected with a strip chart recorder.

9.0 REAGENTS

9.1 All reagents should be made from ACS grade reagents unless otherwise noted. Deionized water should be used whenever water is needed. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Nitric acid, HNO_3, concentrated, trace metals grade.

9.3 Nitric acid, HNO_3, 5.0 M, trace metals grade. Add 32 ml of concentrated nitric acid to approximately 50 ml of DI water. Dilute to a final volume of 100 ml with DI water and mix well. Store at 20-25°C in the dark. Do not use concentrated nitric acid to make up the 5.0 M solution if it has a yellow tinge. The yellow color is indicative of a photo reduction of nitrate to nitrite, a reducing agent for Cr(VI).

9.4 Sodium Carbonate, Na_2CO_3, anhydrous.

9.5 Sodium Hydroxide, NaOH.

9.6 Magnesium Chloride, $MgCl_2$ (anhydrous). Note: 392.18 mg of $MgCl_2$ is equivalent to 100 mg of Mg^{2+}.

9.7 Phosphate Buffer Solution (0.5 M K_2HPO_4/0.5 M KH_2PO_4 buffer at pH 7): Dissolve 87.09 g of K_2HPO_4 and 68.04 g of KH_2PO_4 into 700 ml of distilled deionized water. Transfer to a 1 liter volumetric fiask and dilute to volume.

9.8 Digestion Solution: Dissolve 20.0 g of NaOH and 30.0 g of Na_2CO_3 in distilled deionized water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20 to 25°C and prepare fresh monthly. The pH of this digestion solution must be checked before using. If the pH is not greater than or equal to 11.5, then the digestion solution should be discarded and a new solution should be made up.

9.9 Insoluble hexavalent chromium spike, lead chromate, $PbCrO_4$. The insoluble matrix spike is prepared by adding 10 to 20 mg of $PbCrO_4$ to the insoluble matrix spike aliquot.

9.10 Soluble hexavalent chromium spiking solution stock. A 1000 mg/l stock solution of potassium dichromate can be used as the stock solution for the spiking solution. (Availabie as 1000 mg/l chromium solution, AAS grade from Fisher or equivalent).

9.11 Soluble hexavalent chromium spiking solution, 100 mg/l. Add 10.0 ml of the 1000 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well. One (1.00) ml of this spiking solution can be used to spike the soluble matrix spike aliquot. The approximate level of the spike in the spiked sample will be 40 mg/kg.

9.12 Sulfuric acid, 10 percent (v/v). Add 10 ml of concentrated sulfuric acid to approximately 70 ml of DI water. Mix well and let cool. Dilute to a final volume of 100 ml with DI water.

9.13 Acetone. Do not use acetone that comes in a container with a metal or metal lined cap.

9.14 Diphenylcarbazide solution. Dissolve 0.250 g of 1,5 diphenylcarbazide in 50 ml of acetone. Store in a brown or a foil covered bottle to minimize exposure to light. Discard when the solution becomes discolored or monthly, whichever comes first. (Note: Be sure to check the quality of the diphenylcarbazide solution before adding it to the sample.

9.15 Hexavalent Chromium Calibration Standard Solutions. The calibration standards must be

prepared fresh daily or each time the analysis is run. For instrument calibration, prepare the standards from the stocks as shown below. For all standards, add 50 ml of digestion solution to a labeled plastic beaker and then pipet in the appropriate amount of a stock solution. Do not dilute these standards to the final volume at this time. Refer to step 10.8 in the procedure section for further instructions.

9.15.1 Hexavalent Chromium, 10 mg/l stock solution. Add 1.00 ml of 1000 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well.

9.15.2 Hexavalent Chromium, 1.0 mg/l stock solution. Add 10 ml of 10 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well.

9.15.3 Add the amount of stock specified below to the 50 ml of digestion solution.

Blank: No spike is added to the blank.
0.010 mg/l. Add 1.0 ml of 1.00 mg/l
0.050 mg/l: Add 0.50 ml of 10.0 mg/l.
0.100 mg/l: Add 1.00 ml of 10.0 mg/l.
0.300 mg/l: Add 3.00 ml of 10.0 mg/l.
0.500 mg/l: Add 5.00 ml of 10.0 mg/l.
0.800 mg/l: Add 8.00 ml of 10.0 mg/l.
1.00 mg/l: Add 10.0 ml of 10.0 mg/l.

9.16 Hexavalent Chromium CCV (Continuing Calibration Verification) Solutions. The check standards must be prepared fresh daily or each time the analysis is run. Prepare the standards from the stocks as shown below. All check standards must go through the entire digestion process, starting at step 10.3. A minimum of 4 check standards should be made for a batch of 20 samples. Note: The check standards must be made from a different source than the calibration standards.

9.16.1 Hexavalent Chromium 10.0 mg/l stock solution. Add 2.00 ml of 1000 mg/l hexavalent chromium to a 200 ml volumetric fiask and dilute to volume with DI water. Mix well.

9.16.2 For initial calibration curves that have the 1.00 mg/l standard as the upper limit, a calibration check at 0.500 mg/l must be used. Therefore, add the amount of stock solution specified below to 50 ml of digestion solution. Do not dilute to a final volume. This entire solution should be digested.

0.500 mg/l: Add 5.00 ml of the 10.0 mg/l stock solution

10.0 DIGESTION PROCEDURE

Below is a step-by-step procedure for the digestion of samples for the determination of hexavalent chromium.

10.1 For each sample to be analyzed, weight out 2.5 ± 0.10 g of the sample into a clean, labeled glass beaker. A one or two place balance may be used for this weighing. The sample should be well mixed before the aliquot is removed as described in OQA-042, the representative sample aliquot SOP.

10.1.1 For the sample that is to be used for the quality control sample, weigh out six 2.5 ± 0.10 g aliquots from the well mixed sample. . One aliquot will be for the soluble Cr(VI) matrix spike, one aliquot will be for the insoluble Cr(VI) matrix spike, one aliquot will be for the original sample analysis, one aliquot will be for the duplicate sample analysis, and the remaining two aliquots will be used to complete the procedures required if the initial post-digest spike does not meet the ± 15 criteria.

10.2 Add the spikes to the matrix spikes and the spike blanks.

10.2.1 Spike the soluble Cr(VI) matrix spike with 1.0 ml of the 100 mg/l Cr(VI) spiking solution. (Check with the area supervisor or manger before starting to see if an additional spike level will be needed.)

10.2.2 Spike the soluble Cr(VI) spike blank with 1.0 ml of the 100 mg/l Cr(VI) spiking solution.

10.2.3 Using an analytical balance, weigh out 0.010 to 0.020 g of $PbCrO_4$ onto a clean piece of weighing paper and carefully add the spike into the insoluble matrix spike sample. Make sure to record the weight used.

10.2.4 Note: This second spike blank is optional. Using an analytical balance, weigh out 0.010 to 0.020 g of $PbCrO_4$ onto a clean piece of weighing paper and carefully add the spike into the insoluble spike blank sample. Make sure to record the weight used.

10.3 Add 50 ml of digestion solution to each sample. Also add 0.392 g of $MgCl_2$ and 0.5 ml of the 1.0 M phosphate buffer. In addition to the samples, 3 extra beakers should be prepared for the method blank, the soluble Cr(VI) spike blank, and the insoluble Cr(VI) spike blank.

10.4 In addition to the samples, the CCV (continuing calibration check) standards should also be digested. Add the entire CCV solution (refer to step 9.16) into a clean, labeled glass beaker. Also add approximately 0.392 g of $MgCl_2$ and 0.5 ml of the 1.0 M phosphate buffer.

10.5 Cover all samples and quality control (including the calibration check samples) with watch glasses. Add a stirring bar to each sample and stir the samples for at least 5 minutes without heating.

10.6 Place the samples on a stirring hot plate that has been preheated to 90 to 95°C. Heat the samples with constant stirring for 60 minutes, maintaining a temperature range of 90 to 95°C. The temperature should be measured by placing a calibrated thermometer in an extra beaker containing digestion reagent on the hot plate. The temperature must be recorded at 30 minutes and 60 minutes during the digestion process. Both the start and the stop time of the digestion must be recorded.

10.7 Cool the samples to room temperature. Filter them through 0.45 um filter paper. Rinse the filter and filtration apparatus with DI water and transfer the filtrate into labeled graduated plastic beakers.

10.7.1 If the filters become clogged using the 0.45 um filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to prefilter the samples. However, the final filtration must be through the 0.45 um filters. If a pre-filtration is required, it should be recorded on the digestion log.

10.7.2 The solids and the filter remaining after the filtration of the matrix spikes may need to be saved in a labeled plastic beaker and stored in the refrigerator. If low recoveries are obtained on the matrix spikes, these solids may be needed for additional analyses. Check with the area supervisor or manager for further instructions.

10.7.3 At this point, the digestates are stable and may be held for up to 168 hours before proceeding with step 10.8.

10.8 Do not start this step unless the analysis will be started within one hour after this step has been completed. The calibration standards should also be taken through this process.

10.8.1 Place a stirring bar in the sample and place it on a stirring plate. Adjust the pH of the solution between 7.00 and 8.00 by carefully adding 5.0 M nitric acid to the digestate

while constantly measuring the pH. Do not let the pH of the solution go below 7.00. If the pH goes below 7.00, then the digestate must be discarded and a new digestate prepared. Make sure to record the final pH.

10.8.2 If the pH is changing too rapidly with 5.0 M nitric acid, then a more dilute solution of nitric acid may be used for the pH adjustment.

10.8.3 Carbon dioxide and nitric acid fumes will be evolved during this process. Therefore, this step must be performed in a hood or well ventilated area.

10.9 Quantitatively transfer the contents of the beaker to a 100 ml volumetric flask or class A graduated cylinder and adjust the sample volume to the mark with DI water. Mix well. At this point, a brief description of each sample (color, turbidity, etc.) can be added to the digestion log.

10.9.1 If the same cylinder is used for multiple samples, it must be rinsed with deionized water at least 3 times between samples.

11.0 ANALYSIS PROCEDURE

11.1 Turn on the spectrophotometer and let it warm up for at least 30 minutes. Set the wavelength to 540 nm and adjust the zero.

11.2 Using a class A graduated cylinder, transfer quantitatively 45.0 ml of the sample or standard to be analyzed to a labeled plastic beaker.

11.3 Add 1.0 ml of diphenylcarbazide solution and mix well.

11.4 Slowly add 10 percent sulfuric acid to each sample, mixing well after each addition. Adjust the pH to a range of 1.5 to 2.5. Test the pH of each sample with a pH meter when the effervescence is minimal and record this reading. (On some samples, a small amount of effervescence has been observed several hours after the pH adjustment was completed.)

11.4.1 A background correction point must also be prepared for each sample with 10 ml of sample adjusted to a pH of 1.5 to 2.5 with sulfuric acid. The background correction point should not contain diphenylcarbazide. Make sure to record the adjusted pH of the background correction point.

11.5 If the samples are turbid at this point, filter them through a 0.45 um filter. If the sample aliquot is filtered, the background aliquot must also be filtered.

