WARZYN

Plan
Project No. 60251

# Quality Assurance Project Plan
# Remedial Investigation/ Feasibility Study
# Volume 2 of 2 Laboratory Methods
# American Chemical Services, Inc.
# Griffith, Indiana

Prepared for:

**American Chemical Services**
**Steering Committee**
**Chicago, Illinois**

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September, 1988

# APPENDIX C

## HAZLETON LABORATORIES AMERICA

## STANDARD OPERATING PROCEDURES USING NON - CLP PROTOCOL

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ASSAY TITLE: Determination of Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Drinking Water

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc. Environmental Analysis

SCOPE:

This method covers the determination of the priority pollutant and target compound list (TCL) organochlorine pesticides and PCBs in drinking water sources using gas chromatography with electron capture (GC-EC) detection. The compounds determined by this method are reported with detection limits lower than those generated by the standard pesticide/PCB screen. All positive results reported using this method are reported only following second column confirmation. The following compounds are calibrated and analyzed for under this method:

| | | |
|---|---|---|
| Aldrin | 4,4'-DDT | Methoxychlor |
| alpha-BHC | Dieldrin | Toxaphene |
| beta-BHC | Endosulfan I | PCB-1016 |
| gamma-BHC (Lindane) | Endosulfan II | PCB-1221 |
| delta-BHC | Endosulfan sulfate | PCB-1232 |
| alpha-chlordane | Endrin | PCB-1242 |
| gamma-chlordane | Endrin aldehyde | PCB-1248 |
| Technical chlordane | Endrin ketone | PCB-1254 |
| 4,4'-DDD | Heptachlor | PCB-1260 |
| 4,4'-DDE | Heptachlor epoxide | |

PRINCIPLE:

A 1-L sample is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried with anhydrous sodium sulfate and exchanged to hexane during the concentration step. The final extract volume is taken to 1.0 mL for analysis. The extract is separated by gas chromatography and the analytes of interest are measured with an electron capture detector. This method provides an alumina column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

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SENSITIVITY, PRECISION AND ACCURACY:

The method detection limits presented in Table 1 represent the sensitivities that can be achieved in ground water in the absence of interferences. Precision and accuracy for this method, as generated from an in house validation study, is presented in Table 2.

REFERENCES:

Environmental Protection Agency (EPA) Method 608 (Federal Register, 49(209):43,321-43,336, October 16, 1984).

Environmental Protection Agency (EPA) Contract Laboratory Program, Statement of Work for "Organic Analysis Multi-Media Multi-Concentration, October 1986. Revisions: January 1987; February 1987; July 1987; August 1987. Exhibits: B, D, E.

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SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

INTERFERENCES:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose major problems in pesticide analysis when using the EC detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature and diversity of the site being sampled. Cleanup procedures provided in this method may be used to minimize or overcome such interferences.

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QUALITY ASSURANCE:

The minimum quality assurance quality control (QA/QC) operations necessary to satisfy the analytical requirements associated with the determination of the pesticide/PCB compounds listed in this method are as follows:

- Method Blank Analysis
- Surrogate Spike Recovery and Retention Time Monitoring
- Matrix Spike/Matrix Spike Duplicate Analysis
- Specific QA/QC for Pesticide Analysis

1. Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

A method blank is performed with every 20 samples processed and/or whenever samples are extracted, whichever is most frequent. It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, and glassware are minimized. An acceptable laboratory method blank should contain less than or equal to the reported method detection limit of any single pesticide/PCB target compound.

If a laboratory method blank exceeds the above criteria, the analyst must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control MUST be reextracted and reanalyzed.

2. Surrogate Spike Analysis

All samples, blanks, and matrix spikes are fortified with the surrogate compound dibutylchlorendate (DBC) before extraction to monitor the preparation and analysis of samples. The spiking level is 0.1 µg/L, based on an extraction volume of 1 L, which will produce an extract concentration (before any optional dilutions) of 0.1 µg/mL.

Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the advisory recovery limits listed below.

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Advisory Surrogate Spike Recovery Limits

| Fraction | Surrogate Compound | Water |
|---|---|---|
| Pest. | Dibutylchlorendate | (24-154)* |

* These limits are for advisory purposes only. They are not used to determine if a sample should be reanalyzed.

3. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analysis

In order to evaluate the matrix effect of the sample on the analytical methodology and provide both precision and accuracy information, an MS/MSD analysis is performed with each set of 20 samples. Spiking is performed using a mixture of the following six individual pesticide compounds:

- Heptachlor
- Aldrin
- Dieldrin
- Lindane
- Endrin
- 4,4'-DDT

Individual component recoveries of the matrix spike are calculated using Equation 3.1.

$$\text{Matrix spike percent recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Eq. 3.1}$$

Where: SSR = Spike sample results
SR = Sample result
SA = Spike added from spiking mix

The analyst is required to calculate the relative percent difference (RPD) between the matrix spike and matrix spike duplicate. The RPD for each component is calculated using Equation 3.2.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Eq. 3.2}$$

Where: $D_1$ = First sample value
$D_2$ = Second sample value (duplicate)

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Matrix Spike Recovery Limits

| Fraction | Matrix Spike Compound | Water* |
|---|---|---|
| Pesticide | Lindane | 46-118 |
| Pesticide | Heptachlor | 29-119 |
| Pesticide | Aldrin | 30-108 |
| Pesticide | Dieldrin | 39-133 |
| Pesticide | Endrin | 53-114 |
| Pesticide | 4,4'-DDT | 38-130 |

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be reanalyzed.

4. Pesticide Retention Time Windows

The external standard quantitation method must be used to quantitate all pesticides/PCBs. Before performing any sample analysis, the analyst is required to determine the retention time window for each pesticide/PCB target compound and the surrogate spike compound, DBC. These retention time windows are used to make tentative identification of pesticides/PCBs during sample analysis.

Before establishing retention time windows, the GC operating conditions (oven temperature and flow rate) must be adjusted such that 4,4'-DDT has a retention time of greater than or equal to 12 minutes on packed GC columns, except on OV-1 or OV-101 columns.

Establish retention time windows as follows:

- Before initiating analysis on a GC system and each time a new GC column is installed, make three injections of all single component pesticide mixtures, multi-response pesticides, and PCBs throughout the course of a 72-hour period. The concentration of each pesticide/PCB should be sufficient to provide a response that is approximately half scale. The three injections of each compound are made at approximately equal intervals during the 72-hour period, (i.e., each compound is injected near the beginning, middle, and end of the 72-hour period).

- Verify the retention time shift for DBC in each standard. The retention time shift between the initial and subsequent standards must be less than 2.0% difference for packed columns and less than 1.5% difference for wide-bore capillary columns. If this criterion is not met, continue injecting replicate standards until the criterion is satisfied.

- Calculate the standard deviation of the three absolute retention times for each single component pesticide. For multiresponse pesticides or PCBs, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak.

- The standard deviations determined are used to determine the retention time window for a particular 72-hour sequence. Apply plus or minus three times the standard deviations to the retention time of each pesticide/PCB determined for the first analysis of the pesticide/PCB standard in a given 72-hour analytical sequence. This range of retention times defines the retention time window for the compound of interest for that 72-hour sequence. Note that by definition, the retention time of a pesticide/PCB from the first analysis of that compound in the 72-hour sequence is the center of the retention time window (do not use the retention time measured during the initial determination of the retention time windows as the center of the retention time window). The experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse pesticide/PCBs, the analyst should use the retention time window, but should rely primarily on pattern recognition.

- In those cases where the retention time window for a particular pesticide/PCB is less than 0.01 minutes, the analyst may use whichever of the following formulas apply.

  - For packed columns, the retention time window of the particular pesticide/PCB is calculated as ±1% of the initial retention time of the compound in the 72-hour sequence.

  - For wide-bore capillary columns [inner diameter (i.d.) greater than 0.32 mm], the retention time window of the particular pesticide/PCB is calculated as ±0.75% of the initial retention time of the compound in the 72-hour sequence.

  - For narrow-bore capillary columns (i.d. less than 0.32 mm), the retention time window of the particular pesticide/PCB is calculated as ±0.15% of the initial retention time of the compound in the 72-hour sequence.

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5. Primary GC Column Analysis

Primary analysis determines whether or not pesticides/PCBs are present in the sample, and establishes a tentative identification of each compound. Quantitation may be performed on the primary analysis if the analysis meets all of the QC criteria specified for quantitation. NOTE: To determine that no pesticides/PCBs are present at or above the required quantitation limit is a form of quantitation.

Separation should be greater than or equal to 25% resolution between the peaks. This criteria must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

Evaluation Standard Mixtures

- Prepare Evaluation Standard Mixes A, B, and C (aldrin, endrin, 4,4'-DDT and DBC) at the three concentration levels described in the method. Analyze the three evaluation standard mixes sequentially at the beginning of each 72-hour period (see Figure 1).

- Calculate the calibration factor (ratio of the total area to the mass injected) for each compound in Evaluation Standard Mixes A, B, and C using Equation 5.1.

$$\text{Calibration factor} = \frac{\text{Total area of peak}}{\text{Mass injected (in nanograms)}} \qquad \text{Eq. 5.1}$$

- Using the calibration factors from above, calculate the percent relative standard deviation (%RSD) for each compound at the three concentration levels using Equation 5.2. The %RSD for aldrin, endrin, 4,4'-DDT and DBC must be less than or equal to 10.0%. If the %RSD exceeds 10.0% for 4,4'-DDT, a three-point DDT series (DDT, DDD, DDE) may be run and used to establish a calibration curve for those three compounds; otherwise, corrective action must be taken to bring the DDT %RSD within 10%.

- NOTE: The 10.0% RSD linearity criteria pertains only to columns being used for pesticide/PCB quantitation. If a column is used only for surrogate quantitation, the 10.0% RSD is only required for DBC.

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 5.2}$$

Where: Standard deviation (SD) = $\sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$

$\bar{x}$ = Mean of initial three calibration factors (per compound).

Evaluate the chromatogram from the analysis of the Evaluation Standard Mix B. The appearance of peaks in addition to the four main pesticide peaks indicates a breakdown of endrin and/or 4,4'-DDT.

Calculate the percent breakdown for endrin and/or 4,4'-DDT on the mixed phase (1.5% OV-16/1.95% OV-210 or equivalent) GC column using Equations 5.3 and 5.4. The percent breakdown for endrin or 4,4'-DDT must not exceed 20.0%. Corrective action must be taken before analysis continues if this criterion is not met.

$$\text{\% breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE, DDD)}}{\text{Total DDT peak area (DDT, DDE, DDD)}} \times 100 \qquad \text{Eq. 5.3}$$

$$\text{\% breakdown for Endrin} = \frac{\text{Total eldrin degradation peak areas (endrin aldehyde, endrin ketone)}}{\text{Total endrin peak area (endrin, endrin aldehyde, endrin ketone)}} \qquad \text{Eq. 5.4}$$

Calculate the percent breakdown for endrin and/or 4,4'-DDT on the OV-1 or equivalent GC column using Equations 5.3 and 5.4. The percent breakdown for Endrin or 4,4'-DDT must not exceed 20.0%. Corrective action must be taken before analysis continues if this criterion is not met.

If there is evidence of a peak at the retention time for endrin aldehyde/4,4'-DDD (which coelute on the OV-1 or equivalent GC column), calculate a combined percent breakdown for endrin/4,4'-DDT using Equation 5.5. The combined endrin/4,4'-DDT percent breakdown must not exceed 20.0%, or else corrective action must be taken before analysis continues. The term "peak height" may be substituted for the term "peak area."

$$\text{Combined \% breakdown} = \frac{\text{Total endrin/DDT degradation peak area (DDD, DDE, endrin aldehyde, endrin ketone)}}{\text{Total endrin/DDT peak area (endrin, endrin aldehyde, endrin ketone, DDT, DDD, DDE)}} \qquad \text{Eq. 5.5}$$

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Suggested Maintenance

Corrective measures may require any one or more of the following remedial actions:

- Packed columns. For instruments with off-column injection, replace the demister trap, and clean and deactivate the glass injection port insert, or replace it with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of packing material if any discoloration is noted. Swab out the inside walls of the column if any residue is present. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described below) and/or repack/replace the column.

- Capillary columns. Clean and deactivate the glass injection port insert or replace it with a cleaned and deactivated insert. Break off the first few inches (up to 1 ft) of the injection-port side of the column. Remove the column and backflush with solvent according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

- Metal Injector Body. Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Allow the injection port temperature to come to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsings in the beaker.

Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

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Individual Standard Mixtures A and B

Prepare Individual Standard Mixtures A and B containing the single-component pesticides. One mixture of all of the single component pesticides is acceptable when using a capillary column if resolution of all compounds is achieved. Prepare separate solutions of all multi-response pesticides and PCBs. (Aroclor 1016 and Aroclor 1260 may be combined in a single mixture.)

Analyze Individual Standard Mixtures A and B and all multi-response pesticide/PCBs at the beginning of each 72-hour period (Figure 1) and analyze Individual Standard Mixtures A and B at the intervals specified in the analytical sequence in Figure 1 and whenever sample analysis is completed. The calibration factor for each standard quantitated (Individual Standard Mix A or B) (Equation 5.6), must not exceed a 15.0% difference for a quantitation run, nor exceed a 20.0% difference for a confirmation run during the 72-hour period. Calculate the percent difference using Equation 5.7. Deviations greater than 15.0% require the analyst to repeat the samples analyzed following the quantitation standard that exceeded the criterion.

$$\text{Calibration factor} = \frac{\text{Total area of peak*}}{\text{Mass injected (in nanograms)}} \qquad \text{Eq. 5.6}$$

*For multiresponse pesticide/PCBs, use the total area of all peaks used for quantitation. The term "peak height" may be substituted for the term "peak area."

$$\text{Percent difference} = \frac{R_1 - R_2}{R_1} \times 100 \qquad \text{Eq. 5.7}$$

Where: $R_1$ = Calibration factor from first analysis
$R_2$ = Calibration factor from second or subsequent analysis

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Sample Analysis (Primary GC Column)

Samples are analyzed according to the sequence described in Figure 1.

The retention time shift for DBC must be evaluated after the analysis of each sample. The retention time shift must be less than a 2.0% difference for packed GC columns between the initial standard analysis and any sample or standard analyzed during the 72-hour period. The percent difference for wide-bore capillary columns (i.d. greater than 0.32 mm) must be less than 1.5%. The percent difference for narrow-bore capillary columns (i.d. less than 0.32 mm) must be less than 0.3% (Equation 5.8).

$$\text{Percent Difference} = \frac{RT_1 - RT_S}{RT_1} \times 100 \qquad \text{Eq. 5.8}$$

Where: $RT_1$ = Absolute retention time of DBC in the initial standard (Evaluation Standard Mix A)

$RT_S$ = Absolute retention time of DBC in the sample or subsequent standard

Evaluate the GC column throughout the analysis of samples by injecting Evaluation Standard Mix B at the frequency outlined in Figure 1.

Calculate the percent breakdown for 4,4'-DDT and endrin using Eq. 5.5. Take corrective action when the breakdown for 4,4'-DDT or endrin exceeds 20.0%.

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Figure 1

72-Hour Sequence for Pesticide/PCB Analysis

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A*
5. Individual Standard Mix B*
6. Toxaphene
7. Technical Chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. 5 Samples
15. Evaluation Standard Mix B
16. 5 Samples
17. Individual Standard Mix A or B
18. 5 Samples
19. Evaluation Standard Mix B
20. 5 Samples
21. Individual Standard Mix A or B (whichever was not run in Step 16)
22. 5 Samples
23. Repeat the above sequence starting with Step 14
24. Pesticide/PCB analysis sequence must end with Individual Standard Mixes A and B regardless of number of samples analyzed.

* These may be one mixture (provided adequate separation can be shown)

6. Confirmation Analysis (GC/EC)

Confirmation analysis confirms the presence of all compounds tentatively identified in the primary analysis. Therefore, the only standards required are the evaluation standard mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence described in Figure 1 is therefore modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are necessary.

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Separation should be greater than or equal to 25% resolution between peaks. This criteria must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

For a fused silica capillary confirmation (FSCC), there must be greater than or equal to 25% resolution (valley) between the following pesticide pairs:

- Beta-BHC and delta-BHC
- Dieldrin and 4,4'-DDT
- 4,4'-DDD and endrin aldehyde
- Endosulfan sulfate and 4,4'-DDT

All QC specified previously must be adhered to, i.e., the greater than or equal to 12 minutes retention time for 4,4'-DDT, and the specified criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for DBC. The retention time requirement for 4,4'-DDT does not have to be met if the confirmation column is OV-1 or OV-101.

Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B, and C. The exception to this occurs when toxaphene and/or the DDT series are confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the following sequences must be followed depending on the situation.

Toxaphene only. Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating %RSD. If less than or equal to 10.0% RSD, use the appropriate calibration factor for calculation. If greater than 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

DDT, DDE, DDD only. Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD, and DDT. Calculate linearity and follow the requirements specified earlier under the primary GC analysis for each compound to be quantitated.

DDT series and toxaphene. Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified under the primary GC analysis for each compound to be quantitated.

Other pesticides/PCBs plus DDT series and/or toxaphene. Begin the sequence with Evaluation Standard Mixes A, B, and C. Calculate linearity on the four compounds in the Evaluation Standards mixes. If DDT and/or one or more of the other compounds are greater than 10.0% RSD and/or degradation exceeds the criterion, corrective maintenance as outlined earlier should be performed before repeating the above chromatography evaluation. If only DDT exceeds the linearity criteria and one or more of the DDT series is to be quantitated, inject three concentration levels of the DDT series (DDT, DDE, DDD) as described in the earlier paragraph (do not repeat Evaluation Mix B). If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the %RSD on the proper form. Anytime toxaphene is to be quantitated follow the instructions as given in the paragraph describing toxaphene only.