11.6 Transfer the samples to 50 ml volumetric flasks or class A graduated cylinders and dilute to a final volume of 50 ml with DI water. Let the samples stand for 5 to 10 minutes after the reagents are added for full color development.

11.6.1 If the same cylinder is used for multiple samples, it must be rinsed with deionized water at least 3 times between samples.

11.7 Read the standard calibration curve first, and then a calibration check standard and a reagent blank, making sure to record all results on the strip chart recorder. The correlation coefficient for the curve must be greater than or equal to 0.995, the check standard must be within 10 percent

of the tme value, and the reagent blank must be less than the reporting detection limit before the analysis can be continued.

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

11.8 After the curve and the initial quality control are completed, the samples may be analyzed. First read the sample result. If the result is over the highest point in the calibration curve, do not read the background correction point. If the result is within the calibration curve, the background correction point must be read immediately after the sample analysis is complete and before starting the next sample.

11.9 After every 10 samples or every 20 readings (10 samples plus 10 background correction points), a digested CCV and a reagent blank will be analyzed. The reagent blank must be less than the reporting limit, and the CCV must be within 10% of the true value. If they are outside of this range, do not proceed. Check with the laboratory supervisor or manager for further directions.

11.10 After the quality control sample analysis is completed, prepare a post-digest spike on this sample. The sample should be spiked at 2 times the concentration found in the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater. Then proceed through steps 11.3 to 11.6 and analyze the spiked sample. Calculate the recovery immediately. If the recovery is not within 85 to 115 percent, proceed to steps 11.11 and 11.12.

11.10.1 The 40 mg/kg spike can be made by spiking a 45 ml aliquot of digestate containing 1.125 g of digested sample with 0.45 ml of 100 mg/l Cr(VI) standard (Section 9.10).

11.10.2 This spiking level requirement is taken from method 3060a. A lower level spiking requirement is given in the NJDEP 7196A method, but guidance from the state suggested using the 3060A spiking levels when following the 3060a digestion.

11.11 Dilute by a factor of 1:5 a fraction of the quality control sample. Place 45 ml of the diluted sample into a plastic beaker. Then proceed through steps 11.3 to 11.6 and analyze the sample. Also prepare a background correction point at this dilution and analyze it immediately following the analysis of the diluted sample.

11.12 Take an additional 45 ml aliquot of the sample and adjust the pH to between 8.0 and 8.5 using 1.0 N NaOH. Record the final pH. Then spike the sample at 2 times the concentration found in

the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater. After the sample is spiked, proceed with steps 11.3 through 11.6, and analyze the pH adjusted post-digest spike.

11.13 The calculations should be done as shown below. Values less than the IDL should be treated as zero for all calculations.

11.13.1 Calculation of the sample result.

Cone. Cr(VI) in the sample in mg/kg =

$$\frac{\text{(cone. in digestate in ug/ml) x (final volume in ml) x DF}}{\text{(initial sample weight in g) x (\%soiids/100}}$$

11.13.2 Calculation of amount spiked.

Spike amount (SA) in mg/kg =

$$\frac{\text{(cone. of spiking solution, ug/ml) x (vol. of spike, ml)}}{\text{(initial sample weight in g) x (\%solids/100)}}$$

11.13.3 Calculation of matrix spike recovery.

$$\text{MS Rec.} = \frac{\text{(SSR - SR) x 100}}{\text{SA}}$$

where SSR = Spiked sample result
SR = Sample result and
SA = Spike added.

11.13.4 Calculation of duplicate rpd.

$$\text{Dup RPD.} = \frac{\text{(SR - DR) x 100}}{\text{\{(SR + DR)/2\}}}$$

where SR = Sample result and
DR = Duplicate result.

12.0 QUALITY CONTROL

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements as taken from these methods. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 A new 5 point calibration curve must be analyzed on each analysis day. The calibration curve must have a correlation coefficient greater than or equal to 0.995 percent.

12.2 All samples should initially be analyzed undiluted. If the sample concentration is higher than the highest standard, then the sample should be diluted and reanalyzed. The dilution should be made so that, if possible, the sample is in the mid-range of the calibration curve.

12.3 One preparation blank is required for each set of 20 samples or less or with each batch, whichever is most frequent. The preparation blank must contain all of the reagents in the sample volumes as used in the preparation of the samples. (The preparation blank should never be used to blank correct the samples.) The preparation blank must be less than the reporting limit. If the preparation blank does not meet the criteria, then the entire batch must be redigested.

12.4 A continuing calibration verification (CCV) standard at approximately the mid-point of the curve must be analyzed after every 10 samples or every 20 readings (10 sample readings plus 10 background readings). The CCV standard must be prepared from a different stock than the calibration curve and should be taken through the digestion process as outiined in the procedure section of this SOP. A CCV standard must be analyzed at the beginning of the analysis immediately after the analysis of the calibration curve. All CCV standards must be within 10 percent of the true value for that standard. If they are outside of this range, do not proceed. Check with the laboratory supervisor or manager for further directions.

12.5 A reagent blank (or CCB) must be analyzed after each CCV. The reagent blank must be less than the reporting detection limit. If this criteria is not met do not proceed. Check with the laboratory supervisor or manager for further directions.

12.6 A duplicate sample must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. An acceptance criteria of 20 percent relative percent difference should be applied if the original and duplicate sample values are greater than or equal to 4 times the reporting detection limit. If the values are less than 4 times the reporting detection limit, then a control limit of ± the reporting detection limit should be applied.

12.7 Both a soluble and an insoluble hexavalent chromium matrix spike must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The acceptance range for matrix spike recoveries is 75 to 125 percent recovery. If the matrix spike recoveries for either the soluble or the insoluble spikes are not within these recovery limits, then the lab supervisor or manager must be immediately notified. The client services deparment will then be notified to contact the client. The method requires additional testing as listed below, but the lab should not proceed with this testing until client approval is obtained and the testing is logged into the LIMS system.

12.7.1 All samples and quality control must be rehomogenized, redigested and reanalyzed to verify the original sample results.

12.7.2 Additional tests, such as oxidation-reduction potential, pH, sulfide, ferrous iron, etc., may be requested to help quantify the reducing nature of the sample. For some projects, eH and pH analysis may be specified for all samples at the start of the project. Eh and pH data plots must be provided in the data deliverable if this analysis is specified

12.7.3 A mass balance study for total chromium may be done, using the digested solids remaining after the alkaline digestion and filtration of the matrix spike and from a unspiked aliquot of the sample.

12.8 A post-digest spike must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The acceptance range for post digest spike recoveries is 85 to 115 percent recovery.

12.9 A spike blank or lab control sample must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller The spike blank or lab control can be prepared using either soluble or insoluble hexavalent chromium as the spike. The acceptance range for the spike blanks is 80 to 120 percent recovery. If the spike blanks are not within that range, then the entire batch must be redigested and reanalyzed.

13.0 DOCUMENTATION REQUIREMENTS

13.1 The analyst shouid document ali reievant information, including all sample weights and volumes, digestion times and temperatures, all intermediate and final pH values, all times relevant to the pH adjustment process, all sample and background analysis resuits, and any relevant comments for any section of the digestion or analysis. Sample digestion and analysis sheets are provided.

13.2 Analyses are done using an automated analysis spreadsheet where the sample absorbances are recorded electronically. If this electronic recording option is not available, then the analyst must verify all recorded absorbances. All reagent identification numbers should be recorded on the sample worksheets. In addition, all reagent information such as lot numbers should also be recorded in the reagent logbook.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to analysis (GN) batches in the LIMS system. The analyst should calculate all matrix spike, duplicate, external, and CCV recoveries and review the results of all blanks.

14.2 All documentation must be completed, including reagent references and spike amounts and spiking solution references.

14.3 A data file should be exported to the LIMS system and the spike amounts should be entered into the file at the GNAPP process step.

14.4 A final data package, consisting of the prep and analysis raw data, the LIMS cover page, the reagent reference pages, and the QC summary pages must be turned into the area supervisor or other senior reviewer for review.

14.5 After review by the supervisor, the data is released in the LIMS for access to the clients.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

16.0 ADDITIONAL REFERENCES

16.1 No additional references are required for this SOP.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

FN: EGN230-09
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Lab Manager: Nancy Cole

OA Manager: [signature] for Phil Worby

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TEST NAME: HEXAVALENT CHROMIUM IN WATERS

METHOD REFERENCE: SW846 Method 7196a

Revised Sections: 3.2.2, 10.6.1

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentraiion of hexavalent chromium in aqueous matrices. The hexavalent chromium is determined in the sample by reaction with diphenylcarbazide in acid solution. The diphenylcarbazide complex produces a characteristic pink color that can be measured spectrophotometrically at 540 nm.

2.0 SUMMARY

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenytcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, lhe absorbency index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenytcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at 0.010 mg/l.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentraiion of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study

4.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individuat method SOP's) For most methods, the mid-levet catibration check standard criteria is ± 10 percent of the

true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboraiory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the coritrol limits for a given parameter, all samptes must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboraiory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). ff a duplicate is out of control, fiag the results with the appropriate footnote. ff the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2)} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amouni is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Resuli} - \text{Sample Result})}{(\text{Amouni Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, Ihen the method blank is

equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs are determined approximatety once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent btank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent btank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samptes following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contaci any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboraiory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheeis must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: hexavalent chromium.

6.0 PRESERVATION & HOLDING TIME

6.1 Refrigerate all samples at 4°C until the time of analysis.

6.2 The holding time for this method is 24 hours from the time of collection. Analyze all samples within 24 hours.

7.0 INTERFERENCES

7.1 The hexavalent chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the hexavalent chromium concentraiion is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent: however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can generally be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of hexavalent chromium will not generally cause interference.

7.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

7.3 Reducing substances such as organic matter or sulfides can convert hexavalent chromium to trivalent chromium. These reactions may occur in the natural environment and during the digestion and measurement processes.

8.0 APPARATUS

8.1 Spectrophotometer capable of measurement at 540 nm, providing a light path of 1 cm or longer.

8.2 50 ml graduated cylinder (class A) with a stopper.

8.3 Volumetric flasks, class A.

8.4 Volumetric pipets, class A, for standards preparation.

8.5 Filter paper, 0.45 um and 0.10 um. Acceptable filter papers include the following:

8.5.1 MSI cellulostic white grid filters, 0.45 um, 47 mm (catalog number E04WG047S1)

8.5.2 Porectics polycarbonate membrane filters, 0.10 um, 47 mm (catalog number 13010)

8.6 Filter pump and vacuum filtration apparatus.

8.7 pH meter. Orion pH/ISE Meter Model 710A or equivalent

8.8 Four-place analytical balance. Acculab LA-110 or equivalent.

8.9 Graduated Plastic Beakers.

8.10 One or two place balance. Ohaus Galaxy 4000 or equivalent.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Use deionized water whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Sulfuric acid, 10 percent (v/v): Add 10 ml of concentrated sulfuric acid to approximately 70 ml of DI water. Mix well and let cool. Dilute to a final volume of 100 ml with DI water.

9.3 Diphenylcarbazide Solution: Dissolve 250 mg of 1,5 diphenylcarbazide in 50 ml of acetone. Mix well. Store in a brown bottle or in a foil wrapped container to proiect the solution from the light. Discard when the solution becomes discolored or monthly, whichever comes first. (**NOTE**: Make sure to check the quality of the diphenylcarbazide solution before adding it to the samples.)

9.4 Acetone. Do not use acetone that comes in container with metal or metal-lined caps.

9.5 Hexavalent Chromium Stock Solution. A 1000 mg/L (as Cr(VI))stock solution of potassium dichromate can be used as the stock solution for the spiking solutions and calibration standards. (Available as 1000 mg/L chromium solution, AAS grade from Fisher.)

9.6 Hexavalent Chromium Calibration Standard Solutions: Prepare the calibration standards fresh daily or each time the analysis is run. For instrument calibration, prepare the standards from the stocks as shown below.

9.6.1 Hexavalent Chromium 5.00 mg/L stock solution. Add 1.00 ml of 1000 mg/L hexavalent chromium to a 200 ml volumetric flask and dilute to volume with DI water. Mix well.

9.6.2 Hexavalent Chromium 1.00 mg/L stock solution. Add 10.00 ml of 5.0 mg/L hexavalent chromium to a 50 ml volumetric flask and dilute to volume with Dt water. Mix well.

9.6.3 Hexavalent Chromium 7.5 mg/L stock solution. Dilute 1.50 ml of the 1000 mg/L stock solution to a final volume of 200 ml with DI water and mix well. (For use for spiking.)

9.6.4 Add the amount of stock specified below to the 50 ml volumetrics and bring to a final volume of 50 ml with DI water.

Blank: No spike is added to the blank.
0.010 mg/l: Add 0.50 ml of 1.00 mg/L.
0.050 mg/L: Add 0.50 ml of 5.00 mg/L.
0.100 mg/L: Add 1.00 ml of 5.00 mg/L.
0.300 mg/L: Add 3.00 ml of 5.00 mg/L.
0.500 mg/L: Add 5.00 ml of 5.00 mg/L.
0.800 mg/L: Add 8.00 ml of 5.00 mg/L.
1.00 mg/L: Add 10.0 ml of 5.00 mg/L.
2.00 mg/L: Add 20.0 ml of 5.00 mg/L. (*)

(*) If the curve is more linear without the 2.00 mg/l standard, then do not use this standard.

9.7 Hexavalent Chromium Check Standard Solutions: Prepare the check standards fresh daily or each time the analysis is run. Prepare the standards from the stocks as shown below. NOTE: Prepare the check standards from a different source than the calibration standards.

9.7.1 Hexavalent Chromium 5.0 mg/L stock solution. Add 1.00 ml of 1000 mg/L hexavalent chromium to a 200 ml volumetric flask and dilute to volume with DI water. Mix well.

9.7.2 Add the amouni of stock specified below to DI water and dilute to a final volume of 50 ml.

9.7.2.1 For initial calibration curves that have the 2.00 mg/L standard as the upper limit, a calibration check at 1.00 mg/L is used. Therefore, add the amouni of stock solution specified below to DI water and dilute to a final volume of 50 ml:

1.00 mg/L: Add 10.00 ml of the 5.00 mg/L stock solution .

9.7.1.1 For initial calibration curves that have the 1.00 mg/L standard as the upper limit, a calibration check at 0.500 mg/L is used. Therefore, add the amount of stock solution specified below to DI water and dilute to a final volume of 50 ml.

0.500 mg/L: Add 5.00 ml of the 5.00 mg/L stock solution.

9.8 1.0 N Sodium Hydroxide, NaOH. Add 4.0 g of NaOH pellets to Di water and dilute to a ffnal volume of 100 ml. Mix well.

10.0 ANALYSIS

10.1 Turn on the spectrophotometer and let it warm up for at least 30 minutes. Set the wavelength to 540 nm and adjust the zero.

10.2 Using a graduated cylinder, Iransfer quantitatively 45.0 ml of the sample or standard to be analyzed to a labeled plastic beaker.

10.3 Add 1.0 ml of diphenylcarbazide solution and mix well.

10.4 Slowly add 10 percent sulfuric acid to each sample, mixing well after each addition. Adjust the pH to a range of 1.5 to 2.5. Test the pH of each sample with a pH meter when the effervescence is minimal and record this reading. (No significant effervescence is expected for most aqueous samples, although this will be seen when analyzing soil digestates.)

10.5 If the samples are turbid at this point, filter them through a 0.45 um filter. If they are still turbid after this filtration, a 0.10 um filter may also be used.

10.6 Transfer the samples to 50 ml volumetric flasks or class A graduated cylinders and dilute to a final volume of 50 ml with DI water. Let the samples stand for 5 to 10 minutes after the reagents are added for full color development. If the sample volume is greater than 50 ml, make sure to correct for the volume difference in the calculations.

10.6.1 Make sure to look af the initial color developmeni of the samples. If the sample initially forms a dark color which quickly starts to fade, this indicates that the sample contains a high level of hexavalent chrornium and should be run on dilution.

10.6.2 If the same cylinder is used for multiple samples, it must be rinsed with deionized water at least 3 times between samples.

10.7 Read the standard curve first and then a calibration check standard and a reagent blank, making sure to record all results on the strip chart recorder. The curve correlation coefficient is required to be greater than or equal to 0.995 and the check standard is required to be within 10 percent of the true value before the analysis can be continued.

10.8 After the curve and initial quality controt is completed, the samples may be analyzed. First read the sampte result. ff it is over the calibration curve, do <u>not</u> read a background correction point. If ll is within the calibration curve, a background correction point is prepared with 10 ml of sample adjusted to a pH of 1.5 to 2.5 with sulfuric acid. Make sure to record the adjusted pH of the background correciion point. Do not add diphenylcarbazide reagent to the background correction point. Note: If the sample was filtered, process the background correction sample through the same filtration procedure. Read the background correction point immediately after the sample analysis is completed.

10.9 After every 10 samples, every 20 readings (10 samples plus 10 background correction points) and at the end of the sample analysis sequence a digested calibration check and a reagent blank should be analyzed.

t0.10 Prepare a Method blank per batch of 20 or less. The method blank consists of 50 ml of deionized water.

10.11 Prepare a spike blank per batch of 20 or less. Spike the blank witn t50ug Cr(VI)/L, (The 150 ug/L spike can be made by spiking 1.0 ml of 7.5 mg/L Cr(VI) standard to a final volume of 50 ml.) Then proceed through steps 10.3 through 10.6 and analyze the sample.

10.12 Prepare a matrix spike and a duplicate on at least one sample per batch of 20 or less. Spike the sample selected as the matrix spike sample at 2 times the concentraiion found in the original sample aliquot or 150ug Cr(VI)/L, whichever is greater. (The 150 ug/L spike can be made by spiking 1.0 ml of 7.5 mg/L Cr(VI) standard to a final volume of 50 ml.) Then proceed through steps 10.3

through 10.6 and analyze the sample. Calculate the recovery immediately. If the recovery is not within 85 to 115 percent, proceed to steps 10.13 and 10.14.

10.13 Dilute a fraction of the qualtty control sample 1:5 and place 45 ml of the sample into a plastic beaker. Then proceed through steps 10.3 through 10.6 and analyze the sample. Also prepare a background correction point at this dilution and analyze it.

10.14 Take an additional 45 ml aliquot of the sample and adjust the pH to between 8.0 to 8.5 using 1.0 N NaOH. Record the final pH. Then spike the sample at 2 times the concentration found in the original sample aliquot or 150 ug Cr(VI)/L, whichever is greater. After the sample is spiked, proceed with steps 10.3 through 10.6. ff the sample volume is greater than 50 ml, make sure to correct for the volume difference in the calculations.

11.0 CALCULATIONS

11.1 Calculation of the sample result.

cone. of hexavalent chromium in the sample (mg/l)=

$$\frac{\text{(cone. in ext.(mg/l) x (final ext. vol.(ml)}}{\text{(initial sample vol. (ml))}}$$

11.2 Calculation of amount spiked.

Amount spiked of hexavalent chromium (SA)=

$$\frac{\text{(cone. of spiking solution (ug/ml)) x (vol. of spike (ml)}}{\text{(sample volume in ml)}}$$

11.3 Calculation of Matrix Spike Recovery.

$$\text{Percent recovery} = \frac{(SSR - SR) \times 100}{SA}$$

where SSR = Spiked sample result
SR = Sample result
SA = Spike added

11.4 Calculation of Calibration Check Standard (CCS) recovery.

$$\text{Percent recovery} = \frac{\text{CCS result x 100}}{\text{True Value}}$$

11.5 Calculation of Relative Percent Dtfference (RPD).

$$RPD = \frac{2(|\text{Sample result - Duplicate result}|) \times 100}{\text{(Sample result + Duplicate result)}}$$

12.0 QC REQUIREMENTS

12.1 Analyze a new 5 point calibration curve, at a minimum, on each analysis day. Up to eight calibration standards may be employed. The calibration curve is required to have a correlation coefficient greater than or equal to 0.995 percent. (Note: The 2.0 mg/L standard may be dropped from the curve to increase linearity.)

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

12.2 Initially analyze all samples undiluted. If the sample concentration is higher than the highest standard, then reanalyze the sample as a dilution. Prepare the dilution so that the sample is in the mid-range of the calibration curve.

12.3 One preparation blank is required for each set of 20 samples or less or with each batch. The preparation blank is required to contain all the reagents in the same volumes as used in the preparation of the samples. The preparation blank is required to be less than the RL. If it exceeds this limit do not proceed. Check with the laboratory supervisor or manager for further directions.

12.4 After every 10 samples, every 20 readings (10 samples plus 10 background correction points) and at the end of the sample analysis sequence a digested calibration check and a reagent blank must be analyzed. Prepare the mid-point calibration check from a different stock than the calibration curve. This calibration check standard must also be analyzed at the beginning of the analysis immediately after the calibration curve. The acceptance criteria for the mid-range calibration check standard is 90 – 110% of the true value of the standard. If they are outside of this range, do not proceed. Check with the laboratory supervisor of manager for further directions.

12.5 Analyze a reagent blank after each mid-calibration check standard. The reagent blank is required to be less than the RL. If It exceeds this limit do not proceed. Check with the laboraiory supervisor or manager for further directions.

12.6 Prepare and analyze a duplicate sample for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. An acceptance criteria of 20 percent relative percent difference is applied if the original and duplicate sample values are greater than or equal to 0.050 mg/l.

12.7 Prepare and analyze a matrix spike for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. An acceptance criteria of 85 to 115 percent recovery is applied If the spike amount is greater than one fourth of the sample amount. If the matrix spike does not meet this criteria, then analyze the sample at a 1:5 dilution and a pH adjusted spike should be analyzed.

12.8 A spike blank or lab control must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The spike blank or lab control can be prepared using either soluble or insoluble hexavalent chromium as the spike. The acceptance range for the spike blank is 90 to 110 percent recovery. If the spike blank is not within that range, do not proceed. Check with the laboraiory supervisor or manager for further directions.