After the linearity standards are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified during primary analysis to establish the daily retention time windows for the confirmation analysis. Analyze all confirmation standards for a case at the beginning, at intervals specified in the following paragraph and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The analyst must reanalyze all samples between the standard that exceeds the criterion and a subsequent standard that meets the criterion.

Begin injection of samples at this point of the confirmation analysis sequence. Analyze groups of five samples with a standard pertaining to the samples after each group (Evaluation Mix B is required after the first five samples, and every 10 samples thereafter, e.g., after 5, 15, 25, etc.). The alternating standard's calibration factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the laboratory to repeat the samples analyzed between the standard that exceeds the criterion and a subsequent standard that meets the criterion. The 15.0% criterion only pertains to compounds being quantitated.

If more than one standard is required to confirm all compounds tentatively identified in the primary analysis, include an alternate standard after each 10 samples.

Samples must also be repeated if the degradation of either DDT and/or Endrin exceed 20.0% on the intermittent Evaluation Standard Mix B.

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If the samples are split between two or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

Inject the method blanks (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

APPARATUS:

- Separatory funnel - 2,000 mL with Teflon® stopcock.
- Drying column - Chromatographic column approximately 400 mm x 19 mm i.d., with coarse frit. (Substitution of a small pad of disposable Pyrex® glass wool for the frit will help prevent cross-contamination of sample extracts.)
- Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-57000010500 or equivalent). Attach to concentrator tube with springs.
- Snyder column - Kuderna-Danish, three-ball macro (Kontes D-503000-0121 or equivalent).
- Snyder column - Kuderna-Danish, two-ball micro (Kontes D-569001-0219 or equivalent).
- Chromatographic column for alumina - 8-mL (200 mm X 3 mm i.d.) polypropylene column (Kontes D-520160 or equivalent), or 6-mL (150 mm x 8-mm i.d.) glass column (Kontes K-420155 or equivalent), or 5-mL serological pipettes plugged with a small piece of Pyrex glass wool or polyethylene porous disk (Kontes K-420162).
- Pyrex glass wool - Pre-rinse glass wool with appropriate solvents to ensure its cleanliness.
- Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

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- Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

- Balance - Analytical, capable of accurately weighing ±0.0001 g.

- Nitrogen evaporation device equipped with a water bath that can be maintained at 35- to 40°C. The N-Evap by Organomation Associates, Inc., South Berlin, Massachusetts (or equivalent) is suitable.

- Gas chromatograph - An analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector, and strip-chart recorder with recording integrator. A data system is required for measuring peak areas or peak heights and recording retention times.

- Quantitation and/or confirmation columns:

  Column 1: 6-ft long, 4-mm i.d. glass packed column
  1.5% SP-2250/1.95% SP-2401 on 100/120 Suppelcoport

  Column 2: 6-ft long, 4-mm i.d. glass packed column
  3% SP-2100 on 100/120 Suppelcort

  Column 3: 30-m long, 0.53-mm i.d. fused silica megabore cap column DB-5

  Column 4: 30-m long, 0.53-mm i.d. fused silica megabore cap column DB-608

REAGENTS:

Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the method detection limit of each parameter of interest.

Acetone, hexane, isoctane (2,2,4-trimethylpentane), methylene chloride - Pesticide quality or equivalent.

Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

Alumina - Neutral, Super I Woelm or equivalent. (Universal Scientific, Incorporated, Atlanta, Georgia or equivalent.) Prepare Activity III by adding 7% (v/w) reagent water to the Super I neutral alumina. Tumble or shake in a

wrist-action shaker for a minimum of 2 hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25-cycle Soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide technique indicates any interferences for the compounds of interest.

Alumina Equivalency Check. Check recovery of all single component pesticides following the procedure as outlined under the procedure. The percent recovery for all single component pesticides must be greater than or equal to 80%, except for endosulfan sulfate, which must be greater than or equal to 60%, and endrin aldehyde, which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/w) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

Sodium hydroxide solution (10N)-(ACS). Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least 1 month.

Pesticide surrogate standard spiking solution.

The surrogate standard is added to all samples and calibration solutions; the compound specified for this purpose is DBC.

Prepare a surrogate standard spiking solution at a concentration of 1 µg/1.00 mL in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

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Sulfuric acid solution (1+1)-(ACS). Slowly add 50 mL $H_2SO_4$ (sp. gr. 1.84) to 50 mL of reagent water.

Stock standard solutions (1.00 µg/mL) - Stock standard solution can be prepared from pure standard materials or purchased as certified solutions.

Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10-mL volumetric flask with isoctane. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are traceable to EMSL/LV supplied standards.

Transfer the stock standard solutions into a bottle/vial with Teflon-lined septa. Store at 4°C (±2°C) and protect from light. Stock standard solutions must be replaced after 12 months, or sooner, if comparison with check standards indicate a problem.

Pesticide matrix standard spiking solution. Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentrations specified.

| Pesticide | µg/1.0 mL |
|---|---|
| Lindane | 0.2 |
| Heptachlor | 0.2 |
| Aldrin | 0.2 |
| Dieldrin | 0.5 |
| Endrin | 0.5 |
| 4,4' DDT | 0.5 |

Matrix spikes are also to serve as duplicates by spiking two 1-L portions from the one sample chosen for spiking.

Evaluation Standard Mixtures - Prepare working standard mixtures diluted with hexane containing aldrin, endrin, 4,4'-DDT, and DBC to evaluate the GC column. Prepare three concentration levels as follows:

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| Standard I.D. | Aldrin (µg/ml) | Endrin (µg/ml) | 4,4' DDT (µg/ml) | DBC µg/ml |
|---|---|---|---|---|
| EVAL A | 0.005 | 0.010 | 0.010 | 0.010 |
| EVAL B | 0.025 | 0.050 | 0.050 | 0.050 |
| EVAL C | 0.05 | 0.100 | 0.100 | 0.100 |

Working Standard Solutions:

Individual Standard Mixtures - These include all single-component organochlorine pesticides as well as the surrogate compound DBC. Two mixtures of the individual component standards are prepared to prevent coelution of components when using packed columns. Prepare the two individual standard mixtures, diluted in hexane, containing the following pesticides in the concentrations specified.

| Individual Mix A | | Individual Mix B | |
|---|---|---|---|
| Pesticide | µg/ml | Pesticide | µg/ml |
| gamma-BHC | 0.025 | alpha-BHC | 0.025 |
| Heptachlor | 0.025 | beta-BHC | 0.025 |
| Aldrin | 0.025 | delta-BHC | 0.025 |
| Heptachlor epoxide | 0.025 | p,p'-DDE | 0.05 |
| Endosulfan I | 0.025 | Endrin | 0.05 |
| Dieldrin | 0.05 | p,p'-DDD | 0.05 |
| p,p' DDT | 0.05 | Endosulfan sulfate | 0.05 |
| Endrin aldehyde | 0.05 | Endrin ketone | 0.05 |
| Endosulfan II | 0.05 | alpha-chlordane | 0.025 |
| Methoxychlor | 0.25 | gamma-chlordane | 0.025 |
| Dibutylchlorendate | 0.10 | Dibutylchlorendate | 0.10 |

Multicomponent Standards - All multicomponent standards, e.g., PCB aroclors, toxaphene, and technical chlordane, must be in separate solutions with the exception of aroclors 1016/1260. Dibutylchlorendate is also to be included in each multicomponent standard mixture. Prepare the following standards in hexane at the specified concentrations:

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| Standard I.D. | µg/ml |
|---|---|
| Toxaphene | 0.40 |
| Technical Chlordane | 0.20 |
| PCB 1016/1260 | 0.10 |
| PCB 1232 | 0.10 |
| PCB 1242 | 0.10 |
| PCB 1248 | 0.10 |
| PCB 1254 | 0.10 |
| PCB 1260 | 0.10 |

## Procedure

1. Sample Storage and Holding Times

1.1 Procedures for Sample Storage

1.1.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

1.1.2 After analysis, extracts and unused sample volume must be protected from light and refrigerated at 4°C ±2° for the periods specified in the contract schedule.

1.2 Holding Time

All samples should be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

2. Sample Extraction - Separatory Funnel

2.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extractions, continuous liquid-liquid extraction may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L.

2.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide and/or 1:1 sulfuric acid solution. (Note: Recovery of DBC will be low if pH is outside this range. Alpha-BHC, gamma-BHC, Endosulfan I and II, and endrin are subject to

decomposition under alkaline conditions, and therefore may not be detected if the pH is above nine). Add 100 µL of surrogate standard spiking solution into the separatory funnel and mix well. Add 100 µL of pesticide matrix spiking solution to each of two 1-L portions from the sample selected for spiking. (If insufficient sample is available to perform matrix spikes, prepare duplicate control spikes, using laboratory reagent water and analyze in lieu of the matrix spikes.)

2.3 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third of the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. Drain methylene chloride into a 250-mL Erlenmeyer flask.

2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

2.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all pesticides listed in this method.

2.6 Pour the combined extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

2.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the

proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes.

2.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

2.9 Remove the Snyder column, and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane.

3. Nitrogen Blowdown

3.1 Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with hexane during the operation, and the final volume must be brought to 0.5 mL. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

3.2 Dilute the extract to 1 mL with acetone and proceed to Step 5 Alumina Column Cleanup.

4. Sample Extraction - Continuous Liquid-Liquid Extractor

4.1 When experience with a sample from a given source indicates that a serious emulsion problem will result, or if an emulsion is encountered in Step 2.3 using a separatory funnel, a continuous extractor should be used.

4.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into the continuous extractor. Add 100 µl of surrogate standard spiking solution into the continuous extractor and mix well. Check the pH of the sample with wide-range pH paper and adjust the pH to between 5 and 9 with 10N sodium hydroxide and/or 1:1 sulfuric acid solution.

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4.3 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in Steps 2.5 through 3.2.

5. Alumina Column Cleanup

5.1 Add 3 g of Activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

5.2 Transfer the 1 mL of hexane/acetone extract from Step 3.2 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10-mL concentrator tube.

5.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.

5.4 Concentrate the cleaned-up extract using the nitrogen blowdown technique as described in Step 3.0, adjusting the final volume to 1.0 mL with hexane. The pesticide/PCB fraction is ready for analysis. Store the extracts at 4°C (±2°C) in the dark in Teflon-sealed containers until analyses are performed.

6. Optional Sulfur Cleanup

6.1 Transfer the 1-mL extract from Step 5.4 to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50-mL bottle.

6.2 Add 1 mL of TBA-sulfite reagent and 2 mL of 2-propanol, cap the bottle, and shake it for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

6.3 Add 5 mL of distilled water and shake the sample for at least 1 minute. Allow the sample to stand 5 to 10 minutes. Transfer the hexane layer (top) to a concentrator ampule and go back to Step 5.4.

7. Calibration

7.1 The gas chromatographic system must be calibrated using the external standard technique for all columns used for quantitation.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations found in real samples, or should define the working range of the detector. This should be done on each quantitation column and each instrument used for this analysis.

7.2.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound.

8. GC-EC Primary Analysis (Quantitation may be performed on primary or confirmation analyses.)

8.1 Adjust oven temperature and carrier gas flow rates so that the retention time for 4,4'-DDT is equal to or greater than 12 minutes.

8.2 Table 3 provides examples of operating conditions for the gas chromatograph. Separation should be greater than or equal to 25% resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion can not be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

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8.2.1 Inject 2 to 5 µL of the sample or standard extract using the solvent-flush technique or auto sampler. Smaller (1.0 µL) volumes can be injected only if automatic devices are employed. Record the volume injected and the total extract volume.

8.2.2 Inject Individual Standard Mixes A and B and all multi-response pesticides/PCBs at the beginning of each 72-hour sequence. (See Paragraph 8.2.8.6). To establish the retention time window within each 72-hour sequence for the pesticide/PCB of interest, use the absolute retention time from the above chromatograms as the mid-point, and plus or minus three times the standard deviation as described earlier in Part 4 of the Quality Assurance Section. Individual Standard Mixes A and B are analyzed alternately and intermittently throughout the analysis. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis.

8.2.3 Sample analysis of extracts can begin when linearity and degradation QA/QC requirements specified in the Quality Assurance Section are met.

8.2.4 NOTE: The 10.0% RSD linearity criterion is <u>only</u> required on the column(s) being used for pesticide/PCB quantitation. If a column is used for surrogate quantitation only, the 10.0% RSD is required only for DBC.

8.2.5 Analyze samples in groups of no more than five samples. After the analysis of the first group of up to five samples, analyze Evaluation Mix B. Analyze another group of up to five samples, followed by the analysis of Individual Mix A or B. Subsequent groups of up to five samples may be analyzed by repeating this sequence, alternately analyzing Evaluation Mix B and Individual Mix A or B between the groups as shown in Paragraph 8.2.8.6. The Pesticide/PCB analytical sequence <u>must</u> end with Individual Mix A <u>and</u> B regardless of the number of samples analyzed.

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8.2.6 If a multiresponse pesticide/PCB is detected in either of the preceding groups of five samples, the appropriate multiresponse pesticide/PCB may be substituted for Individual Mix A or B. All standards listed in Paragraph 8.2.8.6 must be included for every sample set and must be analyzed within the same 72-hour period as those samples. If the samples are split between two or more instruments, the complete set of standards must be analyzed on each instrument with the same 72-hour requirement. All standards must be analyzed before the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

8.2.7 Paragraphs 8.2.8.1 and 8.2.8.5 contain GC performance criteria. If it is determined during the course of a 72-hour sequence that one or more of the criteria have been violated, stop the run and take corrective action. After the corrective action has been taken, the 72-hour sequence may be restarted as follows: If a standard violated the criterion, restart the sequence with that standard, determine that the criteria have been met, and continue with sample analyses according to Paragraph 8.2.8.6. If a sample violated the criterion, restart the sequence with the standard that would have <u>followed</u> that group of samples (thereby preserving the sequence of standards in Paragraph 8.2.8.6), determine that the criteria have been met, and continue with sample analyses according to Paragraph 8.2.8.6.

8.2.8 If it is determined <u>after</u> the completion of a 72-hour sequence that one or more of the criteria have been violated, proceed as follows: If a standard violated the criterion, all samples analyzed after that standard must be reanalyzed as part of a new 72-hour sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that <u>did</u> <u>not</u> meet the criterion and the standard that <u>did</u> meet the criterion must be reanalyzed as part of a new 72-hour sequence. If only samples violated the criteria, then those samples must be reanalyzed as part of a new 72-hour sequence.

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8.2.8.1. Differences in the calibration factors for each standard in Individual Standard Mixes A and B must not exceed 20.0% (15.0% for any standard compound used for quantitation) during the 72-hour primary analysis. Calculate the difference using the initial individual standard mix versus all subsequent individual standard mixes analyzed during the 72-hour sequence.

8.2.8.2 The retention time shift of DBC in any standard or sample must be less than 2.0% difference for packed columns, less than 1.5% difference for wide-bore capillary columns (i.d. greater than 0.32 mm), and less than 0.3% difference for narrow-bore capillary columns (i.d. less than 0.32 mm).

8.2.8.3 Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20.0% respectively on the intermittent analysis of Evaluation Standard Mix B.

8.2.8.4 All pesticide standards must fall within the established 72-hour retention time windows.

8.2.8.5 Highly colored extracts may require a dilution.

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8.2.8.6 The 72-hour sequence must be as follows.

72-Hour Sequence for Pesticide/PCB Analysis:

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A
5. Individual Standard Mix B
6. Toxaphene
7. Technical Chlordane
8. Aroclors 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. Five samples
15. Evaluation Standard Mix B
16. Five samples
17. Individual Standard Mix A or B
18. Five samples
19. Evaluation Standard Mix B
20. Five samples
21. Individual Standard Mix A or B (whichever not run in Step 16)
22. Five samples
23. Repeat the above sequence starting with Evaluation Standard Mix B (Step 14 above).
24. Pesticide/PCB analysis sequence must end with Individual Standard Mix A and B regardless of number of samples analyzed.

8.3 Evaluation of Chromatograms.

8.3.1 Consider the sample as negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample is complete at this point. Confirmation is not required.

8.3.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

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8.3.3 Determine if any target pesticides/PCBs are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.

8.3.3.1 If the response for any of these compounds is 100% or less of full scale, the extract is ready for confirmation and quantitation.

8.3.3.2 If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50% and 100% full scale and reanalyze. Also use this dilution for confirmation and quantitation.

8.3.3.3 For dilution greater than 10 fold. Also inject an aliquot of a dilution 10-fold more concentrated to determine if other compounds of interest are present at lower concentrations.

8.3.3.4 Computer reproductions of chromatograms manipulated to ensure all peaks are on scale over a 100-fold range are an accepted substitute. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100-fold range using higher concentrations of the evaluation mixture.

8.3.4 Quantitation may be performed on the primary analysis, with the exception of toxaphene and possibly the DDT series. If DDT exceeds the 10.0% RSD linearity criterion, then quantitations for any DDE, DDD, and DDT in a sample must be on the confirmation analysis. Toxaphene must always be quantitated on the confirmation analysis. See Quality Assurance Section for special QC requirements for quantitations.

8.3.5 If identification of compounds of interest are prevented by the presence of interferences, further cleanup may be required.

8.3.6 When selecting a GC column for confirmation and/or quantitation, be sure that none of the compounds to be confirmed/quantitated overlap, e.g., do not select the 3% OV-1 column if DDE and dieldrin are to be confirmed and/or quantitated.

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9. GC/EC Confirmation Analysis

9.1 Confirmation analysis confirms the presence of all compounds tentatively identified in the primary analysis.

Therefore, the only standards that are required are the evaluation standard mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence in Paragraph 8.2.8.6 is therefore modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in Step 9.5.1.

9.2 Table 3 provides examples of operating conditions for the gas chromatograph. Separation should be greater than or equal to 25% resoluton between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

9.3 For a fused silica capillary column confirmation, there must be greater than or equal to 25% resolution (valley) between the following pesticide pairs:

- Beta-BHC and delta-BHC
- Deildrin and 4,4'-DDT
- 4,4'-DDD and endrin aldehyde
- Endosulfan sulfate and 4,4'-DDT

9.4 All QC requirements specified earlier in the Quality Assurance Section must be adhered to, i.e., the greater than or equal to 12-minute retention time for 4,4'-DDT, the criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for DBC. The retention time criterion for 4,4'-DDT does <u>not</u> have to be met if the confirmation column is OV-1.

9.5 Inject 2 to 5 µL (1 to 2 µL for capillary columns) of the sample extract and standards using the solvent-flush technique or auto samples.

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One-microliter volumes can be injected only if automatic devices are employed. Record the volume injected and the total extract volume. The detector attenuation must provide peak response equivalent to the primary analysis response for each compound to be confirmed.

9.5.1 Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B, and C. The exception to this occurs when toxaphene and/or the DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur; therefore, the following sequences must be followed depending on the situation.

9.5.1.1 Toxaphene only - Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating %RSD.

9.5.1.2 If less than or equal to 10.0% RSD, use the appropriate equation in Paragraph 8 for calculation. If greater than 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

9.5.1.3 DDT, DDE, DDD only - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD, and DDT. Calculate linearity and follow the requirements specified in Paragraph 9.5.1.1 for each compound to be quantitated.

9.5.1.4 DDT series and toxaphene - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in Paragraph 9.5.1.1 for each compound to be quantitated.

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9.5.1.5 Other pesticides/PCBs plus DDT series and/or toxaphene - Begin the sequence with Evaluation Standard Mixes A, B, and C. Calculate linearity on the four compounds in the Evaluation Standard mixes. If DDT and/or one or more of the other compounds are greater than 10.0% RSD and/or degradation exceeds the criterion, corrective maintenance should be performed before repeating the above chromatography evaluations. If only DDT exceeds the linearity criterion and one or more of the DDT series is to be quantitated, follow Paragraph 9.5.1.3 (do not repeat Evaluation Mix B).

9.5.1.6 If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the %RSD on the proper form. Any time toxaphene is to be quantitated, follow Paragraph 9.5.1.1.

9.5.2 After the linearity standards are injected, continue the confirmation analysis sequence by injecting standards for all compounds tentatively identified in the primary analysis, to establish the 72-hour retention time windows. Analyze all confirmation standards for a case at the beginning, at intervals specified in Step 9.5.3., and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The analyst must reanalyze all samples which follow the standard that exceeds the criterion.

9.5.3 After injection of the appropriate standards as described in the proceeding paragraph, begin injection of samples. Analyze groups of five samples. Analyze Evaluation Mix B after the first group of five samples. After the second group of five samples, analyze a standard pertaining to the samples in the preceeding groups (i.e., standard mix containing those compounds requiring confirmation). Continue analyzing groups of five samples, alternately preceding samples between groups of five samples.

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The alternating standard's calibration factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the analyst to repeat the analyses of samples which were analyzed after the standard that exceeds the criterion. The 15.0% criterion only pertains to compounds being quantitated.

9.5.4 If more than one standard is required to confirm all compounds tentatively identified in the primary analysis, alternate the standards with Evaluation Standard Mix B. Samples must also be repeated if the degradation of either DDT and/or endrin exceeds 20.0% on the intermittent Evaluation Standard Mix B.

If the samples are split between two or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

9.5.5 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

9.6 Evaluation of Chromatograms

9.6.1 A compound tentatively identified in the primary analysis is confirmed in the retention time from the confirmation analysis falls within the retention time window of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

9.6.2 Quantitation should be performed on the column (primary or confirmation) that provides the best separation from interfering peaks. Note: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit is a form of quantitation.

9.6.2.1 Quantitation of Chlordane. Because weathering and/or different formulations of chlordane usually modify the pattern exhibited by technical chlordane, this method is not appropriate for determining technical chlordane. Instead, standards for alpha chlordane and gamma chlordane are used for quantitation, and each isomer of chlordane is reported separately.

9.6.3 Computer reproduction of chromatograms that are attenuated to ensure that all peaks are on scale over a 100-fold range are acceptable. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Also, peak response must be greater than 25% of full scale deflection to allow visual pattern recognition of multicomponent compounds, and individual compounds must be visible.

9.6.4 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident, go to Step 6 (Optional Sulfur Cleanup).

9.6.5 If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup is applied.

9.6.6 Calculate surrogate standard recovery on all samples, blanks, and spikes unless the surrogate was diluted out. Determine if recovery is within limits and report.

9.6.7 If target pesticide/PCB compounds were identified in the unspiked sample from which the matrix spike and matrix spike duplicate were prepared, confirmation analysis is required for the matrix spike and matrix spike duplicate. If target pesticide/PCB compounds were not identified in the unspiked sample, confirmation of the matrix spike and matrix spike duplicate is not required.

10. Calculations

10.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

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10.1.1 Water

Concentration (µg/L) $= \frac{(A_x)\ (I_s)\ (V_t)}{(A_s)\ (V_i)\ (V_s)}$

Where:

$A_x$ = Response for the parameter to be measured
$A_s$ = Response for the external standard
$V_t$ = Volume of total extract (µL) (take into account any dilutions)
$I_s$ = Amount of standard injected in nanograms (ng)
$V_i$ = Volume of extract injected (µL)
$V_s$ = Volume of water extracted (mL)

10.2 For multicomponent mixtures (chlordane, toxaphene, and PCB) match retention times of peaks in the standard with peaks in the sample. Quantitate every identifiable peak (greater than 50% of the total area must be used) unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

10.3 Calculation of surrogate and matrix spike recoveries.

Percent recovery $= \frac{Qd}{Qa} \times 100\%$

Where:

Qd = Quantity determined by analysis
Qa = Quantity added to sample

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Table 1

Method Detection Limits

| Compound | Method Detection Limit (µg/L) |
|---|---|
| Aldrin | 0.005 |
| alpha-BHC | 0.002 |
| beta-BHC | 0.003 |
| gamma-BCH (lindane) | 0.005 |
| delta-BHC | 0.002 |
| alpha-chlordane | 0.003 |
| gamma-chlordane | 0.009 |
| Technical chlordane | 0.05* |
| 4,4'-DDD | 0.005 |
| 4,4'-DDE | 0.005 |
| 4,4'-DDT | 0.010 |
| Dieldrin | 0.011 |
| Endosulfan I | 0.004 |
| Endosulfan II | 0.012 |
| Endosulfan sulfate | 0.006 |
| Endrin | 0.007 |
| Endrin aldehyde | 0.012 |
| Endrin ketone | 0.005 |
| Heptachlor | 0.006 |
| Heptachlor epoxide | 0.005 |
| Methoxychlor | 0.060 |
| Toxaphene | 0.10* |
| PCB-1016 | 0.04 |
| PCB-1221 | 0.05* |
| PCB-1232 | 0.05* |
| PCB-1242 | 0.05* |
| PCB-1248 | 0.05* |
| PCB-1254 | 0.05* |
| PCB-1260 | 0.03 |

* Detection limits estimated

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Table 2

Precision and Accuracy Data
Pesticide/PCB Screen

| Compound | Spike Level (µg/L) | Average Recovery (µg/L) | Average Recovery (%) | Standard Deviation (µg/L) |
|---|---|---|---|---|
| Aldrin | 0.0125 | 0.00858 | 69 | 0.00159 |
| alpha-BHC | 0.0125 | 0.0105 | 84 | 0.000706 |
| beta-BHC | 0.0125 | 0.0102 | 82 | 0.000837 |
| gamma-BCH (lindane) | 0.0125 | 0.00955 | 76 | 0.00152 |
| delta-BHC | 0.0125 | 0.0106 | 85 | 0.000561 |
| alpha-chlordane | 0.0125 | 0.0116 | 93 | 0.000866 |
| gamma-chlordane | 0.0125 | 0.0130 | 104 | 0.00298 |
| Technical chlordane | ND | - | - | - |
| 4,4'-DDD | 0.025 | 0.0228 | 91 | 0.00157 |
| 4,4'-DDE | 0.025 | 0.0220 | 88 | 0.00168 |
| 4,4'-DDT | 0.025 | 0.0209 | 84 | 0.00350 |
| Dieldrin | 0.025 | 0.0187 | 75 | 0.00809 |
| Endosulfan I | 0.0125 | 0.0104 | 83 | 0.00129 |
| Endosulfan II | 0.025 | 0.0204 | 81 | 0.00382 |
| Endosulfan sulfate | 0.025 | 0.0212 | 85 | 0.00181 |
| Endrin | 0.025 | 0.0206 | 82 | 0.00245 |
| Endrin aldehyde | 0.025 | 0.0180 | 72 | 0.00370 |
| Endrin ketone | 0.025 | 0.0229 | 92 | 0.00143 |
| Heptachlor | 0.0125 | 0.00930 | 74 | 0.00188 |
| Heptachlor epoxide | 0.0125 | 0.0106 | 85 | 0.00164 |
| Methoxychlor | 0.125 | 0.118 | 94 | 0.0189 |
| Toxaphene | ND | - | - | - |
| PCB-1016 | 0.050 | 0.0675 | 135 | 0.0101 |
| PCB-1221 | ND | - | - | - |
| PCB-1232 | ND | - | - | - |
| PCB-1242 | ND | - | - | - |
| PCB-1248 | ND | - | - | - |
| PCB-1254 | ND | - | - | - |
| PCB-1260 | 0.050 | 0.0626 | 125 | 0.0229 |

ND Not determined.

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Table 3.0

Recommended GC Operating Conditions

Column 1: COLUMN: 6 ft x 4 mm i.d., 1.5% SP-2250/1.95% SP-2401 on 100/120 Suplecoport
TEMP OF: INJ 200°C, COL 210°C, DET 300°C
$Ar/CH_4$: 95/5 FLOW RATE 60 mL/minute
RECORDER: 1 mV full scale; 0.5 cm/minute

Column 2: COLUMN: 6 ft x 4 mm i.d., 3% OV-1% on 80/100 GAS CHROM Q
TEMP OF: INJ 200°C, COL 210°C, DET 300°C
$Ar/CH_4$: 95/5 FLOW RATE 60 mL/minute
RECORDER: 1 mV full scale; 15 in/hour

Column 3: COLUMN: 30 m x 0.53 mm i.d., DB 608 FSOT Megabore
TEMP OF: INJ 150°C, DET 300°C
PROGRAM: INITIAL TEMP 150°C, Hold 0 minutes, RATE 8°C/minute; FINAL TEMP 250°C, HOLD 16 minutes
CARRIER GAS: Helium at 6 mL/minute
MAKE-UP GAS: Nitrogen at 30 mL/minute
RECORDER: 1mV full scale; 10 mm/minute

Column 4: COLUMN: 30 m x 0.53 mm i.d., DB 5 Megabore
TEMP OF: INJ 150°C, DET 300°C
PROGRAM: INITIAL TEMP 150°C
RATE 8°C/minute; FINAL TEMP 250°C, HOLD 16 minutes
CARRIER GAS: Helium at 6.5 mL/minute
MAKE-UP GAS: Nitrogen at 30 mL/minute
RECORDER: 1mV full scale; 10 mm/minute

# DRAFT

ASSAY TITLE: Low Level Semivolatile Analysis of Water Samples by Gas Chromatography/Mass Spectroscopy

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc. Environmental Analysis

SCOPE:

This method covers the determination of the priority pollutant and Target Compound List (TCL) semivolatile organics in drinking water sources using gas chromatography/mass spectrometry (GCMS). The compounds determined by this method are reported with detection limits lower than those generated by the standard GCMS semivolatile screen. The standard list of compounds calibrated and analyzed for are presented in Table 10 as an attachment.

PRINCIPLE:

A 1-L sample is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2, using a separatory funnel or continuous extraction technique. The methylene chloride extracts are dried and concentrated separately and stored at 4°C until instrumental analysis. Just prior to analysis the two extracts (>pH 11 and <pH 2) are combined and reduced to a final volume of 0.5 mL. The extract is separated by gas chromatography and the analytes of interest are measured by a mass spectrometer detector in the electron impact mode.

SENSITIVITY, PRECISION, ACCURACY:

The method detection limits presented in Table 10 represent the sensitivities that can be achieved in ground water in the absence of interferences.

Precision and accuracy for this method, as generated from an inhouse validation study, is presented in Table 10.

REFERENCES:

1. Environmental Protection Agency (EPA) Method 625 (Federal Register 49 (209): 43385-43406, October 16, 1984).

2. Environmental Protection Agency (EPA) Contract Laboratory Program, Statement of Work for "Organic Analysis Multi-Media Multi-Concentration", October 1986. Revisions: January 1987; February 1987; July 1987; August 1987. Exhibits: B, D, E.

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SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

The following parameters 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, and N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

INTERFERENCES:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, that lead to discrete artifacts or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

QUALITY ASSURANCE:

This section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of semivolatile organic TCL compounds in water. The QC operations are as follows:

1. Documentation of GC/MS mass calibration and abundance pattern
2. Documentation of GC/MS response factor stability
3. Internal standard response and retention time monitoring
4. Method blank analysis
5. Surrogate spike response monitoring
6. Matrix spike and matrix spike duplicate analysis

<u>Tuning and GC/MS Mass Calibration</u>

1. It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria before initiating any on-going data collection. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP).

1.1 Decafluorotriphenylphosphine (DFTPP)

1.1.1 Each GC/MS system used for the analysis of semivolatile compounds must be hardware-tuned to meet the abundance criteria listed in Table 1 for a 50-ng injection of DFTPP. DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each 12-hour period, whichever is more frequent, before samples can be analyzed. DFTPP must be injected to meet this criterion.

1.1.2 Whenever corrective action is taken that may change or affect the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-hour tuning requirements.

Table 1. DFTPP Key Ions and Ion Abundance Criteria

| Mass | Ion Abundance Criteria |
|---|---|
| 51 | 30.0 - 60.0% of mass 198 |
| 68 | Less than 2.0% of mass 69 |
| 70 | Less than 2.0% of mass 69 |
| 127 | 40.0 - 60.0% of mass 198 |
| 197 | Less than 1.0% of mass 198 |
| 198 | Base peak, 100% relative abundance |
| 199 | 5.0 - 9.0% of mass 198 |
| 275 | 10.0 - 30.0% of mass 198 |
| 365 | Greater than 1.00% of mass 198 |
| 441 | Present but less than mass 443 |
| 442 | Greater than 40.0% of mass 198 |
| 443 | 17.0 - 23.0% of mass 442 |

Calibration of the GC/MS System

2. Before the analysis of samples and required blanks, and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of three concentrations to determine the linearity of response utilizing TCL compound standards. Once the system has been calibrated, the calibration must be verified each 12-hour time period for each GC/MS system.

2.1 Prepare calibration standards to yield the following specific concentrations.

2.1.1 Semivolatile TCL Compounds

Initial calibration of semivolatile TCL compounds is required at 20, 50, and 100 total nanograms.

2.2 Analyze each calibration standard and tabulate the area of the primary characteristic ion (Tables 2 and 3) against concentration for each compound including all required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late eluting compounds usually will have much better agreement.

Using Table 4, calculate the RRF for each compound at each concentration level using Equation 1.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Equation 1}$$

Where:

$A_x$ = Area of the characteristic ion for the compound to be measured.

$A_{is}$ = Area of the characteristic ion for the specific internal standards from Tables 2 or 3.

$C_{is}$ = Concentration of the internal standard (ng/µL).

$C^x$ = Concentration of the compound to be measured (ng/µL).

2.2.1 Using the relative response factors (RRF) from the initial calibration, calculate the %RSD for compounds labeled as Calibration Check Compounds and shown in Table 4 using Equation 2.

$$\%RSD = \frac{SD}{x} \times 100 \qquad \text{Equation 2}$$

Where:

RSD = Relative Standard Deviation

SD = Standard Deviation of initial response factors (per compound)

Where: $$SD = \sum_{i=1}^{N} \frac{(X_i - \bar{x})^2}{N-1}$$

$\bar{x}$ = Mean of initial relative response factors (per compound)

The %RSD for each individual Calibration Check Compound (see Table 5) must be less than or equal to 30.0%. This criteria must be met for the initial calibration to be valid.

2.3 A system performance check must be performed to ensure that minimum average RRF are met before the calibration curve is used.

2.3.1 For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-Nitroso-Di-n-Propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, and 4-Nitrophenol. The minimum acceptable average RRF for these compounds is 0.050. SPCCs typically have very low RRFs (0.1 - 0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. These compounds are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

2.3.2 The initial calibration is valid only after both the %RSD for CCC compounds and the minimum RRF for SPCC have been met. Only after both these criteria are met can sample analysis begin.