13.0 DOCUMENTATION REQUIREMENTS

13.1 The analyst should document all relevant information, including all sample weights and volumes, digestion times and temperatures, all intermediate and final pH values, all times relevant to the pH adjustment process, all sample and background analysis results, and any relevant comments for any section of the digestion or analysis. Sample digestion and analysis sheets are provided.

13.2 For the analysis, all reagent identification numbers should be recorded on the sample worksheets. In addition, all reagent information such as lot numbers should also be recorded in the reagent logbook.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to GP and GN batches in the LIMS system. The analyst should calculate all matrix spike, duplicate, external, and CCV recoveries and review the results of all blanks. These calculations may be automated or manual.

14.2 All documentation must be completed, including reagent references and spike amounts and spiking solution references.

14.3 A data file should be exported to the LIMS system and the spike amounts should be entered into the file at the GNAPP process step.

14.4 A final data package, consisting of the prep and analysis raw data, the LIMS cover page, the reagent reference pages, and the QC summary pages must be turned into the area supervisor or other senior reviewer for review.

14.5 After review by the supervisor, the data is released in the LIMS for access to the clients.

14.6 The department manager does an additional periodic review on the sample data as appropriate

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

16.0 ADDITIONAL REFERENCES

16.1 Refer to the spectrophotometer instrument manual(s) for additional information.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:_____
QA Manager:_____

Effective Date:_____

TEST NAME: OXIDATION-REDUCTION POTENTIAL

METHOD REFERENCE: ASTM D1498-76 for waters. ASTM D1498-76 modified for soils.

Revised Sections: 9.3, 9.8.2, 9.8.3, 9.8.4

1.0 SCOPE AND APPLICATION

This method is based on ASTM method D t498-76 for waters and on a modification of this method for soils. The oxidation-reduction potential (ORP) of a process solution can be described as the millivolt (mV) signal produced when a noble metals electrode and a reference electrode are placed in water. The ORP measurement establishes the ratio of oxidants and reductants prevailing within a solution. The LIMS system product for oxidation-reduction potential is eH.

2.0 SUMMARY

Oxidation-reduction potential is measured using a meter with a combined oxidation-reduction and reference electrode. The meter is calibrated using a ferrous-ferric reference solution. The calibration is verified using quinhydrone buffer solutions. Samples are then measured with the calibrated electrode. The calibration is again verified with quinhydrone buffer solutions. The results are reported in mv versus a hydrogen electrode.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

No specific reporting limit or method detection limit values are in place for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similariy with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is + 10 percent of the true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of (the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of (20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2)} = \text{Duplicate RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents, which conform to the current specifications of the Committee on Analyticai Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 SAMPLE COLLECTION, PRESERVATION, & STORAGE

6.1 Although this method does not specify a sample preservation procedure, it is recommended that both water and soils samples be stored under refrigeration at 4°C until analysis.

6.2 No specific holding time is specified in the method, but analyses should be done as soon as possible.

7.0 APPARATUS

7.1 pH meter with millivolt output scale. Thermo Orion Star Series or equivalent.

7.2 Oxidation-reduction electrode and reference electrode. Note: a combined electrode can be used which eliminates the need for a separate reference electrode is recommended. One acceptable electrode is the Platinum combination electrode from Fisher Scientific (cat. number 13-620-82) which consists of a platinum wire electrode with an electrolyte of 4M KCl saturated with AgCl.

7.3 Stir plate.

8.0 REAGENTS

8.1 Redox Standard Solution; Ferrous-Ferric Reference Solution. Dissolve 39.21 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$), 48.22 g of ferric ammonium sulfate ($FeNH_4(SO_4)_2.12H_2O$) and 56.2 mL of sulfuric acid in water and dilute to 1 liter.

8.2 Redox Reference Solution; pH 4 Quinhydrone Solution. Mix 200 mL of pH 4 buffer solution with 2.0 g of Quinhydrone. Be sure that excess Quinhydrone is used in the solution so that solid crystals are always present. This solution is stable for only 8 hours.

8.3 Redox Reference Solution; pH 7 Quinhydrone Solution. Mix 200 mL of pH 7 buffer solution with 2.0 g of Quinhydrone. Be sure that excess Quinhydrone is used in the solution so that solid crystals are always present. This solution is stable for only 8 hours.

8.4 pH 4 buffer solution. A potassium hydrogen phthalate pH 4 buffer solution can either be made as described in ASTM 1498 or it can be purchased.

8.5 pH 7 buffer solution. A potassium dihydrogen phosphate/disodium hydrogen phosphate pH solution can either be made as described in ASTM 1498 or it can be purchased.

9.0 PROCEDURE

9.1 Attach the redox electrode to the pH meter and allow the meter to warm up.

9.2 Slide the mode switch to mv (millivolts) and place the electrode in the ferrous/ferric standard solution. Place a small stir bar in the bottom of the beaker and start it stirring gently.

9.3 Measure the millivolts of the solution and record on the worksheet. The ferrous-ferric reference solution should read back at 475 mv at 25 deg. C against the Ag/AgCl electrode. If the solution is not within 5 percent of this value do not continue. Check with the lab supervisor or manager for maintenance of the electrode. Additional electrolyte may need to be added to the electrode.

9.4 Press the cal switch on the pH meter. Both the cal 1 and the rel mv LED should light. The display should read 0.

9.5 Scroll in the ferrous-ferric reference solution value versus the hydrogen electrode (675 mv). Press enter. The meter is now ready for analysis. The absolute mv reading will give the mv versus the Ag/AgCl electrode. The relative mv reading will give the mv versus the standard hydrogen electrode. Both values should be recorded on the worksheet for the standards and for all samples.

9.5.1 The meter adds 200 mV to the absolute mv reading to obtaine the relative mv reading versus the standard hydrogen electrode. The difference between sample absolute and relative mv readings may vary slightly due to solution stability.

9.6 Check the redox measurements by measuring the ORP of the reference Quinhydrone solutions. All measurements should be done at 25 deg. C. The true values of the solutions are shown below. The measured values should be within 10 percent of the true values. If they are not, do not continue, but check with the lab supervisor to determine what corrective action is needed.

Solution	ORP vs Ag/AgCl (absolute mv)	ORP vs Hydrogen (relative mv)
pH 4 Quinhydrone solution	263	462
pH 7 Quinhydrone solution	86	285

9.7 For water samples, pour an aliquot of each sample into a plastic beaker and place a small stir bar in the sample. Slowly stir the sample. Place the electrode into the sampie and measure both the absolute and the relative mv reading. Record the readings on the data sheet.

9.7.1 The difference between sample absolute and relative mv readings may vary slightly due to solution stability, but should be approximately 200 mv.

9.8 For soil samples, follow the procedure shown below.

9.8.1 Weigh out equal amounts of sample and DI water. Normally 50.0 g of sample and 50 mL of deionized water is used. If the sample is hygroscopic (i.e. absorbs water), then add water until the sample can be stirred and record the total volume of water added.

9.8.1.1 Smaller weights can be used if necessary, but the larger weight and volume is recommended for better sample reproducibility.

9.8.2 Hand mix the soil and water with a stirring rod or spatula thoroughly until a sluny is obtained. Make sure that there is no solid material on the bottom of the beaker while stirring.

9.8.3 Put in a stir bar and stir the sample on a stirring plate continuously for 5 minutes at a normal stirring speed. The sample should be mixing well, but there should not be a large vortex.

9.8.3.1 If the sample starts to cake on the bottom during the stirring procedure, hand stir the sample again so that it is as well suspended as possible before proceeding to setp 9.8.4.

9.8.3.2 If the sample contains oii and water, then let it settle and decant off the oily phase and measure the pH of the aqueous phase.

9.8.4 Slow the stirring speed to a slow stir. Place the electrode into the sample and measure both the absolute and the relative mv reading. Record the readings on the data sheet.

9.8.4.1 The difference between sample absolute and relative mv readings may vary slightly due to solution stability, but should be approximately 200 mv.

9.9 After every 10 samples, reanalyze the Quinhydrone solutions. Record both the absolute and relative mv readings. The readings should be within 10 percent of the true values.

10.0 QC REQUIREMENTS:

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality controi requirements.

10.1 Matrix Duplicate. The laboratory must analyze a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below. The control limit for the duplicate recovery are calculated on an annual basis and are used to assess whether a duplicate is in control. Until sufficient duplicate data become available to determine control limits, the laboratory should assess laboratory performance of the duplicate against a relative percent difference of 20 percent. If a duplicate is out of control, then the results should be flagged with the appropriate footnote.

$$\frac{(\text{Sample Result - Duplicate Result}) \times 100}{(\text{Sample Result + Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

10.2 Calibration Checks. The laboratory should analyze a reference or standard solution after approximately every 10 samples. The solution must be within 10 percent of the true value. If the check solution is outside of the acceptable range, then the problem must be corrected, the meter recalibrated and any affected samples reanalyzed and reported from an area with compliant calibration checks.

11.0 DOCUMENTATION REQUIREMENTS:

11.1 All sample results should be entered on a results worksheet. This worksheet should include all sample information and ail quality control information. All reagent references should be included on or attached to this worksheet. In addition, any unusual characteristics of the samples should be noted.

11.2 Standards and Reagents. All standards and reagents must be recorded in the reagent log book.

12.0 DATA REVIEW AND REPORTING

12.1 All samples should be updated to QC batches in the LIMS system.

12.2 The analyst should calculate all duplicate RPD's and all check standard recoveries. All reagent references should be checked and included with the data write-up.

12.3 The data report should be turned in to the area supervisor for entry into the LIMS and data review.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT.

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors; liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 ADDITIONAL REFERENCES.

14.1 Refer also to Standard Methods for the Examination of Water and Wastewater, Method 2580B.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager_____

QA Manager_____

Effective Date:_____

TITLE: HARDNESS AS $CACO_3$ BY TITRATION

REFERENCES: Method 2340C from "Standard Methods for the Examination of Water and Wastewater", *19th* Edition.

Revised Sections: *10.4, 10.4.1, 12.3*

1.0 SCOPE AND APPLICATION

1.1 This method is used as a measure of the hardness in a sample and is applicable to all waters and wastewaters.

1.2 The product for hardness is **HRD**.

1.3 An alternate method for hardness, where the hardness value is calculated from calcium and magnesium values, is cited in the **SOP EGN**259.

2.0 SUMMARY

2.1 A measured aliquot of sample is buffered and then titrated with standardized **EDTA** (disodium ethylenediamine tetraacetate) titrant. The end point of the reaction is determined when the last reddish tint in the sample disappears. The indicator has a red color in the presence of calcium and magnesium ions and a blue color when these ions are sequestered.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method has been established at **4.0** mg/l of hardness as calcium carbonate.