## Table 2

### Characteristic Ions for Semivolatile TCL Compounds

| Parameter | Primary Ion | Secondary Ion(s) |
|---|---|---|
| Phenol | 94 | 65, 66 |
| bis(-2-Chloroethyl)Ether | 93 | 63, 95 |
| 2-Chlorophenol | 128 | 64, 130 |
| 1,3-Dichlorobenzene | 146 | 148, 113 |
| 1,4-Dichlorobenzene | 146 | 148, 113 |
| Benzyl alcohol | 108 | 79, 77 |
| 1,2-Dichlorobenzene | 146 | 148, 113 |
| 2-Methylphenol | 108 | 107 |
| bis(-2-Chloroisopropyl)Ether | 45 | 77, 79 |
| 4-Methylphenol | 108 | 107 |
| N-Nitroso-di-propylamine | 70 | 42, 101, 130 |
| Hexachloroethane | 117 | 201, 199 |
| Nitrobenzene | 77 | 123,65 |
| Isophorone | 82 | 95, 138 |
| 2-Nitrophenol | 139 | 65, 109 |
| 2,4-Dimethylphenol | 107 | 121, 122 |
| Benzoic acid | 122 | 105,77 |
| bis(-2-Chloroethoxy)Methane | 93 | 95, 123 |
| 2,4-Dichlorophenol | 162 | 164, 98 |
| 1,2,4-Trichlorobenzene | 180 | 182, 145 |
| Naphthalene | 128 | 129, 127 |
| 4-Chloroaniline | 127 | 129 |
| Hexachlorobutadiene | 225 | 223, 227 |
| 4-Chloro-3-Methylphenol | 107 | 144, 142 |
| 2-Methylnaphthalene | 142 | 141 |
| Hexachlorocyclopentadiene | 237 | 235, 272 |
| 2,4,6-Trichlorophenol | 196 | 198, 200 |
| 2,4,5-Trichlorophenol | 196 | 198, 200 |
| 2-Chloronaphthalene | 162 | 164, 127 |
| 2-Nitroaniline | 65 | 92, 138 |
| Dimethyl phthalate | 163 | 194, 164 |
| Acenaphthylene | 152 | 151, 153 |
| 3-Nitroaniline | 138 | 108, 92 |
| Acenaphthene | 153 | 152, 154 |
| 2,4-Dinitrophenol | 184 | 63, 154 |
| 4-Nitrophenol | 109 | 139, 65 |
| Dibenzofuran | 168 | 139 |
| 2,4-Dinitrotoluene | 165 | 63, 182 |
| 2,6-Dinitrotoluene | 165 | 89, 121 |
| Diethylphthalate | 149 | 177, 150 |
| 4-Chlorophenyl-phenylether | 204 | 206, 141 |

Table 2 (Continued)

Characteristic Ions for Semivolatile TCL Compounds

| Parameter | Primary Ion | Secondary Ion(s) |
|---|---|---|
| Fluorene | 166 | 165, 167 |
| 4-Nitroaniline | 138 | 92, 108 |
| 4,6-Dinitro-2-Methylphenol | 198 | 182, 77 |
| N-Nitrosodiphenylamine | 169 | 168, 167 |
| 4-Bromophenyl-phenylether | 248 | 250, 141 |
| Hexachlorobenzene | 284 | 142, 249 |
| Pentachlorophenol | 266 | 264, 268 |
| Phenanthrene | 178 | 179, 176 |
| Anthracene | 178 | 179, 176 |
| Di-N-Butylphthalate | 149 | 150, 104 |
| Fluoranthene | 202 | 101, 100 |
| Pyrene | 202 | 101, 100 |
| Butylbenzylphthalate | 149 | 91, 206 |
| 3,3'-Dichlorobenzidine | 252 | 254, 126 |
| Benzo(a)Anthracene | 228 | 229, 226 |
| bis(2-Ethylhexyl)Phthalate | 149 | 167, 279 |
| Chrysene | 228 | 226, 229 |
| Di-N-Octyl phthalate | 149 | - |
| Benzo(b)Fluoranthene | 252 | 253, 125 |
| Benzo(k)Fluoranthene | 252 | 253, 125 |
| Benzo(a)Pyrene | 252 | 253, 125 |
| Indeno(1,2,3-cd)Pyrene | 276 | 138, 227 |
| Dibenz(a, h)Anthracene | 278 | 139, 279 |
| Benzo(g, h, i) Perylene | 276 | 138, 277 |

Table 3

Characteristic Ions for Surrogates and
Internal Standards for Semivolatile Compounds

| | Primary Ion | Secondary Ion(s) |
|---|---|---|
| **Surrogates** | | |
| Phenol-$d_5$ | 99 | 42, 71 |
| 2-Fluorophenol | 112 | 64 |
| 2,4,6-Tribromophenol | 330 | 332, 141 |
| d-5 Nitrobenzene | 82 | 128, 54 |
| 2-Fluorobiphenyl | 172 | 171 |
| Terphenyl | 244 | 122, 212 |
| **Internal Standards** | | |
| 1,4-Dichlorobenzene-$d_4$ | 152 | 115 |
| Naphthalene-$d_8$ | 136 | 68 |
| Acenaphthene-$d_{10}$ | 164 | 162, 160 |
| Phenanthrene-$d_{10}$ | 188 | 94, 80 |
| Chrysene-$d_{10}$ | 240 | 120, 236 |
| Perylene-$d_{12}$ | 264 | 260, 265 |

Table 4

Semivolatile Internal Standards with Corresponding TCL Analytes Assigned for Quantitation

| 1,4-Dichlorobenzene-d | Naphthalene-d | Acenaphthene-d | Phenanthrene-d | Chrysene-d | Perylene-d |
|---|---|---|---|---|---|
| Phenol | Nitrobenzene | Hexachlorocyclo-pentadiene | 4,6-Dinitro-2-methylphenol | Pyrene | Di-n-octyl phthalate |
| bis(2-chloroethyl) ether | Isophorone | 2,4,6-Trichloro-phenol | N-nitrosodi-phenylamine | Butylbenzyl phthalate | Benzo(b)fluor-anthene |
| 2-Chlorophenol | 2-Nitrophenol | 2,4,5-Trichloro-phenol | 1,2-Diphenylhy-drazine | 3,3'Dichloro-benzidine | Benzo(k)fluor-anthene |
| 1,3-Dichlorobenzene | 2,4-Dimethyl-phenol | 2-Chloronaphthalene | 4-Bromophenyl phenyl ether | Benzo(a)-anthracene | Benzo(a)pyrene |
| 1,4-Dichlorobenzene | Benzoic acid | 2-Nitroaniline | Hexachloro-benzene | bis(2-ethyl-hexyl)phthalate | Indeno(1,2,3-c pyrene |
| Benzyl alcohol | bis(2-Chloro-ethoxy)methane | Dimethyl phthalate | Pentachloro-phenol | Chrysene | Dibenz(a, h) anthracene |
| 1,2-Dichlorobenzene | 2,4-Dichloro-phenol | Acenaphthylene | Phenanthrene | Terphenyl-$d_{14}$ (surr) | Benzo(g,h,i) perylene |
| 2-Methylphenol | 1,2,4-Trichloro-benzene | 3-Nitroaniline | Anthracene | | |
| bis(2-Chloroiso-propyl)ether | Naphthalene | Acenaphthene | Di-n-butyl phthalate | | |
| 4-Methylphenol | 4-Chloroaniline | 2,4-Dinitrophenol | Fluoranthene | | |
| N-nitroso-Di-n-propylamine | Hexachloro-butadiene | 4-Nitrophenol | | | |
| Hexachloroethane | 4-Chloro-3-methylphenol | Dibenzofuran | | | |
| 2-Fluorophenol (surr) | 2-Methylnaphth-alene | 2,4-Dinitrotoluene | | | |
| Phenol-$d_6$ (surr) | Nitrobenzene-$d_5$ (surr) | 2,6-Dinitrotoluene | | | |
| | | Diethyl phthalate | | | |
| | | 4-Chlorophenyl-phenyl ether | | | |
| | | Fluorene | | | |
| | | 4-Nitroaniline | | | |
| | | 2-Fluorobiphenyl (surr) | | | |
| | | 2,4,6-Tribromo phenol | | | |

## 2.4 Continuing Calibration

A calibration standard(s) containing all semivolatile TCL compounds, including all required surrogates, must be analyzed each 12 hours during analysis. Compare the RRF data from the standards each 12 hours with the average RRF from the initial calibration for a specific instrument. A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum RRFs are not met, the system must be evaluated and corrective action must be taken before sample analysis begins.

2.4.1 Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the from end of the analytical column, and active sites in the column or chromatography system. This check must be met before analysis begins. The minimum RRF for semivolatile SPCC is 0.050.

2.4.2 Calibration Check Compounds (CCC)

After the system performance check is met, CCCs listed in Table 5 are used to check the validity of the initial calibration. Calculate the percent difference using Equation 2.3.

$$\% \text{ Difference} = \frac{RRF_I - RRF_C}{RRF_I} \qquad \text{Equation 3}$$

Where:

$RRF_I$ = Average response factor from initial calibration

$RRF_C$ = Response factor from current verification check standard.

2.4.2.1 If the percent difference for any compound is greater than 20%, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than or equal to 30%, the initial calibration is assumed to be valid. If the criteria are not met (>30% difference), for any one calibration check compound, corrective action <u>MUST</u> be taken.

Table 5 Calibration Check Compounds

| Base/Neutral Fraction | Acid Fraction |
|---|---|
| Acenaphthene | 4-Chloro-3-Methylphenol |
| 1,4-Dichlorobenzene | 2,4-Dichlorophenol |
| Hexachlorobutadiene | 2-Nitrophenol |
| N-Nitroso-di-n-phenylamine | Phenol |
| Di-n-octylphthalate | Pentachlorophenol |
| Fluoranthene | 2,4,6-Trichlorophenol |
| Benzo(a)pyrene | |

Continuing calibration: 20 ng except for the following: Benzoic acid, 2,4-Dinitrophenol, 2,4,5-trichlorophenol, all three nitroaniline isomers, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, and pentachlorophenol which are to be injected at 50 ng.

2.5 Documentation

Calculate and report the RRF and percent difference (%D) for all compounds. Ensure that the minimum RRF for semivolatile SPCCs is 0.050. The %D for each CCC compound must be less than or equal to 30.0%.

3. Internal Standard Evaluation

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

Method Blank Analysis

4. A method blank is a volume of deionized, distilled laboratory water, carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes or sample weights being processed.

4.1 A method blank is performed with every 20 samples processed and/or whenever samples are extracted, whichever is most frequent.

Surrogate Spike (SS) Analysis

5. Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

5.1 Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds before extraction. The surrogate spiking compounds shown in Table 6 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Table 6 Surrogate Spiking Compounds

| Compounds | Amount in Sample | |
|---|---|---|
| | Fraction | Water (ug) |
| Nitrobenzene-$d_5$ | BNA | 25 |
| 2-Fluorobiphenyl | BNA | 25 |
| p-Terphenyl-$d_{14}$ | BNA | 25 |
| Phenol-$d_5$ | BNA | 50 |
| 2-Fluorophenol | BNA | 50 |
| 2,4,6-Tribromophenol | BNA | 50 |

5.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the recovery limits listed in Table 7.

Table 7 Required Surrogate Spike Recovery Limits

| Fraction | Surrogate Compound | Water |
|---|---|---|
| BNA | Nitrobenzene-$d_5$ | 35-114 |
| BNA | 2-Fluorobiphenyl | 43-116 |
| BNA | p-Terphenyl-$d_{14}$ | 33-141 |
| BNA | Phenol-$d_5$ | 10-94 |
| BNA | 2-Fluorophenol | 21-100 |
| BNA | 2,4,6-Tribromophenol | 10-123 |

5.3 The analyst must take the actions listed below if either of the following conditions exists:

- o Recovery of any one surrogate compound in <u>either</u> base neutral or acid fraction is below 10%.
- o Recoveries of two surrogate compounds in <u>either</u> base neutral or acid fractions are outside surrogate spike recovery limits.

5.3.1 The analyst shall document (in this instance, document means to write down and discuss the problem and corrective action taken in the Case Narrative) deviations outside of acceptable quality control limits and take the following actions:

5.3.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc., also check instrument performance.

5.3.1.2 If the steps in 5.3.1.1 fail to reveal a problem, then reanalyze the extract. If reanalysis of the extract solves the problem, then the problem was within the analyst's control. Therefore, <u>only</u> <u>submit</u> data from the analysis with surrogate spike recoveries <u>within</u> the control windows. This shall be considered the <u>initial</u> analysis and shall be reported as such on all data deliverables.

5.3.1.3 If the steps in 5.3.1.2 fail to solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis solves the problem, then the problem was in the analyst's control. Therefore, <u>only</u> <u>submit</u> data from the extraction and analysis with surrogate spike recoveries <u>within</u> the control windows. This shall be considered the <u>initial</u> analysis and shall be reported as such on all data deliverables.

5.3.1.4 If the reextraction and reanalysis of the sample does not solve the problem, i.e., surrogate recoveries are outside the control windows for both analyses, then submit the surrogate spike recovery data and the sample data from <u>both</u> analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables.

5.4 Documentation

The laboratory shall report surrogate recovery data for the following:

- o Method blank analysis
- o Sample analysis
- o Matrix spike/matrix spike duplicate analysis
- o All sample reanalyses that substantiate a matrix effect

## Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

6.1 MS/MSD Frequency of Analysis

A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, once:

- o Each case of field samples received, OR
- o Each 20 field samples in a case, OR

whichever is most frequent.

6.2 Use the compounds listed in Table 8 to prepare matrix spiking solutions. Optional dilution steps must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

Table 8 Matrix Spiking Solutions

| Base/Neutrals | Spike Amount (µg) | Acids | Spike Amount (µg) |
|---|---|---|---|
| 1,2,4-Trichlorobenzene | 25 | Pentachlorophenol | 50 |
| Acenaphthene | 25 | Phenol | 50 |
| 2,4-Dinitrotoluene | 25 | 2-Chlorophenol | 50 |
| Pyrene | 25 | 4-Chloro-3-Methyl-phenol | 50 |
| 1,4-Dichlorobenzene | 25 | 4-Nitrophenol | 50 |

6.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

6.3 Individual component recoveries of the matrix spike are calculated using Equation 4

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Equation 4}$$

Where:

SSR = Spike sample results.
SR = Sample result.
SA = Spike added from spiking mix.

6.4 Relative Percent Difference (RPD)

The analyst is required to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using Equation 5.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad \text{Equation 5}$$

Where:

RPD = Relative percent difference
$D_1$ = First sample value
$D_2$ = Second sample value (duplicate)

6.5 The matrix spike (MS) results (concentrations) for nonspiked semivolatile TCL compounds shall be reported and the matrix spike percent recoveries shall be summarized (Table 9).

Table 9 Matrix Spike Recovery Limits

| Fraction | Matrix Spike Compound | Water |
|---|---|---|
| BN | 1,2,4-Trichlorobenzene | 39-98 |
| BN | Acenaphthene | 46-118 |
| BN | 2,4-Dinitrotoluene | 24-96 |
| BN | Pyrene | 26-127 |
| BN | N-Nitroso-Di-n-Propylamine | 41-116 |
| BN | 1,4-Dichlorobenzene | 36-97 |
| Acid | Pentachlorophenol | 9-103 |
| Acid | Phenol | 12-89 |
| Acid | 2-Chlorophenol | 27-123 |
| Acid | 4-Chloro-3-Methylphenol | 23-97 |
| Acid | 4-Nitrophenol | 10-80 |

APPARATUS:

- Separatory funnel - 2,000 mL, with Teflon® stopcock.
- Drying column - 19 mm ID chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)
- Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-570001 0500 or equivalent). Attach to concentrator tube with springs.
- Snyder column - Kuderna-Danish, three-ball macro (Kontes K503000 0121 or equivalent).
- Snyder column - Kuderna-Danish, two-ball micro (Kontes K569001 0219 or equivalent).
- Vials - amber glass, 2 mL capacity with Teflon-lined screw-cap.
- Continuous liquid-liquid extractors - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ, P/N 6841-10 or equivalent).
- Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- Water bath - heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.
- 3.4 Balance - analytical, capable of accurately weighing ±0.0001 g.
- 3.5 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, Maryland (or equivalent) is suitable.
- Gas chromatograph/mass spectrometer system.
- Gas chromatograph - an analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.
- Column - 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 1.0 micron is recommended because of its larger capacity. A film thickness of 0.25 micron may be used.

- Mass spectrometer - capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

- NOTE: DFTPP criteria must be met before any sample extracts are analyzed. Any samples analyzed when DFTPP criteria have not been met will require reanalysis.

- Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

REAGENTS:

- Reagent water - reagent water is defined as a water in which an interferent is not observed at or above the method detection limit of each parameter of interest.

- Sodium hydroxide solution (10N) - dissolve 40 g NaOH in reagent water and dilute to 100 mL.

- Sodium thiosulfate - (ACS) granular.

- Sulfuric acid solution (1+1) - slowly add 50 mL of $H_2SO_4$ (sp gr.1.84) to 50 mL of reagent water.

- Acetone, methanol, methylene chloride - pesticide quality or equivalent.

- Sodium sulfate - (ACS) powdered, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator, and store in a glass bottle. Baker anhydrous powder, Catalog No. 73898 or equivalent.

- Surrogate standard spiking solution.

- Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are phenol-$d_6$, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-$d_5$, terphenyl-$d_{14}$, and 2-fluorobiphenyl.

- Prepare a surrogate standard spiking solution that contains the base/neutral compounds at a concentration of 100 µg/mL, and the acid compounds at 200 µg/mL. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicates a problem.

- BNA Matrix standard spiking solution. The matrix spike solution consists of:

| Base/Neutrals | Acids |
|---|---|
| 1,2,4-trichlorobenzene | pentachlorophenol |
| acenaphthene | phenol |
| 2,4-dinitrotoluene | 2-chlorophenol |
| pyrene | 4-chloro-3-methylphenol |
| N-nitroso-di-n-propylamine | 4-nitrophenol |
| 1,4-dichlorobenzene | |

- Prepare a spiking solution that contains each of the base/neutral compounds above at 100 µg/1.0 mL in methanol and the acid compounds at 200µg/1.0 mL in methanol.

- Internal standards - 1,4-dichlorobenzene-$d_4$, naphthalene-$d_8$, acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{12}$, perylene-$d_{12}$. An internal standard solution can be prepared by dissolving 200 mg of each compound in 50 mL of methylene chloride. It may be necessary to use 5 - 10% benzene or toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard a concentration of 4,000 ng/µL. A 10-µL portion of this solution should be added to each 1 mL of sample extract (5 µl to 0.5 mL). This will give a concentration of 40 ng/µL of each constituent.

- Prepare calibration standards at three concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard.

  NOTE: Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10° to -20°C in screw-cap amber bottles with Teflon-liners. Fresh standards should be prepared every 12 months at a minimum. The continuing calibration standard should be prepared weekly and stored at 4°C (±2°C).