3.2 Method Detection Limit. Experimentally determine **MDL**s using the procedure specified in **40 CFR**, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental **MDL**s must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For **QC** purposes, if the number of

samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve or the spike blank that is used to verify the accuracy of the method. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specifled in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). MDLs should be established for all appropriate methods, using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of three replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

5.0 HEALTH & SAFETY

5.1 The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses.

6.0 COLLECTION, PRESERVATION, & HOLDING TIME

6.1 Water samples should be acidified to a pH of less than 2 by the addition of concentrated nitric acid.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 APPARATUS & MATERIALS

7.1 25 ml microburet, class A.

7.2 Erlenmeyer flasks or disposable beakers

7.3 Stir plates and stir bars.

7.4 Analytical balance, 4 place. The balance calibration must be checked daily before use. If the calibration checks on the balance are not within limits as supplied in the balance logs, then the balance must be taken out of service until it can be recalibrated.

7.5 Narrow range pH paper to read between 10.0 and 10.1.

8.0 STANDARDS & REAGENTS.

8.1 All chemicals listed below are reagent grade unless otherwise specified. Distilled water should be used whenever water is required.

8.2 Buffer solution. Dissolve 1.179 g of analytical grade disodium EDTA (disodium ethylenediamine tetraacetate, $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) and 0.780 g of $MgSO_4 \cdot 7H_2O$ (or 0.644 g of $MgCl_2 \cdot 6H_2O$) in 50 ml of DI water. Add this solution to a 250 ml volumetric flask containing 16.9 g of ammonium chloride (NH_4Cl) and 143 ml of concentrated ammonium hydroxide (NH_4OH) with mixing and dilute to the mark with DI water. Store in a plastic bottle for no longer than 1 month.

8.2.1 Anhydrous magnesium chloride may also be used in the above buffer solution as long as the weights are adjusted accordingly.

8.2.2 An alternate buffer solution may be prepared by dissolving 16.9 g of ammonium chloride (NH_4Cl) in 143 ml of concentrated ammonium hydroxide (NH4OH). Add 1.25 g of magnesium salt of EDTA (available commercially) and dilute to 250 ml with DI water. Mix well

8.2.3 Commercial buffer solutions are also available. Refer to the method for additional information on these buffer solutions.

8.2.4 One to 2 ml of buffer with the sample should give a pH of 10.0 to 10.1. If the buffer is not obtaining that pH on most samples, it may have deteriorated and fresh buffer should be made.

8.3 Inhibitor solutions. These are to be used only if interferences are evident during the titration. These inhibitor solutions help to give a clear sharp change in color at the end point. Check with the lab supervisor or manager before using any of these inhibitor solutions

8.3.1 Inhibitor I: NaCN powder. (Caution – extremely poisonous). Flush solutions of sample containing this solution down the drain using large quantities of water. Make

sure that there are no acids present that might liberate HCN. Always work in the hood when using this solution.

8.3.2 Inhibitor II: Dissolve 5.0g of $Na_2S \cdot 9H_2O$ in 100 ml of DI water. Cover container with a tightly fitted rubber stopper. This inhibitor deteriorates through air oxidation and can produce a sulfide precipitate that obscures the end point when appreciable concentrations of heavy metals are present.

8.3.3 Inhibitor III: MgCDTA (magnesium salt of 1,2-cylclohexanediamnetetraacetic acid). Add 0.250 g of MgCDTA to each 100 ml of sample before analysis and dissolve completely before adding the buffer solution.

8.4 Indicator. Solid calmagite (1-(1-hydroxy-4-methyl-2phenylazo)-2-maphthol-4-sulfonic acid or a calmagite indicator solution can be used.

8.4.1 Calmagite solution can be prepared by dissolving 0.10 g of Calmagite in 100 ml of DI water.

8.5 Standard EDTA titrant, 0.020 N (0.010 M). Place 3.723 g of analytical grade disodium EDTA in a 1 liter volumetric flask and dilute to the mark with DI water. Check with standard calcium solution by titration as described in the procedure section below. Store in a polyethylene bottle.

8.6 Standard Calcium solution (1000 mg/l). Place 1.000 g of anhydrous calcium carbonate in a 500 ml erlenmeyer fiask. Slowly add 1+1 HCl until all of the calcium carbonate has dissolved. Add 200 ml of DI water and boil for several minutes to expel the carbon dioxide. Cool. Then add a few drops of methyl red indicator and adjust to an intermediate orange color by adding 3N ammonium hydroxide or 1 +1 HCl as required. Transfer quantitatively to a 1 liter volumetric flask and dilute to a final volume of 1 liter with DI water. Mix well.

8.7 Hydrochloric acid solution, 1+1. Add one part hydrochloric acid to one part water.

8.8 Methyl Red Indicator. Dissolve 0.10 g of methyl red in DI water in a 100 ml volumetric flask and dilute to the final volume with DI water and mix well. This may aiso be purchased commercially.

8.9 Ammonium Hydroxide solution, 3 N. Dilute 210 ml of concentrated ammonium hydroxide (NH_4OH) to 1 liter with DI water.

8.10 Ammonium hydroxide solution, 1N. Dilute 70 ml of concentrated ammonium hydroxide to 1 liter with DI water.

9.0 INTERFERENCES

9.1 Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric comsumption of EDTA. These interferences can be reduced by adding certain inhibitors before titration.

9.2 Conduct titrations at or near room temperature. Color change may be impractically slow at low temperatures.

9.3 Calcium carbonate precipitation may cause a drifting endpoint. Completion of the titration within 5 minutes minimizes the tendency for calcium carbonate to precipitate. Dilution can also minimize this problem. Alternatively, do a preliminary titration and add 90 percent of the expected titrate to the sample before adjusting the pH with the buffer. Then finish the titration.

10.0 PROCEDURE

10.1 Check the standardization of the EDTA solution and make sure that it has been standardized within the past month. If it has not been standardized within a month, or if it is a new lot of EDTA, standardize the solution following the procedure outiined below.

10.1.1 Place 10.0 ml of standard calcium solution in a container containing about 50 ml of DI water. Add 1 ml of the buffer solution and a few crystals of calgamite. Titrate slowly with continuous stirring with the EDTA until the last reddish tinge disappears. Add the last few drops at 3 to 5 second intervals. At the end point, the color should be blue. The total titration duration should be no more than 5 minutes from the time of the buffer addition.

10.1.2 Calculate the normality of the EDTA as shown below.

N of EDTA = (0.200)/(ml of EDTA added)

10.2 Start the titration of the samples and the quality control. A method blank and a spike blank must be analyzed at the beginning of every run and a second spike blank must be analyzed with every 10 additional samples. (For example, if you are running 20 samples, you should analyze a spike blank at the beginning of the run and after the first 10 samples.) A duplicate and a matrix spike must be analyzed with every 20 samples. For some clients and some states, additional QC may be required. (10% duplicates are required for New York samples.)

10.3 Measure 25.0 ml of sample or quality control into the titration vessel. Blank spikes and matrix spikes should be spiked with 4.00 ml of the standard calcium carbonate solution at this point. Neutralize the samples with 1 N ammonium hydroxide and dilute to a final volume of approximately 50 ml.

10.3.1 Highly polluted samples should first go through a metals digestion step before analysis. Check with the lab supervisor or manager if you feel the sample needs extra pretreatment.

10.4 Add 1 to 2 ml of buffer solution and mix. The pH of the samples at this point should be 10.0 to 10.1. Check the pH with narrow range pH paper and verify that it is within the range of 10.0 to 10.1. Document that the pH is within range on the sample worksheet. Then add a few grains of the Calgamite to each sample.

10.4.1 If the pH is not within range, add additional buffer or use a smaller sample size and recheck the pH. Do not proceed with the titration until the pH is within the required range.

10.5 Titrate the sample slowly with continuous stirring with the standard EDTA titrant until the last reddish tint disappears. The solution is normally blue at the end point. Note: Make sure that the titration is complete within 5 minutes of the time that the buffer solution is added in order to minimize calcium carbonate precipitation.

10.5.1 If the endpoint is indistinct or fades, an inhibitor may be needed. Check with the lab supervisor or manager and refer to Standard Methods 2340C, Section 2B. Add the inhibitor immediately after the addition of the buffer and proceed with the analysis as outlined above.

10.6 Calculate the final results using the equation shown below. Make sure to use the normality and not the molarity of the EDTA titrant in this calculation.

Hardness as mg $CaCO_3$/liter = (A x N X 50000)/(ml sample)

Where
A = ml of EDTA titrant
N = normality of EDTA titrant.

11.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.1 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level . MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

11.2 Quality Control Sample (also referred to as the external). At a minimum of once per quarter, a standard from a different source than the spike blank must be analyzed. Note: It is recommended that this standard be analyzed with each run if sufficient standard is available. This sample should be within the manufacturers limits. If no manufacturer's limits are available, then default limits of 90 to 110% should be applied.

11.3 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples or on each analysis day. The method blank must contain hardness as calcium carbonate at a level less than the reporting limit. If the method blank contains over that limit, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.4 Spike Blank. The laboratory must analyze a spike blank with each set of 10 samples. The laboratory should assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. If the spike blank recovery is high and the results of the samples to be

reported are less than the reporting limit, then the sample results can be reported with no flag. Otherwise, all associated samples must be reanalyzed.

11.5 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. The matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.6 Matrix Duplicate. The laboratory must digest a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below.

11.6.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.6.2 The duplicate RPD should be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \text{\% RPD}$$

12.0 DOCUMENTATION

12.1 All reagent and standard information, including the manufacturer, lot, and expiration date should be recorded in a general chemistry reagent log.

12.2 Reagent and standard reference numbers should be recorded all on analysis write-ups.

12.3 All initial volumes, dilutions, and final volumes should be recorded on the analysis write-ups. The verification of the pH after the addition of the buffer should also be documented on the analysis write-up.

12.4 Any problems or comments about the samples should be included on the analysis write-ups.

12.5 Balance checks and calibrations should be recorded on the balance logs provided with each balance. Each balance must be checked at least once per day before use. The balance checks should be within the criteria listed in the balance log book.

13.0 DATA REPORTING

13.1 All samples should be updated to QC batches in the LIMS system. The analyst should calculate all duplicate RPD's and spike recoveries.

13.2 All documentation must be completed. The data report should be turned in to the area supervisor for review.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT.

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, ESM003. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes

14.2.3 Chlorinated organic solvents

14.2.4 Non-chlorinated organic solvents

14.2.5 Hazardous solid wastes

14.2.6 Non-hazardous solid wastes

15.0 REFERENCES

15.1 No additional references were required for this method.

Mercury Determination in Tissue and Soil/Sediment Samples by Cold Vapor Atomic Fluorescence Technique (CVAF)

References: Method 7474, Mercury in Sediment and Tissues by Atomic Fluorescence Spectrometry. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Revision 0, Update IV, 1998.

Method 7471A, Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique). SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Revision 1, 1994.

Determination of Mercury in Seawater at Sub-Nanogram per Liter Levels. Bloom, N.S. and E.A. Crecilius, Marine Chemistry, 14, 49-59. 1983.

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Signature: Joseph Watkins Date: 7/11/11

ISSUE AMENDMENTS

Changes since last issue:

Edited signatories.