PROCEDURE:

1. Sample Storage and Holding Times

1.1 Procedures for Sample Storage

1.1.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

1.2 Holding Times

2.1 The extraction of water samples shall be completed within 5 days of sample receipt or within 7 days of sample collection.

2. Sample Extraction - Separatory Funnel

2.1 Samples are extracted using separatory funnel techniques. The separatory funnel extraction scheme described below assumes a sample volume of 1-L.

2.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into a 2-L separatory funnel. Add 250 µl of surrogate standard spiking solution into the separatory funnel and mix well. Add 250 µl of BNA matrix spiking solution to each of two 1-L portions from the sample selected for spiking. Check the pH of the sample with wide range pH paper and adjust to pH> 11 with 10N sodium hydroxide.

2.3 Add 60 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

2.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Serially extract three times with 60-mL aliquots of methylene chloride, as per Paragraph 5.3. Collect and combine the extracts in a 250 mL Erlenmeyer flask and label the combined extract as the acid fraction.

2.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

2.7 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in the separate K-D concentrators. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

2.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

2.9 Micro Snyder column technique - add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GC/MS analysis will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extracts will be stored longer than 2 days, they should be transferred to individual Teflon-sealed screw-cap bottles and labeled base/neutral or acid fraction, appropriate.

3. Calibration

3.1 Each GC/MS system must have the hardware tuned to meet the criteria listed in Table 1 for a 50-ng injection of decafluorotriphenyl phosphine (DFTPP). No sample analyses can begin until all these criteria are met. This criteria must be demonstrated each 12-hour shift. DFTPP has to be injected to meet this criterion. Post-acquisition manipulation of abundances is not acceptable.

3.2 The internal standards should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantification (Table 2.2). If interferences are noted, use the next most intense ion as the secondary ion, i.e., for 1,4-dichlorobenzene-$d_4$ use m/z 152 for quantification.

3.2.1 The internal standards are added to all calibration standards and all sample extracts just prior to analysis by GC/MS. A 10-µL aliquot of the internal standard solution should be added to a 1-mL aliquot of calibration standards.

3.3 Analyze 1 µL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Equation 1}$$

Where:

$A_x$ = Area of the characteristic ion for the compound to be measured.

$A_{is}$ = Area of the characteristic ion for the specific internal standard from Table 3.

$C_{is}$ = Concentration of the internal standard (ng/µL).

$C^x$ = Concentration of the compound to be measured (ng/µL).

3.3.1 The average relative response factor (RRF) should be calculated for all compounds. A system performance check must be made before this calibration curve is used. Four compounds (the system performance check compounds) are checked for a minimum average relative response factor. These compounds (the SPCC) are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.

3.3.2 A % relative standard deviation (%RSD) is calculated for 11 compounds labeled the calibration check compounds (CCC) on Form VI SV and in Table 2.3. a maximum %RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.

3.4 A check of the calibration curve must be performed once every 12 hours during analysis. These criteria are described in detail under the Quaity Assurance section of this method. The minimum RRF for the system performance check compounds must be checked. If this criteria is met, the RRFs of all compounds are calculated. A percent difference of the daily (12 hour) RRF compared to the average RRF from the initial curve is calculated. A maximum percent difference of 30% is allowed for each compound flagged as 'CCC'. Only after both these criteria are met can sample analysis begin.

3.5 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

4. <u>GCMS Analysis</u>

4.1 The following instrumental parameters are required for all performance tests and for all sample analyses:

| | |
|---|---|
| Electron energy | - 70 volts (nominal) |
| Mass range | - 35 to 500 amu |
| Scan time | - not to exceed 1 second/scan |

4.2 Combine the base/neutral extract and the acid extract and concentrate or adjust for a final volume of 0.5 mL.

4.3 Internal standard solution (5 µL) is added to each sample extract. Analyze the extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

| | |
|---|---|
| Initial column temperature hold | - 40°C for 4 minutes |
| Column temperature program | - 40-270°C at 10°/minute |
| Final column temperature hold | - 270°C for 10 minutes |
| Injector temperature | - 250-300°C |
| Transfer line temperature | - 250-300°C |
| Source temperature | - according to manufacturer's specifications |
| Injector-Grob-type, splitless | |
| Sample volume | - 1 - 2 µL |
| Carrier gas | - Helium at 30 $cm^3$/second |

5. Qualitative Analysis

5.1 The compounds listed in the Target Compound List (TCL), shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

5.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

5.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the analyst's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

5.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

5.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

5.1.3.2 The relative intensities of ions specified in 5.1.3.1 must agree within plus or minus 20% between the standard and sample spectra. (Example: for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%.)

5.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the MDL report the actual value followed by "J", e.g., "3J".

5.1.4 If a compound cannot be verified by all of the criteria in 5.1.3, but in the technical judgement of the mass spectral interpretation specialist the identification is correct, then the Contractor shall report that identifications and proceed with quantification.

5.2 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or a more recent release), containing 42,261 spectra, shall be used.

5.2.1 Up to 20 nonsurrogate organic compounds of greatest apparent concentration not listed for the combined base/neutral/acid fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

5.2.2 Guidelines for making tentative identification:

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

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

5.2.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

5.2.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

5.2.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

5.2.3 If in the technical judgement of the mass spectral interpretation specialist no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

## 6. Quantitation

6.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Tables 2 and 3 are used.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

6.2 The RRF from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a RRF is calculated using the secondary ion. When TCL compounds are below quantitation limits but the spectra meets the identification criteria, report the concentration with a "J".

6.2.1 Calculate the concentration in the sample using the RRF as determined in Paragraph 4.3 and the following equation:

$$\text{Concentration } \mu g/L = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_o)(V_i)}$$

$A_x$ = Area of the characteristic ion for the compound to e measured

$A_{is}$ = Area of the characteristic ion for the internal standard

$I_s$ = Amount of internal standard injected in nanograms (ng)

$V_o$ = Volume of water extracted in milliliters (mL)

$V_i$ = Volume of extract injected (µL)

$V_t$ = Volume of total extract

6.3 An estimated concentration for Non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard <u>free of interferences</u> shall be used.

6.3.1 The formula for calculating concentrations is the same as in Paragraph 6.2.1. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RRF of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

6.4 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits and report.

6.4.1 If recovery is not within limits (i.e., if two surrogates from either base/neutral or acid fractions are out of limits or if recovery of any one surrogate in either fraction is below 10%), the following is required.

- o Check to be sure there are not errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.
- o Reanalyze the sample if none of the above reveal a problem.

6.4.2 If none of the steps above solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the control windows. This shall be considered the initial analysis and shall be reported as such.

6.4.3 If the reextraction and reanalysis of the sample does not solve the problem, i.e., the surrogate recoveries are outside the control limits for both analyses, then submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the reanalysis on all data deliverables.

6.4.4 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document in the narrative the similarity in surrogate recoveries.

DRAFT

ASSAY TITLE: The Analysis of Volatile Organics with Low Detection Limits by Purge and Trap Gas Chromatography/Mass Spectrometry Method

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc.
Mass Spectrometry Section

SCOPE:

This purge and trap gas chromatography-mass spectrometry (GC-MS) method is applicable to the determination of volatile organic compounds in municipal (drinking) water and groundwater. The compounds listed in Table 1 (see attachments) represent the standard list of analytes determined by this method.

This method is restricted to use by, or under the supervision of, analysts who are experienced in the operation of a purge and trap system, by GC-MS, and in the interpretation of mass spectra.

PRINCIPLE:

An inert gas is bubbled through a 25-mL water sample contained in a specially 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 trap where the purgeables are trapped. After purging is completed, the trap is heated and back flushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables, which are then detected with a mass spectrometer.

SENSITIVITY:

The method detection limits presented in Table 6 represent the sensitivities that can be achieved in ground water in the absence of interferences.

PRECISION, ACCURACY:

Precision and accuracy for this method, as generated from an inhouse validation study, is presented in Table 7.

**REFERENCES:**

1. Environmental Protection Agency (EPA) Method 624 (Federal Register, 49 (209): 43373-43384, October 16, 1984).

2. Environmental Protection Agency (EPA) Method 524.1, Revised 1985, "Methods for Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", September 1986.

3. Environmental Protection Agency (EPA) Contract Laboratory Program, Statement of Work for "Organic Analysis Multi-Media Multi-Concentration", October 1986. Revisions: January 1987, February 1987, July 1987, August 1987. Exhibits: B, D, E.

APPROVED BY: _____ DATE: _____
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Quality Assurance Unit

(1066D)

SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined.

- o Treat each chemical as a potential health hazard, and minimize exposure to these chemicals.

Maintain an awareness of Occupational Safety and Health Administration (OSHA) regulations regarding safe handling of chemicals used in this method.

- o Make a reference file of material data handling sheets available to all personnel involved in the chemical analysis.
- o Additional references to laboratory safety are available for the information of the analyst.

The following parameters covered by this method have been tentatively classified as known, or suspected, human or mammalian carcinogens: benzene, tetrachloroethene, trichloroethene, carbon tetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromomethane and vinyl chloride.

- o Prepare primary standards of these compounds under a hood. Wear a toxic gas respirator, approved by the National Institute of Occupational Safety and Health/Mining Enforcement and Safety Administration (NIOSH/MESA) when handling high concentrations of these toxic compounds.

Observe all laboratory safety precautions as outlined in the Hazleton Laboratories America, Inc., Safety Training Manual.

INTERFERENCES:

Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. Non-Teflon® plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system are not used.

QUALITY ASSURANCE:

The minimum quality assurance/quality control (QA/QC) operations necessary to satisfy the analytical requirements associated with the determination of the volatile compounds listed in this method are as follows:

- o Documentation of GC/MS Mass Calibration and Abundance Pattern
- o Documentation of GC/MS Response Factor Stability

- Internal Standard Response and Retention Time Monitoring
- Method Blank Analysis
- Surrogate Spike Recovery Monitoring
- Matrix Spike and Matrix Spike Duplicate Analysis

1. GCMS Tuning and Mass Calibration

Establish that the GC-MS system meets the standard spectral abundance criteria before initiating any data collection. Tune the GC-MS system hardware to meet the abundance criteria listed in Table 1 for a maximum of a 50 ng injection of 4-bromofluorobenzene (BFB). Do not analyze the BFB simultaneously with any calibration standards or blanks. Demonstrate this criteria daily.

- Meet the BFB criteria before any standards, samples, or blanks are analyzed.
- Document the GC-MS tuning and mass calibration each time the system is tuned.
- Demonstrate that the GC-MS system can generate easily recognizable spectra using 1.5 µg/L for VOA's.

Table 1

BFB Key Ions and Abundance Criteria

| Mass Criteria | Ion Abundance |
|---|---|
| 50 | 15.0 - 40.0 percent of the base peak |
| 75 | 30.0 - 60.0 percent of the base peak |
| 95 | base peak, 100 percent relative abundance |
| 96 | 5.0 - 9.0 percent of base peak |
| 173 | less than 2.0 percent of mass 174 |
| 174 | greater than 50.0 percent of the base peak |
| 175 | 5.0 - 9.0 percent of mass 174 |
| 176 | greater than 95.0 percent but less than 101.0 percent of mass 174 |
| 177 | 5.0 - 9.0 percent of mass 176 |

## 2. Calibration of GC-MS System

### 2.1 Initial Standard Calibration

Calibrate the GC-MS system at a minimum of three concentrations to determine the linearity of response using TCL compound standards before the analysis of samples and required blanks, and after the tuning criteria have been met.

Prepare calibration standards (using 50 µg/mL HSL mix and 50 µg/mL Purgeables ABC mix) to yield the following specific concentrations: 5, 10, and 20 µg/L. Include surrogates and internal standards at 10 µg/L with each of the calibration standards.

Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including all required surrogate compounds. The relative retention time (RRT) of each compound in each calibration run must agree within 0.06 RRT units.

Use Table 2 and Equation 1 to calculate the relative response factors (RRF) for each compound at each concentration level.

Equation 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

$A_x$ = Area of the characteristic ion for the compound to be measured
$A_{is}$ = Area of the characteristic ion for the specific internal standards from Table 2 (attachments)
$C_{is}$ = Concentration of the internal standard (ng/µL)
$C_x$ = Concentration of the compound to be measured (ng/µL)

Use Equation 2 and the relative response factors (RRF) from the initial calibration to calculate the percent relative standard deviation (% RSD) for the calibration compounds.

Equation 2

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

Where:

RSD = Relative standard deviation.

SD = Standard deviation of initial relative response factors

Equation 3

$$\text{Where: } SD = \sum_{i=1}^{N} \frac{(x_i - x)^2}{N-1}$$

x = Mean of initial relative response factors (per compound)

All RF must be above 0.05 except 2-Butanone.

The initial calibration is valid only after the percent RSD for calibration compounds are <40%. Common laboratory solvents (methylene chloride and acetone) are known to bias the results to more than 40% RSD.

Table 2

Volatile Internal Standards with Corresponding TCL Analytes Assigned for Quantitation

| Bromochloromethane | 1,4-Difluorobenzene | Chlorobenzene-$d_5$ |
|---|---|---|
| Chloroethane | 2-Butanone | 2-Hexanone |
| Bromomethane | 1,1,1-Trichloroethane | 4-Methyl-2-Pentanone |
| Vinyl chloride | Carbon tetrachloride | Tetrachloroethene |
| Chloroethane | Vinyl acetate | 1,1,2,2-Tetrachloroethane |
| Methylene chloride | Bromodichloromethane | Toluene |
| Acetone | 1,2-Dichloropropane | Chlorobenzene |
| Carbon disulfide | trans-1,3-Dichloropropene | Ethylbenzene |
| 1,1-Dichloroethene | Trichloroethene | Styrene |
| 1,1-Dichloroethane | Dibromochloromethane | Xylene (total) |
| 1,2-Dichloroethene (total) | 1,1,2-Trichloroethane | Bromofluorobenzene (surr) |
| Chloroform | Benzene | Toluene-$d_8$ (surr) |
| 1,2-Dichloroethane | cis-1,3-Dichloropropene | |
| 1,2-Dichloroethane-d4 (surr) | Bromoform | |

(surr) = Surrogate compound

2.2 Continuing Calibration Check

A calibration standard(s) containing all volatile TCL compounds, including all required surrogates must be analyzed every 12 hours during analysis. (The concentration for each TCL compound is 10 µg/L). Compare the relative response factor data taken from the standards each twelve hours with the average relative response factor from the initial calibration for a specific instrument.

Use Equation 4 to calculate the percentage difference (% difference) for all compounds and check the validity of the initial calibration.

Equation 4

$$\% \text{ Difference} = \frac{RRF_i - RRF_c}{RRF_i} \times 100$$

Where:

$RRF_i$ = Average relative response factor from initial calibration

$RRF_c$ = Relative response factor from current calibration check standard

If the percentage difference is less than, or equal to, 25.0%, assume that the initial calibration is valid. If the criteria are not met, take corrective action. This may involve rerunning the initial three-point curve.

3. Evaluate the internal standard responses and retention times in all samples immediately after, or during, data acquisition. If the retention time for any internal standard changes by more than 30 seconds; inspect the chromatographic system for malfunctions and make corrections. Monitor the area of the extracted ion current profile (EICP) of the internal standards and evaluate the EICP for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP for any of the internal standard changes from the latest calibration check standard by more than a factor of two (-50% to 100%), inspect the mass spectrometer for malfunction, and make corrections.

4. Method Blank Analysis

Analyze the method blank (consists of reagent water) once for each 12-hour period. Ensure that the method blank volume is approximately equal to the sample volume being processed. Demonstrate that the method blank is free of contamination.

5. Surrogate Spike Analysis

Perform surrogate recovery determinations on all samples and blanks. Add the surrogate compound to each sample, matrix spike, matrix-spiked duplicate, and blank. Use the amount of the surrogate standard and the acceptable percentage recovery limits that are listed in Table 3.

Acceptable surrogate recovery limits are in Table 3. In the case of highly concentrated or "dirty" samples, the recovery limits may not be applicable. Make a professional judgment as to whether the sample is to be reanalyzed to demonstrate a matrix problem. Check the GC-MS system by analyzing a method blank.

Table 3

Surrogate Spike Compounds,
Concentrations and Recovery Limits

| Compounds | Concentration (ppb) | Percentage of Recovery |
|---|---|---|
| Toluene-$d_8$ | 10 | 80 - 120 |
| 4-Bromofluorobenzene | 10 | 80 - 120 |
| 1,2-dichloroethane-$d_4$ | 10 | 76 - 120 |

6. Matrix Spike/Matrix Spike Duplicate Analysis

In order to evaluate the matrix effect of the sample on the analytical methodology and provide both precision and accuracy information, a matrix spike and matrix spike duplicate (MS/MSD) analysis is performed with each set of 20 samples. Spiking is performed at a level of 10 µg/L, using a mixture of the following compounds:

- Benzene
- Toluene
- Trichloroethene
- Chlorobenzene
- 1,1-Dichloroethene

Calculate the individual component recoveries of the matrix spikes using Equation 5.

Equation 5

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample results
SR = Sample results
SA = Spike added from spiking mix

Calculate the relative percentage difference (RPD) for each component using Equation 6.

Equation 6

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = Relative percentage difference
$D_1$ = First sample value
$D_2$ = Second sample value (duplicate)

Table 4
Matrix Spike Recovery Limits

| Fraction | Matrix Spike Compound | Control Limit* |
|---|---|---|
| VOA | Benzene | 66-142 |
| VOA | Toluene | 76-125 |
| VOA | Trichloroethene | 71-120 |
| VOA | Chlorobenzene | 75-130 |
| VOA | 1,1-Dichloroethene | 61-145 |

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be re-analyzed.

APPARATUS:

Sample Containers

- Vials, 40 mL, screw-cap vials with PTFE-faced silicone septum seals.

Purge and Trap System (Tekmar LSC-2 or equiavlane)

- Purging device, all-glass, capable of accepting 25-mL samples with a water column of at least 5 cm deep, and with a glass frit (3-cm diameter at origin). Wash vials and seals with detergent, rinse with tap water and then distilled water, dry at 105°C, and then allow to cool in an area free of organic vapors.

- Volatile trap, at least 25 cm long, with an inside diameter of at least 0.105 inches. The trap requires two phases: tenax and silica gel. Before daily use, condition the trap for 10 minutes at 220°C and back flood with an inert gas flow of at least 20 mL/minute Vent the trap effluent to the room through a charcoal trap.

- Desorber, capable of rapidly preheating the trap to 180°C, and then desorbing the trap to the GC column, and maintaining a trap temperature of 180°C.

GC-MS System

- Gas chromatograph, Hewlett-Packard 5993 or equivalent, must be capable of temperature programming and achieving an initial column temperature of 30° to 45°C. Use variable constant differential-flow controllers capable of maintaining constant flow rates throughout the desorbtion and temperature program.

- Gas chromatography column, 8 ft x 1/8 O.D. glass column, packed with 1% SP-1000 on Carbopack B (60/80 mesh), or equivalent.

- Mass spectrometer, Finnigan 5100 or equivalent, capable of scanning from 20 to 260 amu every 7 s or less, using 70 V (nominal) of electron energy in the electron impact ionization mode, and producing a mass spectrum that meets all the criteria in Table 3 (attachments) when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

- GC-MS interface, constructed of all-glass or glass-lined materials. Glass is deactivated by silanizing with dichloro- dimethylsilane.

Data System

- Computer system, interfaced to the mass spectrometer, allows continuous acquisition and storage of on machine-readable media of all mass spectra obtained through the duration of the chromatographic program. Use a computer with software that can search for any GC-MS data file for specific m/z (masses) and plot such m/z abundance versus time or scan number. Software must also be able to integrate the abundance, between

Syringe and Syringe Valves

- Syringes, 5- and 25-mL glass hypodermic with luerlock tip (two each)
- Micro syringes, 25 and 100 µL
- Gas syringes, 1.0 and 5.0 mL gas tight, with shut off valve

Miscellaneous

- Standard storage containers, 3.7-mL screw-cap amber vials
- Mini-inert valves, screw cap.

REAGENTS:

- Reagent water, producing less than a 0.4-µg/L response for the compounds being monitored, except those compounds recognized as common laboratory solvents (methylene chloride, acetone, 2-butanone, toluene).

- Methanol, demonstrated to be free of analytes (Spike 100 µL into 25 mL of reagent water and analyze. This produces a response of less than 0.4 µg/L.)

Stock Standards

- Prepare the working standard for the HSL mix separately, or add to the purgeables (A, B, or C) working standards. It is convenient to prepare them separately because the purgeables working standards must be replaced more frequently than the HSL mix.

Preparation of a 50 µg/mL HSL Mix

The solution provided from Supelco has 2 mg/mL of each compound. Place approximately 9 mL of methanol in a 10-mL volumetric flask. Using a 500 µL gas tight syringe, add exactly 250 µL of Supelco HSL Standard Mix to the volumetric flask. Ensure that the drops fall directly into the alcohol without touching the side of the flask. Dilute the flask to volume with methanol, stopper and invert three times. This yields a solution with each compound at 500 µg/mL. Store at 0°C. This standard should be replaced monthly.

Preparation of a 50 µg/mL Purgeables A, B, and C

Mixtures A, B, and C contain a different group of compounds. All are at 200 µg/mL. Place Purgeables C (the gases) in dry ice for 10 minutes. Using a 500-µL gas-tight syringe, add 250 µL each of methanol, Purgeables A, Purgeables B and Purgeables C to a milliliter micro-reaction vessel equipped with a mini-inert valve closure. Store the vial at 0°C. Replace Purgeables A, B, and C standards weekly to maintain proper concentration of the gases.

Preparation of a 50 µg/mL Internal Standard Mix

Supelco Purgeables Internal Standard Mix-624 provides the desired compounds in methanol at 1,000 µg/mL. Place approximately 9 mL methanol in a 10-mL volumetric flask. Using a 500-µL gas-tight syringe, add exactly 500 µL of the internal standard mix to the methanol. Ensure that the drops fall directly into the alcohol without touching the sides of the flask. Dilute volume with methanol, stopper, and invert three times. Store at 0°C.

Preparation of a 25 µg/mL Surrogates Standard Mix

Supelco Purgeables Surrogate Standard Mix provides the desired compounds in methanol at 250 µg/mL. Place approximately 8 mL methanol in a 10-mL volumetric flask. Using a 500- or 1,000-µL gas-tight syringe, add exactly 1.0 mL of surrogate standard mix to the methanol using the technique described previously. Dilute to volume with methanol, stopper, and invert three times. Store at 0°C.

Sample Spiking or Matrix Spike Standard

- Matrix spike solution, containing the five compounds listed in Table 2 (Attachment B). No mix is commercially available that has only these compounds. Prepare the stock standard from neat.

Preparation of a Matrix Spike Stock Standard (2 mg/mL)

Place approximately 24 mL methanol in a 25-mL volumetric flask. Allow flask, allow to stand unstoppered for 10 minutes, or until all alcohol-wetted surfaces have dried and tare. Using a 100-µL syringe, add 50 mg of the first compound; ensure that all of the drops fall directly into the alcohol without touching the flask neck. Re-tare the flask, and add 50 mg of the next compound. Repeat the process until all of the compounds have been added. Dilute to volume with methanol, stopper, and invert three times. Transfer contents to appropriate storage containers with no headspace and store at 0°C.

Preparation of a Matrix Spike Working Standard (50 µg/mL)

Place approximately 9 mL of methanol in a 10-mL volumetric flask. Using a 500-µL gas-tight syringe, add 250 µL of the 2.0 mg/mL stock solution to the flask using the technique described previously. Dilute to volume with methanol, stopper, and invert three times. Store at 0°C.

SAMPLE COLLECTION, PRESERVATION, AND STORAGE:

Sample Collection

- Include trip blanks with each sample set (composed of the samples collected from the same general sampling site at approximately the same time). Fill at least of two sample bottles with reagent water and seal at the laboratory, and then ship these to the sampling site along with the empty sample bottles. Whenever a set of samples is shipped and stored, it is accompanied by trip blanks.

- Collect one field blank sample, which is composed of deionized laboratory water per group of 20 or fewer samples. Prepare this blank in the field as follows: Allow deionized laboratory water to contact the sampling equipment and then pour it into the sampling vial. Ensure that no air bubbles are trapped in the field blank sample when the vial is sealed.

- Collect all samples in duplicate (triplicate when high levels requiring screening and dilution are suspected). Fill sample bottles to overflowing. Ensure that no air bubbles pass through the sample as the bottle is filled, or become trapped in the sample when the bottle is sealed.

- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes). Adjust the flow to above 500 mL/minute and collect duplicate samples from the stream.

- When sampling from an open body of water, fill a 1-qt wide-mouth bottle or 1-L breaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-qt container.

Sample Preservation

- Chill the samples to 4°C on the day of collection and maintain them at that temperature until analysis. Package the field samples that are not received at the laboratory on the day of collection for shipment with sufficient ice to ensure that they are at 4°C on arrival at the laboratory.

- Analyze all samples within 10 days of sample receipt or within 14 days of sample collection.

SAMPLE ANALYSIS:

1. Quality Control Requirements

Analyze the samples after the initial quality assurance activities are successfully completed. Twelve hours after the completion of the initial tuning, conduct an instrument tuning and calibration-check analysis. Any major system maintenance, such as a source cleaning or installation of a new column, requires re-tuning and recalibration, irrespective of the 12-hour requirement (see Initial Calibration). Only the calibration verification is done for minor maintenance (Continuing Calibration).

1.1 For highly concentrated or "dirty" samples, the EICP area for any internal standard may change by more than a factor of two. Make a professional judgment as to whether the sample is to be reanalyzed to demonstrate a matrix problem. Check the GC-MS system by analyzing a method blank.

1.2 Check each analytical run for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

1.3 If any compound in any sample exceeds the initial calibration range, dilute that sample. Re-adjust the internal standard concentration and reanalyze the sample.

**PROCEDURE:**

1. Upon receipt, samples should be stored at 4°C.

2. Sample Analysis

All standards, blanks, and samples should be analyzed in the following fashion:

2.1 Purging

2.1.1 Set up the purge and trap system. Adjust the purge gas (helium) flow rate to 40 mL/minute.

2.1.2 Allow the sample to come to ambient temperature before injecting it into the syringe.

2.1.3 Remove the plunger from a 25-mL syringe and attach a closed syringe valve to it.

2.1.4 Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing.

2.1.5 Replace the syringe plunge and compress the sample.

2.1.6 Hold the syringe in an upright position with the syringe valve set on top of the syringe. Open the syringe valve, vent any residual air and adjust the sample volume to 25 mL.

2.1.7 Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data.

2.1.8 Add 10 µl of the surrogate spiking solution (25 ng/µl) and 5 µl of the internal standard spiking solution (50 ng/µl) through the valve bore and then close the valve.

2.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device.

2.1.10 Open the syringe valves and inject the sample into the purging chamber. Close both valves.

2.1.11 Purge the sample for 11.0 ±0.1 minutes at ambient temperature.

2.1.12 After the 11-minute purge, attach the trap to the chromatograph and adjust the purge and trap system to the desorb mode.

2.2. Gas Chromatography-Mass Spectrometry Analysis

2.2.1 Set up the GC-MS operating parameters.

Carrier gas flow rate: 40 mL/minute
Injector temperature: 220°C
Oven temperature: Hold at 45°C for 3 minutes and then heat to 220°C at 8°C/minute. Hold at 200°C until the programmed run time expires.
Transfer line temperature: 225°C
Ion source temperature: 200°C
Scan range: 35-250 amu
Electron energy: 70 V
Scan Time: To give at least 5 scans per peak but not to exceed 7 seconds per peak.

2.2.2 Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while back flooding the trap with an inert gas between 20 and 60 mL/minute for 4 minutes. If rapid heating of the trap cannot be achieved, use the GC column as a second trap by cooling it to 30°C, or subambient temperature (cryogenic trapping) if the problem persists, instead of the initial program temperature of 45°C.

2.2.3 As the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 25-mL flushes of reagent water.

2.2.4 After desorbing the sample from the trap for 4 minutes, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, and then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

2.2.5 If the response for any m/z exceeds the working range of the system, prepare dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

3. Daily Analysis Scheme

3.1 Achieve acceptable abundance criteria (see Table 4) for BFB at the beginning of each day that analyses are performed. This test must be passed prior to analysis of any standards, blanks, or samples.

3.2 Upon achieving the key abundance criteria for BFB, calibrate the instrument as described in the Quality Assurance section, paragraph 2.

3.3 After the instrumental calibration requirements are met, analyze a method blank (25 mL aliquot of reagent water plus 250 ng each internal standards mix and surrogate standards mix) to demonstrate that the instrument is free of contamination.

3.4 Proceed with sample analysis.

4. Qualitative Identification

4.1 Obtain EICPs for the primary m/z (Table 5, attachments) and at least two secondary masses for each parameter of interest. The following criteria must be met:

4.2 Ensure that the characteristic masses of each parameter of interest is maximized in the same, or within one, scan of each other.

4.3 Ensure that the relative retention time fall within ±.06 units of the relative retention time of the standard component.

4.4 Ensure that the relative peak heights of the three characteristic masses in the EICPs fall within ±20% of the relative intensity of these masses in a reference mass spectrum.

4.5 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or a more recent release), containing 42,261 spectra, shall be used.

4.6 Up to 10 nonsurrogate organic compounds of greatest apparent concentration not listed as target volatile compounds shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. NOTE: Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

4.7 Guidelines for making tentative identification:

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

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

4.7.3 Molecular ions present in reference spectrum should be present in sample spectrum.

4.7.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

4.7.5 Ions present in the reference spectum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

4.8 If in the technical judgment of the mass spectral interpretation specialist no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

5. Quantitation

5.1 When a parameter has been identified, the quantitation of that parameter is based on the integrated abundance from the EICPs of the primary characteristic m/z given in Table 5.

5.2 Equation 7 is used to calculate the concentration in the sample using the response factor (RF) determined in Calibration of GC-MS System section.

Equation 7

$$\text{Concentration } (\mu g/L) = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

Where:

$A_s$ = Area of the characteristic m/z for the parameter or surrogate standard to be measured

$A_{is}$ = Area of the characteristic m/z for the internal standard

$C_{is}$ = Concentrations of the internal standard

Report result is given in µg/L without correction for recovery data.

5.3 An estimated concentration for Non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used. The formula for calculating concentrations is the same as in Equation 7. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RRF of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

CALCULATIONS:

Description of calculations has been included in the previous section.

## Table 5

### Characteristic Ions for Volatile Compounds

| Parameter | Primary Ion | Secondary Ion(s) |
|---|---|---|
| Chloromethane | 50 | 52 |
| Bromomethane | 94 | 96 |
| Vinyl chloride | 62 | 64 |
| Chloroethane | 64 | 66 |
| Methylene chloride | 84 | 49, 51, 86 |
| Acetone | 43 | 58 |
| Carbon disulfide | 76 | 78 |
| 1,1-Dichloroethene | 96 | 61, 98 |
| 1,1-Dichloroethane | 63 | 65, 83, 85, 98, 100 |
| 1,2-Dichloroethene (total) | 96 | 61, 98 |
| Chloroform | 83 | 85 |
| 1,2-Dichloroethane | 62 | 64, 100, 98 |
| 2-Butanone | 72 | 57 |
| 1,1,1-Trichloroethane | 97 | 99, 117, 119 |
| Carbon tetrachloride | 117 | 119, 121 |
| Vinyl acetate | 43 | 86 |
| Bromodichloromethane | 83 | 85 |
| 1,1,2,2-Tetrachloroethane | 83 | 85, 131, 133, 166 |
| 1,2-Dichloropropane | 63 | 65, 114 |
| trans-1,3-Dichloropropene | 75 | 77 |
| Trichloroethene | 130 | 95, 97, 132 |
| Dibromochloromethane | 129 | 208, 206 |
| 1,1,2-Trichloroethane | 97 | 83, 85, 99, 132, 134 |
| Benzene | 78 | -- |
| cis-1,3-Dichloropropene | 75 | 77 |
| Bromoform | 173 | 171, 175, 250, 252, 254, 256 |
| 2-Hexanone | 43 | 58, 57, 100 |
| 4-Methyl-2-pentanone | 43 | 58, 100 |
| Tetrachloroethene | 164 | 129, 131, 166 |
| Toluene | 92 | 91 |
| Chlorobenzene | 112 | 114 |
| Ethyl benzene | 106 | 91 |
| Styrene | 104 | 78, 103 |
| Total xylenes | 106 | 91 |

a The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

Table 6

Analytes and Detection Limits
by GC-MS Method

| Parameter | CAS Number | Detection Limits Water (µg/L) |
|---|---|---|
| Chloromethane | 74-87-3 | .712 |
| Bromomethane | 74-83-9 | .223 |
| Vinyl Chloride | 75-01-4 | .423 |
| Chloroethane | 75-00-3 | .924 |
| Methylene Chloride | 75-09-2 | .747 |
| Acetone | 67-64-1 | .697 |
| Carbon Disulfide | 75-15-0 | .255 |
| 1,1-Dichloroethene | 75-35-4 | .289 |
| 1,1-Dichloroethane | 75-35-3 | .238 |
| t,2-Dichloroethene (total) | 156-60-5 | .217 |
| Chloroform | 67-66-3 | .269 |
| 1,2-Dichloroethane | 107-06-2 | .660 |
| 2-Butanone[a] | 78-93-3 | 5.0 |
| 1,1,1-Trichloroethane | 71-55-6 | .876 |
| Carbon Tetrachloride | 56-23-5 | .303 |
| Vinyl Acetate | 108-05-4 | 1.100 |
| Bromodichloromethane | 75-27-4 | .279 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | .392 |
| 1,2-Dichloropropane | 78-87-5 | .309 |
| trans-1,3-Dichloropropene | 10061-02-6 | .240 |
| Trichloroethene | 79-01-6 | .206 |
| Dibromochloromethane | 124-48-1 | .268 |
| 1,1,2-Trichloroethane | 79-00-5 | .262 |
| Benzene | 71-43-2 | .248 |
| cis-1,3-Dichloropropene | 10061-01-5 | .385 |
| 2-Chloroethyl vinyl ether | 110-75-8 | .355 |
| Bromoform | 75-25-2 | .684 |
| 2-Hexanone | 591-78-6 | .479 |
| 4-Methyl-2-Pentanone | 108-10-1 | .541 |
| Tetrachloroethene | 127-18-4 | .336 |
| Toluene | 108-88-3 | .244 |
| Chlorobenzene | 108-90-7 | .182 |
| Ethyl benzene | 100-41-4 | .876 |
| Styrene | 100-42-5 | .266 |
| Total xylenes | | .741 |

a Based on laboratory experience.