Sections 9.5 and 11: Edited QC Acceptance Criteria.

Mercury Determination in Tissue and Soil/Sediment Samples by Cold Vapor Atomic Fluorescence Technique (CVAF)

References: Method 7474, Mercury in Sediment and Tissues by Atomic Fluorescence Spectrometry, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Revision 0, Update IV, 1998.

Method 7471A, Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique). SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Revision 1, 1994.

Determination of Mercury in Seawater at Sub-Nanogram per Liter Levets. Bloom, N.S. and E.A. Crecilius, Marine Chemistry, 14, 49-59. 1983.

1. Scope and Application

Matrices: The method is applicable to total mercury in tissue and soil/sediment samples.

Definitions: Refer to Alpha Analytical Quality Manual.

Two procedures for the analysis of mercury by cold vapor atomic fluorescence spectrometry are discussed in this SOP.

Mercury in Tissues - This method utilizes a microwave digestion followed by bromine chloride oxidation. Samples are then decolorized using hydroxylamine hydrochloride and analyzed following reduction with stannous chloride. Elemental mercury is then purged from solution and analyzed by atomic fluorescence spectrometry.

Mercury in Soil/Sediments - This method utilizes a hot plate digestion with aqua regia followed by bromine chloride oxidation. Samples are then decolorized using hydroxylamine hydrochloride and analyzed following reduction with stannous chloride. Elemental mercury is then purged from solution and analyzed by atomic fluorescence spectrometry.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Mercury analyzer and in the interpretation of Mercury data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

Parameter	CAS
Mercury	7439-97-6

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2. Summary of Method

Mercury in tissue samples is determined by cold vapor atomic fluorescence spectrometry from an aliquot of a microwave digestion (see SOP MP-003). A 10 mL aliquot of the digest is added to a 50 mL screw cap polyethylene digestion tube along with 2 mL of an acidic bromine chloride solution. Bromine chloride is prepared by mixing potassium bromide with potassium bromate solutions with hydrochloric acid producing a yellow solution. Bromine chloride is know to oxidize inorganic and organomercury compounds. If a yellow color does not persist after addition of bromine chloride, then additional solution must be added until a yellow color persists. The same volume of bromine chloride solution is added to all samples and standards. This solution is allowed to stand for at least 12 hours. After digestion is complete, bring to 50 mL, add 0.4 mL of 12% hydroxyl amine hydrochloride splution and shake. Additional hydroxyl amine hydrochloride is added if the yellow color from the bromine chloride solution persists.

Samples and standards are placed in the autosampler rack for analysis following stannous chloride reduction and analysis by cold vapor atomic fluorescence spectrometry at a wavelength of 253.7 nm.

Mercury in soil/sediment samples is determined by cold vapor atomic fluorescence spectrometry from a hot plate digestion utilizing aqua regia. A 0.5 – 1 g wet sediment aliquot is added to a 50 mL screw cap polyethylene digestion tube along with 5 mL of DI water, 3.75 mL concentrated HCl and 1.25 mL of concentrated HNO_3. Samples are heated on the hot block for 2 minutes and allowed to cool. 25 mL of Di water are then added, the samples placed back pn the hot block and heated for 30 minutes. The samples are then cooled and brought to 50 mL with DI water. A 10 mL aliquot of the digest is added to a 50 mL digestion tube along with 2 mL of an acidic bromine chloride solution. If a yellow color does not persist after addition of bromine chloride then additional solution must be added until a yellow color persists. The same volume of bromine chloride solution is added to all samples and standards. This solution is allowed to stand for at least 12 hours. After digestion is complete, bring to 50 mL, add 0.4 mL of 12% hydroxyl amine hydrochloride solution and shake. Additional hydroxyl amine hydrochloride is added if the yellow color from the bromine chloride solution persists.

Samples and standards are placed in the autosampler rack for analysis following stannous chloride reduction and analyzed by cold vapor atomic fluorescence spectrometry at a wavelength of 253.7 nm.

2.1 Method Modifications from Reference

Method 7474 calls for a microwave digestion for both tissues and soils/sediments with nitric and hydrochloric acids. The method has been modified for tissues to use an aliquot of a microwave digest utilizing nitric acid only. The method has been modified for soils/sediments to use a hot block digestion similar to that used for Method 7471A but withoui the addition of potassium permanganate. The change allows for more rapid preparation of samples and yields equivalent data to the referenee method as indicated by the performance of PT samples.

The procedure used to prepare the bromine chlonde solution has been modified from the method reference to that used in the Bloom and Crecelius, 1983 reference. The solution is equivalent the reference method and requires less time to make. There is no impaci to the data as indicated by the performance of PT samples.

3. Reporting Limit

The Reporting limit for mercury in tissues is 0.05 pg/L (0.0125 mg/kg) and the linear range of the analysis is 10 pg/L (2.5 mg/kg).

The Reporting limit for mercury in soil/sediment is 0.05 pg/L (0.0125 mg/kg) and the linear range of the analysis is 10 pg/L (0.5 mg/kg).

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4. Interferences

4.1 Gold, silver and iodide are known interference.

4.1.1 High concentrations of gold and silver in a sample may suppress mercury reduction.

4.1.2 Samples with iodide concentrations greater than 3 mg/L shouid be pre-reduced with stannous chloride to clarify the brown color. It may be necessary to clean the analytical system with 4N HCl following analysis of a sample with iodide concentrations greater than 30 mg/L.

4.1.3 Sulfide concentrations up to 24 mg/L produce no interference problems.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples knowri to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The use of laboratory equipment and chemieals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratpry area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept alphabetically in a centrally located file storage.

Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at *all* times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting device and/or secondary outer container. Chemical storage is properiy segregated and adequateiy ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Department Manager Supervisor immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Department Manager Supervisor immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

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Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

Compressed gas cylinders shall only be moved with the doily supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

All additional company safety practices shall be followed at all times as written in the *Chemical Hygiene Plan.*

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

A minimum of 10g of sample must be collected in a pre-cleaned 2oz or 4oz glass jar with a Teflon lined screw cap.

6.2 Sample Preservation

No preservatives are used. See Section 6.4.

6.3 Sampie Shipping

No special sample shipping requirements.

6.4 Sample Handling

Samples are stored at 4°C ± 2°C. The hold time for soil/sediment and tissue samples is 28 days. Sediment and tissue samples may be stored frozen at -20°C ± 10°C. The hold time for solid samples stored frozen inay be extended unless specifically noted by project or client requirements.

7. Equipment and Supplies

7.1 Instrument: The PSA Millennium Merlin Atomic Fluorescence Analyzer equipped with a PC loaded with instrumental software, gold-amalgamation attachment (Millennium Gallahad) and PSA 20.400 autosampler. The instrument is connected to a source of high-purity, mercury free argon regulated to 50 PSI.

7.2 Santoprene Peristaltic Pump Tubing: Green/Green (PSA part number M025T002 or equivalent) for blank and autosampler rlnse, Grey/Grey (PSA part number M055T005 or equivalent) for sample and stannous chlorlde.

7.3 Electric Hot Plate: Adjustable and capable of maintaining a temperature of 90-95°C equipped with graphite carbon blocks that each have 36 positions to hold the sample tubes.

NOTE: Hotplate/Block temperatures are monitored regularly using NIST calibrated and traceable thermometers. If any thermometer is suspected to not be reading the temperatures correctly, it is replaced with another certified thermometer.

7.4 Milestone Ethos E Microwave Oven: Equipped with temperature control probe and high pressure perfluoropolymer vessels.

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7.5 Digestion Tubes: 50mL disposable polyethylene screw cap digestion tubes.

7.6 Other: Adjustable Eppendorf pipettes and replacement tips

8. Reagents and Standards

ACS Trace Metal grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, arialyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

Solutions below expire six months from preparation unless noted.

Stock standard solutions are stored in a cabinet, out of direct light

8.1 Deionized (DI) water: The Barnstead NANO-pure system provides Type I water used in the preparation of samples and standards.

8.2 Hydrochloric acid, concentrated (HCl): ACS reagent grade, Fisher #A508-212, or equivalent. Hydrochloric acid (1:1 HCl) - Add 500mL concentrated HCl to 400mL DI water and dilute to 1L. 10% HCl – Add 100 mL concentrated HCl to approximately 500 mL DI and bring to 1 L with DI. Lots should be checked for purity prior to use and the results stored in a reagent check log book.

8.3 Nitric acid, concentrated (HNO_3): ACS reagent grade, Fisher #A509-212, or equivalent. Nitric Acid (1:1 HNO_3) - Add 500mL concentrated HNO_3 to 400mL DI water and dilute to 1L. Prepare 1% Nitric Acid by diluting 1mL of concentrated HNO_3 up to t00mL in DI water. Lots should be checked for purity prior to use and the results stored in a reagent check log book.

8.4 Hydroxylamine hydrdchloride ($NH_2OH{\cdot}HCl$): ACS reagent grade, VWR #HX0770-1, or equivalent. Prepare 12% solution by adding 12 g per 100 mL of DI.

8.5 Stannous Chloride ($SnCl_2{\cdot}H_20$): ACS reagent grade, Fisher #T142-500, or equivalent. Prepare 2% solution by adding 20 g to 1L of 10% HCl. Prepare daily. Solution may be purged with argon at 2 L/minute for 30 minutes to remove Hg impurities.

8.6 Potassium Bromate ($KBrO_S$): ACS grade, Fisher #P207-250. May be baked in muffle furnace at 250°C for 8 hours to remove mercury impurities.

8.7 Potassium Bromide (KBr): ACS grade, Fisher #P205-500. May be baked in muffle furnace at 250°C for 8 hours to remove mercury impurities.

8.8 Bromine Chloride (BrCl): Prepare in a BOD bottle under a fume hood by adding 1.5 g KBr and 1.1 g $KBrO_3$ to 20mL DI water and mix. Slowly add 80mL of concentrated HCl and mix. Solution will turn yellow. Free Halogens are generated from this solution. Seal the bottle when taking out of fume hood.

8.9 Stock and Working Standards:

The 1000 pg/L working standards must be prepared in the same manner as samples. These standards are then diluted to make calibration and calibration check standards. After preparation, the 1000 pg/L working standards can be used for one week.

8.9.1 1000 mg/L Stock Calibration Mercury Standard: Ultra Scientific #ICP-080, or equivalent.

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8.9.1.1 1000 pg/L **Working Standard for Tissues:** Prepare by adding 0.05mL of 1000 mg/L stock to a microwave digestion vessel containing t0mL of concentrated HNO_3. This standard is digested along with samples according to Method 3051 (SOP MP-003). The standard is then brought to a 50mL final volume with DI water in a screw cap digestion tube. This standard is identified as **C-date-VM** in the Mercury Standards Preparation Log.

8.9.1.2 1000 pg/L **Working Standard for Soils/Sediments:** Prepare by adding 0.05 mL of 1000 mg/L stock (Section 8.9.1) to a 50 mL screw cap digestion tube containing 5 mL of DI water, 1.25 mL of concentrated HNO_3 and 3.75 mL of concentrated HCl. This standard is digested along with samples. The standard is then brought to a 50 mL final volume with DI water. This standard is identified as **C-date-VH** in the Mercury Standards Preparation Log.