Table 7

Precision and Accuracy Data Low Level GCMS Volatiles
(25 mL Sample Purge)

| Compound | Spike Level (µg/L) | Average Recovery (µg/L) | (%) | Standard Deviation (µg/L) |
|---|---|---|---|---|
| Chloromethane | 1.0 | 0.806 | 80.6 | 0.237 |
| Bromomethane | 1.0 | 0.904 | 90.4 | 0.0743 |
| Vinyl Chloride | 1.0 | 0.788 | 78.8 | 0.141 |
| Chloroethane | 1.0 | 1.14 | 114 | 0.308 |
| Methylene Chloride | 1.0 | 1.32 | 132 | 0.249 |
| Acetone | 1.0 | 1.48 | 148 | 0.232 |
| Carbon Disulfide | 1.0 | 1.05 | 105 | 0.0851 |
| 1,1-Dichloroethene | 1.0 | 0.881 | 88.1 | 0.0963 |
| 1,1-Dichloroethane | 1.0 | 0.917 | 91.7 | 0.0793 |
| Total 1,2-Dichloroethene | 1.0 | 0.930 | 93 | 0.0722 |
| Chloroform | 1.0 | 1.05 | 105 | 0.0897 |
| 1,2-Dichloroethane | 1.0 | 0.89 | 89.4 | 0.220 |
| 2-Butanone | ND | ND | ND | ND |
| 1,1,1-Trichloroethane | 1.0 | 0.917 | 91.7 | 0.292 |
| Carbon Tetrachloride | 1.0 | 0.836 | 83.6 | 0.101 |
| Vinyl Acetate | 1.0 | 1.31 | 131 | 0.367 |
| Bromodichloromethane | 1.0 | 0.948 | 94.8 | 0.0958 |
| 1,2-Dichloropropane | 1.0 | 0.952 | 95.2 | 0.103 |
| Trans-1,3-Dichloropropene | 0.78 | 0.746 | 95.7 | 0.0799 |
| Trichloroethene | 1.0 | 0.924 | 92.4 | 0.0686 |
| Dibromochloromethane | 1.0 | 0.997 | 99.7 | 0.0892 |
| 1,1,2-Trichloroethane | 1.0 | 1.00 | 100 | 0.0875 |
| Benzene | 1.0 | 0.954 | 95.4 | 0.0828 |
| Cis-1,3-Dichloropropene | 1.22 | 1.09 | 89.3 | 0.128 |
| 2-Chloroethyl vinyl ether | 1.0 | 0.925 | 92.5 | 0.108 |
| Bromoform | 1.0 | 0.958 | 95.8 | 0.228 |
| 4-Methyl-2-Pentanone | 1.0 | 1.15 | 115 | 0.180 |
| 2-Hexanone | 1.0 | 0.916 | 91.6 | 0.160 |
| Tetrachloroethene | 1.0 | 0.911 | 91.1 | 0.112 |
| 1,1,2,2-Tetrachloroethane | 1.0 | 0.968 | 96.8 | 0.130 |
| Toluene | 1.0 | 0.952 | 95.2 | 0.0814 |
| Chlorobenzene | 1.0 | 0.986 | 98.6 | 0.0606 |
| Ethyl benzene | 1.0 | 0.854 | 85.4 | 0.292 |
| Styrene | 1.0 | 1.05 | 105 | 0.0888 |
| Total xylenes | 1.0 | 0.967 | 96.7 | 0.247 |

ND = Not Determined

# APPENDIX D

## WARZYN ENGINEERING INC
## STANDARD OPERATING PROCEDURES
## USING NON-CLP PROTOCOL

# ATOMIC ABSORPTION SPECTROMETRY
## FURNACE - DIRECT INJECTION

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame, furnace or hydride techniques. The furnace - direct injection technique allows for lower detection limits. The use of the graphite platform in furnace analysis can improve sensitivity and reduce some matrix interferences.

Method: Furnace; direct injection

Reference: EPA 1983, Section 200

"Analytical Methods for Furnace Atomic Absorption Spectroscopy", 1980, Perkin-Elmer Corporation

"Model 2380 Atomic Absorption Spectrophotometer", 1981, Perkin-Elmer Corporation

"Techniques in Graphite Atomic Absorption Spectroscopy", 1985, Perkin-Elmer Corporation

Sample Handling: Acidify with concentrated nitric acid to pH<2. Drinking waters and filtered groundwater samples free of particulate matters and organics may be analyzed directly, while wastewaters, leachates, solids, etc., must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months.

Reagents and Apparatus:

1. 2380 Perkin-Elmer spectrophotometer
2. Required metal lamp and power source
3. HGA 400 Perkin-Elmer furnace and programmer
4. AS40 Perkin-Elmer Autosampler
5. 024 Perkin-Elmer recorder
6. Stock and standard solutions for required metal
7. Class A volumetric glassware
8. Instra-analyzed nitric acid
9. Milli-Q water
10. Argon gas-prepurified
11. Graphite tubes (pyrolytically coated)
12. Graphite tubes and platforms (pyrolytically-coated)
13. Eppendorf 100-1000 microliter pipeter
14. Disposable 10 mL beakers

Procedure:

A. Installation of Furnace

1. Remove the sample compartment door and tray.

2. Disconnect the tiedown cable, drainhoses.

3. Remove the burner head unit by loosening the 2 side knurled knobs and the unit should pull out. Store below the A.A. Lower the platform to lowest possible stage.

4. Loosen the locking screw on the furnace stand.

5. Lift the furnace up, and position the furnace on the pegs in the sample compartment, and screw into place.

6. Turn on water.

7. Attach the drain hose to auto sampler.

8. Attach the D.I. water supply to auto sampler.

Note - See the furnace maintenance procedures. The maintenance must be done with each day of use of the furnace.

B. Furnace Alignment

1. Plug in the lamp.

2. Dial in the desired wavelength. Adjust the wavelength with the fine adjust knob to the highest energy reading on the GAIN control. Adjust the lamp using the knobs in the lamp compartment in the above manner.

3. Turn ON the programmer and auto sample unit.

4. Turn on the gas supply (Argon) with the pressure at 350kPa.

5. Remove the furnace windows.

6. Pull the furnace unit out of the light path. (Make sure all wires are out of light path.)

7. A.Z. the instrument.

8. Put the furnace unit back into position.

9. Adjust the furnace with the two gray knobs on the unit. Adjust the furnace to the nearest 0.000 Absorbance you can obtain.

10. Replace the windows. The absorbance should be about 0.100.

11. Switch the gas to open.

12. Pull the right hand furnace half to the side.

13. Insert the graphite tube.

14. Insert the tube alignment tool into the sampling opening; carefully turning the tube so the tip of the tool goes into the sample hole in the tube.

15. Close the furnace.

16. Switch the gas to ON.

17. Remove the alignment tool.

## C. Conditioning a Graphite Tube

Conditioning of the graphite tube should be done when you begin the day, change to a new tube, or change to another element. The conditioning of a tube removes impurities on the tube's surface.

1. Push and hold for 5 seconds the MANUAL TEMP key at 100°C. Do this 4 times. Do the same at 2700°C repeatedly until smoking has stopped, and no absorbance signal is obtained when the tube is taken through the element's program.

## D. Aligning the Auto-Sampler Arm

1. Connect the drain bottle and the distilled water reservoir to the auto sampler.

2. Turn ON the auto sampler. The sampler will go through a five step rinse cycle.

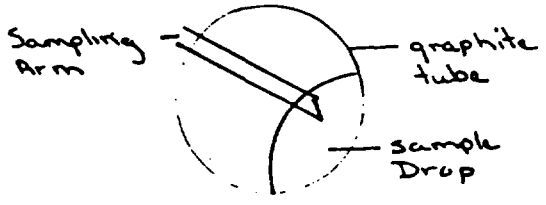
3. Manually move the arm towards the furnace.

4. Adjust the arm so that the tip goes smoothly into the graphite tube.

   a. Unlock the arm by turning the red knob clockwise.

   b. Adjust the arm vertically and horizontally using the gray knobs at the front end left of the sampler.

   c. The height is adjusted using the silver knurled knob. The tip of the arm will be close to the tube wall but not touching. This can be checked using the dental mirror. See figure below:



Notes:

1. See the separate procedures involved with programming elements for the furnace, and programming the auto sampler.

2. Use 1:1 nitric for all glassware cleaning and standard preparation.

E. Programming the Auto Sampler

1. Push STAND-BY to get into operating mode.

2. Enter Method 1.

3. Enter the number of standards used (if in concentration mode only!).

4. Enter the number of the last cup in the run.

5. Enter two replicates.

6. Enter sample volume-usually 20 unless otherwise stated by procedures.

7. Push RESET-this brings the tray back to the starting position.

8. Push START to begin the run.

9. Turn on the Perkin-Elmer 024 recorder.

10. Insert blanks, standards and samples in the autosampler tray. Start the auto sampler and analyze the blanks, standards and samples. Analyze an EPA reference standard to verify the curve. This standard must be within the 95% confidence limits before continuing with the analysis of the samples.

11. Analyze samples by methods described in the furnace section of this manual. Refer to specific metal operating procedures for notes on interferences, use of matrix modifiers, quality control and any other adjustments to this instrument operation procedure.

## Terminology

ALT. VOLUME may be used to specify a volume of an alternate solution to be added to the sample (ex. Matrix Modifier).

MANUAL may be used as follows:

a. to move tray to a specific number. Push the number of the space then the manual button.

b. to inject one sample repeatedly. When the sampler is aligned with the number you want to repeat, push the manual button once to start the repeats.

c. to stop repeats - push manual button again.

CHECK when pushed, the indicator light flashes. Push the operator button and the numbers entered will be displayed.

## F. Auto-Concentration - Furnace

The machine is calibrated against one to three standards. The standard curve is drawn as a straight line between the zero and $S_1$. Again, a straight line is drawn between $S_1$ to $S_2$, and $S_2$ to $S_3$. (Refer to Figure 1 in the MetalF1 SOP, page 7.)

If you should encounter an error code during calibration, the operator's manual has a listing of error codes and their meanings.

| | |
|---|---|
| Signal - Conc. | t = see specific SOP's |
| Mode - pk Ht or pk area (see specific SOP's) | Ave - 2 |

Type the $S_1$ (first standard) value and push $S_1$ button
Type the $S_2$ (second standard) value and push the $S_2$ button

### Procedure

1. Analyze the blank and auto-zero (AZ) Type in $S_1$ value, push the $S_1$ button. Repeat with desired standards.

2. Analyze $S_1$ standard, the A.A. will standardize $S_1$, after the 2 readings. Repeat until desired number of standards are standardized (usually have 2 standards for calibration).

3. Analyze samples, check standards periodically during the run, re-standardize if necessary.

### Notes

You can AZ any time during a run.
If you re-standardize this $S_1$ value, you have to re-standardize the $S_2$ and $S_3$.

## G. Method of Standard Addition - Furnace

The method of standard additions is a useful tool which enables us to achieve an accurate determination of an element in the presence of an interference. Standard additions are required for EP Toxicity metals.

For an accurate value of an element, the working curve must be linear throughout the range of concentration encountered by the samples plus the additions.

SIGNAL - ABS  t = (see specific SOP's)
Ave - 2

MODE - pk Ht or pk area (see specific SOP's)

Procedure

1. Take four aliquots of the sample at a set volume.

2. Add the same volume of blank to the first beaker.

3. Add the same volume of successive standards to the remaining beakers.

4. Mix by swirling.

Example -

| Beaker 1 | Beaker 2 | Beaker 3 | Beaker 4 |
|---|---|---|---|
| 1/2 ml sample | 1/2 ml sample | 1/2 ml sample | 1/2 ml sample |
| 1/2 ml blank | 1/2 ml 1 PPM Std. | 1/2 ml 2 PPM Std. | 1/2 ml 4 PPM Std. |

5. Aspirate the reagent blank and Auto-zero (A.Z.)

6. Aspirate the sample beakers from the blank to the highest spiked beaker.

7. Record all four absorbance readings for the sample.

Calculations

Plot the absorbance readings against the concentrations of the standards added. The intercept of the concentration axis equals the concentration of the element in the sample. (See figure 2 on MetalFL1-7). Linear Regression may be used.

H. Furnace Shut Down

At the end of furnace work, follow the shut down procedure:

1. Turn the B.G. corrector to the Atomic Absorption position.

2. Turn SIGNAL to the lamp position. TURN lamp current to zero, EDL Lamps - turn power pack off. Be careful to store hot EDL's in a horizontal position.

3. Turn off water system.

4. Turn off Argon gas.

5. Turn off hood.

6. Turn off programmer and auto sampler unit.

7. Disconnect drain hose, and unscrew D.I. water supply from the auto sampler.

8. Remove the furnace by loosening the 4 screws. Pull furnace straight out of the compartment. Position furnace on the stand. Tighten the locking screws into position.

9. Insert burner head unit.

10. Connect tiedown cable and drain hoses.

11. Replace compartment door and tray. The AA is now ready for flame analysis.

## I. Furnace Maintenance

The following maintenance is to be done each day the furnace is operated.

1. Clean the furnace windows.

   a. Pop out furnace windows from furnace unit.

   b. Unscrew window casting - gently dislodge windows from casting.

   c. Put windows in alcohol.

   d. Clean with Kim-wipe.

   e. Rinse with D.I. water - dry

   f. Place windows in casting. Screw in finger tight.

2. Check machine windows and clean if needed (same as procedure in A.A. maintenance).

3. Check cones - change the cones if they appear pitted (see P.E. Furnace Manual).

4. Empty drain bottle.

5. Rinse D.I. water bottle and fill with new D.I. water.

6. Clean cones with alcohol on a Q-tip. Rinse with D.I. water. Be Careful! Cones are very fragile.

Quality Control:

1. Refer to specific metal standard operating procedures.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum range.

2. Standards must be prepared in the same acid concentrations as the samples being analyzed.

3. Refer to the Perkin-Elmer Procedures Manual for further instructions and troubleshooting.

| | Revision Date |
|---|---|
| Michael J. Linskens<br>Laboratory Manager | 11-14-86 |
| Kim D. Finner<br>Analytical Laboratory QA/QC Officer | 4-13-87 |
| QA Officer | |

[ALM-3-4]

# ATOMIC ABSORPTION SPECTROMETRY
## FLAME - DIRECT ASPIRATION

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame or furnace techniques. The flame-direct aspiration can be used for most metals but is generally not as sensitive as the furnace method. Both the air-acetylene and nitrous oxide-acetylene flame techniques are described in this operating procedure as well as the use of emission spectroscopy.

Method: Flame; direct aspiration

Reference: EPA 1983, Section 200

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Model 2380 Atomic Absorption Spectrophotometry", 1981, Perkin-Elmer Corporation

Sample Handling: Acidify with concentrated nitric acid to pH<2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months from sampling date.

Reagents and Apparatus:

1. 2380 Perkin-Elmer Spectrophotometer
2. Stock and standard metal solutions
3. Class A volumetric glassware
4. Instra-analyzed nitric acid
5. Milli-Q water
6. Required lamp and power source
7. Disposable 10 mL beakers
8. Eppendorf 100-1000 uL nipeter
9. Acetylene gas
10. Air supply
11. Nitrous oxide gas
12. Air-acetylene burner head with impact bead or nitrous oxide-acetylene burner head with flow spoiler

Procedure:

A. Instrument Set-up Procedure for Flame Atomic Absorption

1. Turn power button to the ON position.

2. Plug in lamp.

   a. Hollow Cathode Lamp: Have the signal control in the lamp position. Turn the lamp knob until the desired mAmps is shown on the lamp/energy display. Warm lamp for 15 minutes.

   b. Electrodless Electrode Discharge Lamp (EDL) Turn on the EDL power supply unit. Adjust the power to the watts needed. Warm up one half hour. Make sure the watts are at or slightly higher than the recommended watts. Otherwise, this will shorten the life of the lamp and elements can appear noisy.

3. Turn Signal to Set-up.

   a. Turn the slit knob to the designated slit (see SOPs). Normal Slit settings are for flame and hydride work Alternate Slit setting are for furnace work.

   b. Adjust the Coarse Adjust knob to the desired wavelength.

   c. Using the Fine Adjust knob - turn to the highest energy level reading on the lamp/energy display. The Gain control may be used to decrease or increase the energy as needed.

   d. Adjust the lamp position; using the two knobs on the lamp holder. Again, adjust to the highest energy reading on the lamp/energy display. Alignment is critical for high quality results and ease of use.

4. Turn signal to Abs. (Absorbance).
   Turn Mode to cont. (Continuous read).
   Insert .5 sec t.
   Push AZ (Auto-zero).

B. Burner Head Set-up and Alignment

Insert appropriate burner head (5cm burner head for the nitrous-oxide/acetylene flame, 10cm burner head for the air/acetylene flame) so the small peg on the burner chamber fits into the slot in the base of the burner head. Tighten the outer ring.

1. Snap the safety chains in place.

2. Insert the plug into the hole at the right rear of the burner platform.

3. Using the right-hand silver knob - raise the burner head until a reading above 0.000 appears on the read-out display.

4. Turn the knob back to a reading of 0.000. Lower the burner head 1/4 turn below this 0.000 reading. (This adjusts the burner head to a position below the light path.)

Turn ON the Background Corrector if running an element with a wavelength below 350 mm.

1. AAEN - shows the lamp energy.

2. BGEN - shows the background corrector's energy.

*These two readings should be approximately the same. (Usually close to 75/74).

If the BG CORR - (to the right of the read-out display) begins to flash, pull the lever (inside the lamp compartment) forward. This moves a filter into place.

C. Air-Acetylene Flame Ignition and Analysis

1. Set fuel flow to specifications (approximately 10-20 psi)

2. Set oxidant flow to specifications (approximately 40-50 psi)

3. Ignite the flame.

4. Let the flame stabilize a few minutes.

D. Alignment of Burner Head

Adjust the burner head to the best position as follows:

1. Auto-zero the machine while aspirating a blank.

   Enter in 0.5 sec t on the keyboard
   Put signal in Abs.
   MODE in CONT.

2. Aspirate a standard with an absorbance of about 0.200 and adjust the burner head towards the back of the instrument. Adjust to the highest Abs. reading on the display.

E. Nebulizer Adjustment

With the first element of the day, clean neubulizer with brass cleaning wire and adjust the neubulizer as follows:

1. Aspirate the standard and open the neubulizer with the silver ring until air bubbles begin to appear in the standard.

2. Adjust the silver ring to the highest Abs. reading that can be obtained.

3. Tighten locking nut.

Now the instrument is ready for the day. The following two methods can be used to determine the metals content.

1. Auto-concentration.

2. Standard-additions.

See the section on each procedure for further instructions.

F. Nitrous Oxide-Acetylene Flame Ignition and Analysis

1. Follow A, B and C (steps 1-3) of this instrument operating procedure through the ignition of the air-acetylene flame using the 5 cm burner head and flow spoiler for nitrous oxide-acetylene analysis.