8.9.1.3 100 pg/L **Intermediate Standard:** Prepare by adding 0.1 mL of the 1000 pg/L working standard (Section 8.9.1.1 or 8.9.1.2) to 0.9 mL DI water. This intermediate standard is used for calibration standards preparation and then discarded.

8.9.1.4 10 pg/L **Intermediate Standard:** Prepare by adding 0.1 mL of the 100 pg/L working standard (Section 8.9.1.3) to 0.9 mL DI. This intermediate standard is used for calibration standards preparation and then discarded.

8.9.1.5 5 pg/L **Intermediate Standard:** Prepare by adding 0.25 mL of the 1000 pg/L working standard (Section 8.9.1.1 or 8.9.1.2) to 50 mL graduated digestion tube containing 2% HCl. Bring to 50 mL final volume.

8.9.2 1000 mg/L **Stock ICV Mercury Standard:** Inorganic Ventures #CGHG-1, or equivalent

8.9.2.1 1000 pg/L **ICV Working Standard for Tissues:** Prepare by adding 0.05 mL of 1000 mg/L stock to a microwave digestion vessel containing 10 mL of concentrated HNO_3. This standard is digested along with samples according to Method 3051 (SOP-MP-003). The standard is then brought io a 50 mL final volume with DI water in a screw cap digestion tube. This standard is identified as **I-date-VM** in the Mercury Standards Preparation Log.

8.9.2.2 1000 pg/L **ICV Working Standard for Soils/Sediments:** Prepare by adding 0.05 mL of 1000 mg/L stock to a 50 mL screw cap digestion tube containing 5 mL of DI water, 1.25 mL of concentrated HNO_3 and 3.75 mL of concentrated HCl. This standard is digested along with samples. The standard is then brought to a 50 mL final volume with DI water. This standard is identified as **t-date-VH** in the Mercury Standards Preparation Log.

8.9.2.3 5 pg/L **Intermediate Standard:** Prepare by adding 0.25 mL of the 1000 pg/L working standard (Section 8.9.2.1 or 8.9.2.2) to 50 mL graduated digestion tube containing 2% HCl. Bring to 50 mL final volume.

8.9.2.4 1000 pg/L **LCS and Matrix Standard for Tissues and Soils/Sediments:** Prepare by adding 0.1 mL of 1000 mg/L stock (8.9.2) to a 100 mL volumetric fiask containing 2% HCL. This standard is identified as **I-date-V** in the Mercury Standards Preparation Log.

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8.10 Calibration and Calibration Check Standards

8.10.1 Standards Preparation for Method 7474 Tissues

To 50 mL screw cap digestion tubes, add 10 mL of DI water and 2 mL of concentrated HNO3. Add the volumes of each standard as indicated in the table below, 2 mL of BrCl solution and bring to 50 mL. The standard set is designated in the Mercury Standards Preparation Log as C-date-VM1,2,3... (for calibration standards) and I-date-VM1,2,3... (for the ICV) as successive sets of standards are prepared from the stock. The same volume of the 1000 pg/L ICV stock is added to the preparation batch LCS and matrix spike sample.

If more than 2 mL of BrCl solution was added to samples to maintain the yellow color, add the same amount to standards. 0.2 mL of 12% hydroxyl amine hydrochloride is added to each vial and shaken. The yellow color should disappear.

8.10.2 Standards Preparation for Method 7474 Soils/Sediments

To 50 mL screw cap digestion tubes, add 10 mL of DI water, 0.75 mL of concentrated HCl and 0.25 mL of concentrated HNO_3. Add the volumes of each standard as indicated in the table below, 2 mL of BrCl solution and bring to 50 mL. The standard set is designated in the Mercury Standards Preparation Log as C-date-VH1,2,3... (for calibration standards) and I-date-VH1,2,3... (for the ICV) as successive sets of standards are prepared from the stock. The same volume of the 1000 pg/L ICV stock is added to the preparation batch LCS and matrix spike sample.

If more than 2 mL of BrCl solution was added to samples to maintain the yellow color, add the same amount to standards. 0.2 mL of 12% hydroxyl amine hydrochloride is added to each vial and shaken. The yellow color should disappear.

8.10.3 Calibration, Calibration Check Standards, LCS and Matrix Spike

Calibration and calibration check standards are prepared by adding standard volumes to vials prepared for tissues and soils/sediments as designated in the following table:

Standard ID	Vol. 1000 µg/L (mL) (Sec. 8.9.1.1 or 8.9.1.2)	Vol. 100 µg/L (mL) (Sec. 8.9.1.3)	Vol. 10 µg/L (mL) (Sec. 8.9.1.4)	Final Concentration (µg/L)
STD0	-	-	-	0.0
STD1	-	-	0.25	0.05
STD2	-	0.05	-	0.1
STD3	-	0.25	-	0.5
STD4	0.1	-	-	2.0
STD5	0.25	-	-	5.0
STD6	0.50	-	-	10.0
ICV, CCV	0.25 (Sec. 8.9.2.1 or 8.9.2.2)			5.0
LCS, MS	0.25 (Sec. 8.9.2.4)			5.0

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Lower detection limits and analytical reporting limits may be required at times for some samples. Lower limits are attained by increasing the instrumental gain from 10 to 100 and by calibrating using lower concentration standards. Calibration standards and the LCS and MS are prepared as in the following table:

Standard ID	Vot. 5 pg/L Standard (Section 8.9.1.5) (mL)	Finat Concentration (µg/L)
STD0	-	0.000
STD1	0.05	0.005
STD2	0.10	0.010
STD3	0.20	0.020
STD4	0.50	0.050
STD5	1.0	0.100
STD6	2.0	0.200
ICV,CCV,LCS, MS	1.0 (Section 8.9.2.3)	0.100

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blanks

9.1.1 Method Blank

A method blank must be prepared once per every 20 samples or per digestion batch, whichever is more frequent.

Mercury must not be detectable in the method blank at a concentration greater than the reporting limit.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. Digestion of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if lhe samples associated with the out of control method blank are non-detect for the elements of interest, or if sample concentrations are greater than t0x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

9.1.2 Initiat Catibration Btank (ICB)

An initial calibration blank must be analyzed immediately following the ICV (see **9.3**).

Mercury must not be detectable in the ICB at a concentration greater than the reporting limit.

Corrective Action: May reanalyze the standard once. If the concentration still exceeds the acceptance limit, stop and recalibrate the instrument. Samples cannot be analyzed until an acceptable ICB analysis is obtained. Exceptions may be made with approval of the Metals Departmeni Manager, Laboratory Director or QAO, if the samples associated with the out of control blank are non-detect for mercury, or if sample concentrations are greater than t0x the blank levels. In such cases, the sample results are accepted withoui

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corrective action for the high blank and the client is notified in a project narrative associated with the sample results.

9.1.3 Continutng Caltbration Blank

A continuing calibration blank must be analyzed immediately following the CCV (see 9.4).

Mercury must not be detectable in the CCB at a concentration greater than the reporting limit.

Corrective Action: May reanalyze the standard once. If the concentration still exceeds the acceptance limit, stop, recalibrate the instrument and reanalyze all associated samples. Samples cannot be analyzed until an acceptable CCB analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with the out of control blank are non-detect for the elements of interest, or if sample concentrations are greater than t0x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

9.2 Laboratory Control Sample (LCS)

Laboratory control sample (LCS) must be prepared once per every 20 samples or per digestion batch, whichever is more frequent, and spiked with a solution prepared from a second source or lot number, other than the source used to verify the accuracy of the standard curve for the determinative analytical method. The LCS contains all target elements of interest, and is digested along with the samples as verification of the accuracy of the entire digestion procedure.

The acceptable recovery QC limits are 80 – 120%. The recovery limits are continuously monitored and documented in-house through control charts. The *Control Limit Generation* SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the LCS recovery is still out of control, re-prepare and re-analyze the LCS and all associated samples. Samples cannot be reported until an acceptable LCS is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with the out of control LCS are also associated with a matrix spike that is in control. This is an acceptable measure of accuracy of the digestion and analytical procedures. An explanation of the out of control LCS recovery must be included in the project narrative to the client and the sample data reported noting the acceptable MS results as batch QC.

9.3 Initial Calibration Verification (ICV)

An initial calibration verification standard from a source different from that used to calibrate the instrument (see 8.9.2) must be analyzed immediately following calibration as an independent check of instrument performance. Nominal acceptance limits are 90% - 110% of the true value.

Corrective Action: May reanalyze the standard once. If the concentration still exceeds the acceptance limit, stop and recalibrate the instrument. Samples cannot be analyzed until an acceptable ICV analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with a high recovery ICV are non-detect. In such cases, the sample results are accepted without corrective action for the high ICV recovery and the client is notified in a project narrative associated with the sample results.

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9.4 Continuing Calibration Verification (CCV)

A continuing calibration verification standard must be analyzed after analysis of no more than 10 samples as an on-going check of instrument performance. Nominal acceptance limits are 90% - 110% of the true value.

Corrective Action: May reanalyze the standard once. If the concentration still exceeds the acceptance limit, stop, recalibrate the instrument and reanalyze all associated samples. Results cannot be accepted until an acceptable CCV analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with a high recovery CCV are non-detect. In such cases, the sample results are accepted without corrective action for the high CCV recovery and the client is notified in a project narrative associated with the sample results.

9.5 Matrix Spike

A matrix spike (MS) sample must be performed once per 20 samples (5% frequency), or per digestion batch, whichever is more frequent. The MS contains all target elements of interest.

The acceptable % recovery QC limits are 75% – 125%. The % recovery QC limits are continuously monitored and documented in-house through cbritrol charts. The *Control Limit Generation* SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the % recovery still exceeds the control limits and the LCS is compliant, include a project narrative with the results to the client noting that there may be potential matrix effects on the accuracy of the reported results as evidenced by MS recovery outside of QC limits.

9.6 Laboratory Duplicate

Duplicate analyses (matrix or sample duplicate) must be performed once per 20 samples 5% frequency), or per digestion batch, whichever is more frequent.

Acceptable relative percent differences (RPD) of duplicates is $\leq$ 20%. This acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate the RPD as follows:

$$RPD = \frac{R1 - R2}{\frac{fR1 + R21}{2}} \times 100$$

where:

R1 = sample Replicate #1
R2 = sample Replicate #2

The RPD limits are continuously monitored and documented in-house through control charts. The *Control Limit Generation* SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis may be repeated once to see if an analytical error has occurred. If the % RPD still exceeds the control limits; include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the reported metals results as evidenced by the matrix duplicate %RPD exceedance.

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9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- ICV
- ICB
- Method Blank
- Laboratory Control Sample
- Matrix QC Sample
- Matrix Duplicate
- Matrix Spike
- Samples 2-5
- CCV
- CCB
- Samples 6-15
- CCV
- CCB

10. Procedure

10.1 Equipment Set-up

Samples are prioritized by the Metals Departmeni Manager or Preparation Group Leader for digestion based on hold time arid client due date. The analyst must be familiar with instrument software and hardware as described in the user manuals supplied with the instrument before attempting to perform an analysis.

Power to the instrument, autosampler , PC and the argon gas supply are turned on. Peristaltic pump windings are inspected for wear and replaced if necessary. The winding clips are relaxed in between usage. The instrument manufacturer suggests that the pump tubing be changed once per month or more frequently as needed.

The starinous chloride solution is attached to the grey/grey pump tubing, 10% HCl is attached to the green/green autosampler rinse and DI is attached to the geen/green rinse blank. The autosampler probe line is attached to a grey/grey pump tubing. The pumps are turned on via the software and the flow is checked to insure that solutions are delivered to the mixing valve.

10.1.1 Sampte Preparation

10.1.1.1 Tissues

Tissue samples are prepared by microwave oven assisted acid digestion according to SOP MP-003. The LCS and MS are spiked as indicated in the table in 8.10.3.

A 10 mL aliquot of each digest is added to a 50 mL screw cap digestion tube along with 2 mL of BrCl solution. The vial contents should remain a yellow color. If a yellow color does not remain, add more BrCl solution. This solution is

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allowed to stand for 12 hours. Bring the vial to 50 mL with DI water . The vials are then decolorized with 0.4 mL of 12% hydroxyl amine hydrochloride and shaken. The yellow color should disappear. If the solution remains yellow, add more hydroxyl amine until the color disappears. Add the same amount to all samples and standards.

10.1.1.2 Soils/Sediment

A 0.5 – 1.0 g wet weight well mixed aliquot of soil/sediment is added to a 50 mL screw cap digestion tube with 5 mL of DI water. The LCS and MS are spiked as indicated in the table in 8.10.3. A 3.75 mL volume of concentrated HCl and 1.25 mL of concentrated HNO_3 are added and the tube placed on the hot block set to 95 ± 3 °C for 2 minutes. Samples are allowed to cool and then 25 mL of DI water is added to each vial and placed back on the hot block for 30 minutes.

After cooling bring to a final volume of 50 mL with DI water. Then a 10 mL aliquot of each digest is added to a 50 mL screw cap digestion tube along 2 mL of BrCl solution. The vial contents should remain a yellow color. If a yellow color does not remain, add more BrCl solution. Bring the vial to 50 mL with DI water. The vials are then decolorized with 0.4 mL of 12% hydroxyl amine hydrochloride and shaken. The yellow color should disappear. If the solution remains yellow, add more hydroxyl amine until the color disappears. Add the same amount to all samples and standards

10.2 initial Calibration

The instrument is calibrated prior to sample analysis and at least once every 24 hours. A linear least squares regression calibration curve is selected for Method 7474.

In all cases, a correlation coefficient ≥ 0.995 is required before the analysis of samples can begin. The calibration blank is included as a point in the calibration curve.

An ICV (Section 9.3) and ICB (Section 9.1.2) are analyzed after calibration.

10.3 Equipment Operation and Sample Processing

After initializing the Millennium software, the instrument is turned on via the software and allowed to warm up for 30 minutes. The analysis method is selected and the autosampler template is selected. Method 7474 is set up in the software which specifies delay, read and rinse times as well as pump speeds. An autosampler template is set up specifying calibration standard, QC standards and positions on the autosampler rack. Once sample ID's have been typed in, the file is saved as the Job number.

A Work Group is obtained from LIMS and used as the data file name.

The analysis is initiated by clicking on the start button on the analysis page.

Following analysis, the data file is exported to the LIMS on the O:Metals\Millennium drive for data processing. The instrument and autosampler are then rinsed with DI water and turned off

10.4 Continuing Calibration

Periodically (after no more than 10 samples) and at the end of the analysis, CCV standards (Section 9.4) and CCB standards (Section 9.1.3) are analyzed.

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10.5 Preventive Maintenance

Inspect pump tubing for signs of wear and replace monthly or more frequentiy if necessary.

Clean glass liquid separator when glass appears coated with yellow film.

Replace dryer tube annually.

11. Data Evaluation, Calculations and Reporting

Procedures for data and record management must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP (08-01). All records must be stored in such a manner as to be safe and accessible for at least 10 years.

The digestion batch bench sheets and other relevant laboratory notebooks must follow the specifications in the *Laboratory Notebook Usage* Work Instruction (108-01), and all record keeping and document control practices.

Sample concentrations are calculated as follows:

Sample Concentration = ((Dc*Df)*Dv)/((Md*(S%/100)*1000))

Where:

Dc = digest Concentration in pg/L
Df = Dilution factor
Dv = Digest volume in mL
Md = Mass of sample digested in g
S% = percent solid of the sample (if reported on wet weight basis then percent solid = 100)

All results are reportable without qualification if digestion and analytical holding times are met, preservation (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is not suspected during digestion or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

QC Parameter	Acceptance Criteria
Method Blank	< reporting limit
Laboratory Control Sample	80%-120% Recovery
Matrix Duplicate	≤ 20% RPD
Matrix Spike	75% - 125% Recovery
Matrix Spike Duplicate (if needed)	≤ 20% RPD, 75% - 125% Recovery

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12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 outlines sample batch QC acceptance criteria. If non-compliant results are to be reported, the Metals Departmeni Manager and/or the Laboratory Director, and the QA Manager must approve the reporting of the results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The instrument analyst or Departmeni Manager performing the secondary analytical review initiates the project narrative, and the narrative must clearly documeni the non-compliance and provide a reason for acceptance of these results.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initiat (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method

13.3 instrument Detection Limits

The instrument detection limit (IDL) is the smallest signal above the background noise that an instrument can detect. The IDL can be calculated taking the average of the standard deviations for three measuremerits of a reagent blank solution analyzed on three analytical runs on three non-consecutive days. Seven consecutive measurements must be taken per day. The IDLs are not required to go through sample digestion. Each measurement must be performed as though it were a separate sample.

14. Pollution Prevention and Waste Management

The *Hazardous Waste* and *Sample Disposal* SOP (G-006) must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

Once sample batches have completed digestion, the sample containers are stored in the metals lab and held for 30 days. If there is no sample remaining in the sample collection bottle, it may be rinsed and thrown away. It must be noted in the *Internal* COC that there is no sample remaining in the bottle, and the bottle was discarded.

Once satisfactory results have been generated, the digestates are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled "Corrosive Liquid".

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All reagent waste generated during digestion must be stored in satellite containers in the metals preparation laboratory.

Once the reagent waste satellite containers are full, they must be emptied into 55-gallon drums marked "Corrosive Liquid".

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/01-01 Sample Receipt & Log-In

SOP/08-01 Documeni Control

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-07 Control Limit Generation

SOP/08-12 IDC/DOC Generation

SOP/G-006 Hazardous Waste and Sample Disposal

SOP/MP-003 Microwave Assisted Acid Digestion of Sediments, Soils, Tissues and Waters

WI/108-01 Laboratory Notebook Usage

16. Attachments

None.

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Soil Field Screening Procedures

Each soil core should be screened with a properly calibrated direct reading instrument (DRI) equipped with a PID or FID detector or other suitable field-screening instrument capable of detecting the contaminants of concern pursuant to N.J.A.C. 7:26E-2.1(b).

To obtain the most representative monitor reading, use a decontaminated stainless steel spoon, knife or other appropriately constructed device and make a longitudinal score deep enough to expose a porous surface the length of the core. Or optionally, make very small divots at six-inch intervals to expose a porous surface. Simultaneously, place the probe of the DRI immediately above the opened area being careful not to touch the sample, and move the probe slowly above the lateral scoring and note any peaks. Record results of peaks in 6-inch intervals to determine sample location. Instrument readings will be biased low and not representative of in-situ conditions if the soil core is not scored or inner core not exposed for proper field screening. Other methods of field screening (e.g., bag headspace, jar headspace, warming, UV light, dye testing etc.) should be discussed with the appropriate regulatory authority for approval before sample collection.

The Technical Requirements for Site Remediation N.J.A.C. 7:26E-3.6(a)4.(ii), instruct one to select a six-inch increment of soil for volatile organic laboratory analysis based on field screening with a DRI. If a boring is continuously cored to 20 feet below grade where ground water is first encountered, then 4 to 5 individual 48" - 60" soil core segments will have to be opened and screened before determination as to which six-inch increment is to be selected for sampling and analysis. Special attention must be paid to labeling and storage of individual core samples when continuous soil samples are collected from a single boring. In many instances soil cores can be produced faster than they can be opened, logged, screened and sampled by a technician. In those instances when a backlog of cores are being generated, care must be made to protect the cores from direct sunlight, excessive ambient temperatures and rain. These conditions may have an adverse effect on highly sensitive volatile organics within the core or the instruments used for screening. Always keep the cores labeled so that the up/down orientation is not lost. Proceeded carefully, but quickly when field screening. If necessary, log soils for lithology information *after* sample collection. Always calibrate the DRI at the start of each day.

Another option is to select (using the DRI), and sample (using a small diameter coring device), a six-inch increment from every individual core segment, and only submit the sample required from that particular boring for analysis as directed in 7:26E-3.6(a)4(ii). This option can be more costly as several sample containers will have to be discarded at the end of the each boring. If chemical preservation is used (methanol), proper disposal could be an issue. Sampling every individual core first, prior to determining which increment to ship for laboratory analysis will also require additional labor. This particular option, to collect a representative six-inch incremental sample from every individual segment of a continuous core with its associated cost, makes the first option to carefully protect and manage the cores to control the loss of volatile organics even more critical. (Section 6.2.6)

Water Quality Parameter Procedures

N.J.A.C. 7:18 requires that any environmental laboratory* submitting analytical data to the Department, regardless of quality level, must be certified by the Office of Quality Assurance. This applies to those firms using LFPS instruments associated with the "analyze immediately" category of water quality indicator parameters (WQIPs) including pH, temperature, and dissolved oxygen. Regardless of whether or not the equipment in question is rented or privately owned the requirement for certification cannot be ignored. All certification documentation must accompany the instrument into the field and accompany all WQIP data submitted to the Department. (*Environmental laboratory is defined as any laboratory, facility, consulting firm, government or private agency, business entity or other person that the

Department has authorized, pursuant to N.J.A.C. 7:18, to perform analysis in accordance with the procedures of a given analytical method using a particular technique as set forth in a certain methods reference document and to report the results from the analysis of environmental samples in compliance with a Departmental regulatory program). (Section **6.9.2.2.4**)

Prior to sample collection, water body characteristics (e.g., size, depth, and flow) should be recorded in the field logbook. Water quality measurements shall include temperature, pH, total hardness (as $CaCO_3$), alkalinity (as $CaCO_3$), salinity (parts per thousand, 0/00), conductivity (as *u*mhos/cm), and dissolved oxygen (mg/l). These measurements must be properly documented as per Chapter 10, *Documentation*. Non-aqueous data must be accompanied by laboratory-analyzed total organic carbon (TOC) and particle grain size for each sample. (Section **6.8.1.2**)