2. Set the nitrous oxide tank output regulator to between 40 to 85 psig.

3. With the air-acetylene flame lit adjust fuel and oxidated rates until a white flame is achieved, then switch over to the nitrous oxide-acetylene flame.

4. Once the nitrous oxide-acetylene flame is ignited, adjust the oxidant and fuel rates to achieve a flame with a rose-red inner core approximately 1/2-3/4 in. high.

5. Aspirate a standard with an absorbance of about 0.200. Maximize this reading by adjusting the burner head (do not raise or lower the head) and aspiration rate.

6. While aspirating a blank, press the auto zero button. Aspirate standards and record the absorbances. Analyze an EPA reference standard to verify the curve. The reference standard must be within the 95% confidence limits before continuing.

7. Analyze samples. Refer to specific metal standard operating procedures for notes on interferences, use of matrix modifiers, quality control and any other adjustments to this instrument operating procedure.

8. Switch back to the air-acetylene flame when done.

G. Flame Emission Analysis

1. Follow parts A, B and C (steps 1-4) as if you were setting up to run copper. All conditions (burner head alignment, fuel and oxidant rates, aspiration rate, etc) must be maximized before switching to emission.

2. Unplug the copper lamp.

3. Set the required wavelength and slit width for the metal which is to be analyzed by emission spectroscopy.

4. Set the signal to EM, mode to CONT.
   While aspirating a blank, press the auto zero button.

5. While aspirating a standard of concentration at the high end of the optimum range, set the gain to about 75. Using the wavelength fine adjustment knob, maximize the gain reading. Turn the gain back to 75. This peaks out the wavelength.

6. Then aspirate standards and record the emission readings (The gain readings and emission readings will increase as the concentrations of standards aspirated increase.) Analyze an EPA reference standard to verify the curve. The reference standard must be within the 95% confidence limits before continuing. Refer to standard operating procedures for each metal for specific requirements.

7. Analyze samples. Refer to standard operating procedures for quality control and any other specific requirements and notes.

## H. Auto-Concentration

The machine is calibrated against one to three standards. The standard curve is drawn as a straight line between the zero and $S_1$. Again, a straight line is drawn between $S_1$ to $S_2$, and $S_2$ to $S_3$.

(See Figure 1) MetalFl1-7

If you should encounter an error code during calibration, the operator's manual has a listing of error codes and their meanings.

| | |
|---|---|
| Signal - Conc. | t = 2 sec. |
| Mode - Hold | Ave - 3 |

Type the $S_1$ value and push $S_1$ button
Type the $S_2$ value and push the $S_2$ button

### Procedure

1. Aspirate the blank and auto-zero (AZ)

2. Aspirate $S_1$ standard, push the $S_1$ button. Repeat until desired number of standards are entered.

3. Aspirate samples, check standards during the run, re-standardize if necessary.

## Notes

You can AZ any time during a run.
If you re-standarize this $S_1$ value, you have to re-standardize the $S_2$ and $S_3$.

## I. Method of Standard Addition

The method of standard additions is a useful tool which enables us to achieve an accurate determination of an element in the presence of an interference. Standard additions are required for EP Toxicity metals.

For an accurate value of an element, the working curve must be linear throughout the range of concentration encountered by the samples plus the additions.

SIGNAL - ABS t - 2 sec.

MODE - HOLD Ave - 3

## Procedure

1. Take four aliquots of the sample at a set volume.
2. Add the same volume of blank to the first beaker.
3. Add the same volume of successive standards to the remaining beakers.
4. Mix by swirling.

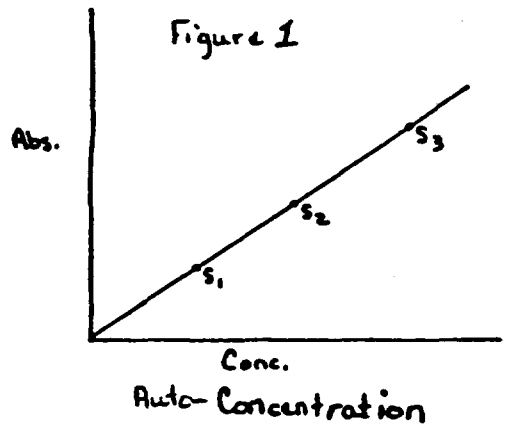
| Example - | Beaker 1 | Beaker 2 | Beaker 3 | Beaker 4 |
|---|---|---|---|---|
| | 3 ml sample<br>3 ml blank | 3 ml sample<br>3 ml 1 PPM Std. | 3 ml sample<br>3 ml 2 PPM Std. | 3 ml sample<br>3 ml 4 PPM Std. |

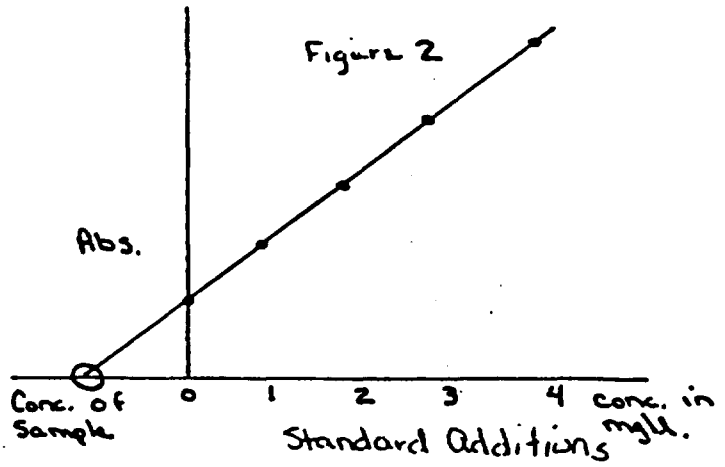
5. Aspirate the reagent blank and Auto-zero (A.Z.)
6. Aspirate the sample beakers from the blank to the highest spiked beaker.
7. Record all four absorbance readings for the sample.

## Calculations

Plot the absorbance readings against the concentrations of the standards added. The intercept of the concentration axis equals the concentration of the element in the sample. (See figure 2 on following page). Linear regression may be used.

Note: When doing furnace Std. Additions, pipet 1/2 ml of sample and standard directly into the cups. Mix thoroughly.




J. General Instrument Shut-down

1. Turn off the air-acetylene flame by first turning off the fuel supply, then turning off the oxidant supply. (The order is important or a flashback may occur!) Turn B.G. corrector to the A.A. Position, Signal to Lamp.

2. Turn off the gas tanks and air supply. Bleed lines of all gases.

3. Turn off the lamp. Be careful to store hot EDL's in a horizontal position. Put lamps away.

4. Turn the gain counter clockwise as far as it will go.

5. Turn off the P.E. 2380 power switch.

6. Put burner head in D.I. water overnight.

7. Rinse the burner chamber with D.I. water.

K. Atomic Absorption - Maintenance

The daily and weekly and monthly maintenance procedures are discussed in this section.

## Daily Cleaning Schedule

### 1. Burner Heads

Due to the nature of our samples (mainly high dissolved solids) clean the burner head daily. Proceed as follows:

a. Soak the burner heads in a weak detergent solution, overnight.

b. In the morning, rinse the burner head with D.I. water and wipe dry.

c. Replace the burner head in the burner chamber.

d. Using a name card or equivalent, clean the burner head slot.

e. Press the oxidant button on the A.A. (this forces air through the burner head) wipe off excess water expelled.

### 2. Burner Chamber

a. Rinse the chamber at the end of each day.

1. Remove burner head.

2. Pour D.I. water into burner chamber. This flushes the drain system as well as the burner chamber.

### 3. Windows

Check the windows of the A.A., if they are dirty, clean with isopropol alcohol; rinse with D.I. water.

### 4. Nebulizer

Each morning, push the brass wire through the capillary. This will dislodge any solid particles.

If you notice a low sensitivity reading or the capillary isn't aspirating as fast as before, repeat the above procedure.

## Weekly Cleaning Schedule

### 1. Empty the drain jug

a. Empty jug into sink, being careful due to the acid content.

b. Rinse the jug with tap water.

c. Fill the jug with D.I. water to a few inches above the drain hose. Water must cover the hose or a flashback may occur.

2. Cleaning the neubilizer

a. Remove neubulizer from the burner.

b. Unscrew the neubilizer.

c. Carefully pull out the needle assembly (good picture in P.E. Model 2380 Atomic Absorption Manual page 12-6.)

d. Remove front end cap and O-ring.

e. Clean each section with soap and water. Rinse thoroughly.

f. Lightly grease the O-rings ( may be found in top drawer by A.A.)

3. Cleaning the Neubilizer Assembly

a. Put the neublizer together, being careful the needle into the main component with the needle or face is facing the opening in the body.

b. Continue to reassemble the nebulizer.

c. Insert the nebulizer in the burner

d. Adjust the aspiration rate as described in the set-up procedure

Monthly Cleaning Schedule

1. Clean the entire A.A. burner and drain system.

a. Aspirate a ten percent detergent for 10-15 minutes.

b. Aspirate D.I. water for 30 minutes to flush system thoroughly.

2. Drain air compressor and change the air filter if necessary.

3. Nebulizer (Refer to figure 2)

a. Cleaning the nebulizer

1. Remove the black nebulizer oxidant tubing and loosen the clamp screw. Remove the nebulizer from the burner end cap.

2. Unscrew and remove the knurled knob (1) and washer (3)

3. Carefully pull out the needle assembly (4) and inspect the inner end for deposits. Clean if required and lay aside.

4. Remove O-ring from the other end (12), unscrew and remove the front end cap (11), and pull out the venturi (10).

5. Remove the insert (8) by pushing out with a wooden probe (pencil).

6. Clean all components with soap and water, gently using a scrub pad and without scratching metal (soaking may be used on difficult deposits.

7. Inspect O-rings (replace when necessary), clean with soap and water, dry and lightly grease (special grease is in top drawer by A.A.)

b. Assembling the nebulizer

1. Slide the needle assembly into the insert as far as it will go, and replace into the left end of the nebulizer body.

   Note Make sure the slanted needle opening is facing the opening of the body.

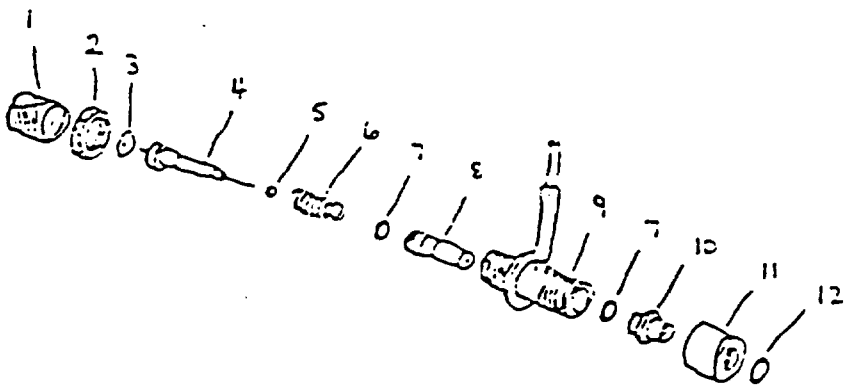
2. Replace the washer and knurled knob (the needle tip should protrude from the small aperture in the insert end).

3. Install the venturi over the needle tip; put on and tighten the front end cap and replace the o-ring on the end of the venturi.

4. Insert the nebulizer back in the burner, connect the oxidant tubing and tighten the clamp screw.

5. Adjust the aspiration rate and lock setting with the locking ring (2).

Nebulizer




1) Knurled Knob
2) Locking Ring
3) Washer
4) Needle Assembly
5) O-Ring
6) Spring
7) O-Ring (2)
8) Insert
9) Nebulizer Body
10) Venturi
11) Front End Cap
12) O-Ring

Quality Control:

1. Refer to specific metal standard operating procedures.

Notes:

1. Refer to Perkin-Elmer Operating Procedures manual for further instructions.

2. Intermediate standards must be prepared fresh from purchased stock solutions every 6 months. Working standards must be prepared fresh every 2 months.

3. Standards are to be prepared in the same acid concentration as the samples being analyzed.

| | Revision Date |
|---|---|
| Michael Linskens<br>Michael J. Linskens<br>Laboratory Manager | 11-14-86 |
| Kim Finner<br>Kim D. Finner<br>Analytical Laboratory QA Officer | 4-13-87 |
| Thomas J. Lynch<br>Thomas J. Lynch<br>QA Officer | |

# ALUMINUM

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 202.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.20 mg/L

**Optimum Concentration Range:** 0.20 - 50.0 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Aluminium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 309.3 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 5.00, 10.0, 20.0, 50.0 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Aluminum Solution (100 mg/L Aluminum): Pipet 10 mL of the 1000 ppm stock aluminum solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Aluminum Standard | Dilute to |
|---|---|---|
| 5.00 mg/L | 0.5 mL of 1000 mg/L Al | 100 mL |
| 10.0 mg/L | 1 mL of 1000 mg/L Al | 100 mL |
| 20.0 mg/L | 2 mL of 1000 mg/L Al | 100 mL |
| 50.0 mg/L | 5 mL of 1000 mg/L Al | 100 mL |

3. Potassium Chloride Solution: In a 1 liter volumetric flask, dissolve 95g KCL in Milli-Q water and dilute to the mark.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentration as the samples being analyzed.

3. The use of background correction is required.

4. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem can be controlled by the addition of potassium. Add 2 mL of 1000 ppm potassium to 100 mL samples, blanks and standards.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If aluminum is to be run in concentration mode, use the 10.0 and 50.0 mg/L aluminum standards for standardization and follow the procedure for analyzing in concentration mode.

To 10 mL of samples, blanks and standards, add 0.2 mL KCL solution. Mix and analyze.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 10.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

[ALM-8-15]

# ANTIMONY

**Method**: AA - Furnace; Direct Injection

**Reference**: EPA 1983, Method 204.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contact Laboratory Program, "Statements of Work", July, 1985

**Detection Limit**: 0.005 mg/L

**Optimum Concentration Range**: 0.005 - 0.050 mg/L

**Instrument Conditions**:

1. Antimony electrodeless discharge lamp with lamp energy set at 7.
2. Wavelength: 217.6 nm
3. Slit Width: 0.2 Alternate
4. Mode: Peak Height
5. HGA Furance Programming:

   Step 1: 120 (dry temp) 10 (ramp time) 20 (hold time)
   Step 2: 900 (char temp) 5 (ramp time) 20 (hold time)
   Step 3: 2400 (atom temp) 0 (ramp time) 3 (hold time)

   * Also press the read, record and stop flow buttons; t = 3 sec.

   Step 4: 2400 (max temp) 0 (ramp time) 3 (hold time)

   Press the record button.

6. Sample Volume : 20 uL
7. Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.
8. Platform is required.

**Sample Handling**: Acidify with nitric acid to pH <2. Analyze within 6 months.

[C-600-91a]

Reagent Preparation:

1. Standard Antimony Solution (1000 ug/L Antimony): Pipet 1.00 mL of the 1000 ppm stock antimony solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$ and dilute to the mark with D.I. water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Antimony Standard | Dilute to |
|---|---|---|
| 10.0 ug/L | 1 mL of 1000 ug/L Sb | 100 mL |
| 20.0 ug/L | 2 mL of 1000 ug/L Sb | 100 mL |
| 50.0 ug/L | 5 mL of 1000 ug/L Sb | 100 mL |

3. Nickel Nitrate 5% Solution: Dissolve 25.0g of nickel nitrate in 100 mL of D.I. water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The use of halide acids should be avoided.

5. Nickel nitrate is added as a matrix modifier to control interferences.

6. Platform technique is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

To 5 mL of samples, blanks, and standards add 0.1 mL of Ni $(NO_3)_2$ solution.

For the use of concentration mode, use the 20.0 and 50.0 standards and follow the procedure for using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If

not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Digest a duplicate and spike; a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within an acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85-115%, standard additions are not required.

   b. If the spike recovery is outside 85-115%, standard additions are required.

5. An EPA reference standard will be analyzed with each analysis.

<u>Calculations</u>:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# ANTIMONY

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 204.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.50 mg/L

**Optimum Concentration Range:** 0.50 - 20.0 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Antimony electrodeless discharge lamp with lamp energy set at 7.
2. Wavelength: 217.6 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 2.00, 5.00, 10.0, 20.0 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Antimony Solution (100 mg/L Antimony): Pipet 10 mL of the 1000 ppm stock antimony solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Antimony Standard | Dilute to |
|---|---|---|
| 2.00 mg/L | 2 mL of 100 mg/L Sb | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Sb | 100 mL |
| 10.0 mg/L | 10 mL of 100 mg/L Sb | 100 mL |
| 20.0 mg/L | 20 mL of 100 mg/L Sb | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where high concentrations of antimony are expected and low detection limits are not required.

5. Lead, in concentrations of >100 mg/L, may interfere. Use an alternate wavelength of 231.1 nm in this situation.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If antimony is to be analyzed in concentration mode, use the 10.0 and 20.0 standards for standardization and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

# ARSENIC

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 206.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Analyzed within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

1. Arsenic electrodeless discharge lamp with lamp energy set at 8.
2. Wavelength: 193.7 nm
3. Slit Width: 0.7 Alternate
4. Mode: Peak height
5. HGA Furnace Programming:

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1: | 130 | (dry temp) | 10 | (ramp time) | 20 | (hold time) |
| Step 2: | 1300 | (char temp) | 10 | (ramp time) | 10 | (hold time) |
| Step 3: | 2500 | (atom temp) | 0 | (ramp time) | 3 | (hold time) |

* Also press the read, record and stop flow buttons; enter t = 3 sec.

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 4: | 2500 | (max temp) | 0 | (ramp time) | 3 | (hold time) |

Press record button.

6. Sample Volume: 20 uL
7. Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.
8. Pyrolytic tubes must be used.

Reagent Preparation:

1. Standard Arsenic Solution (1000 ug/L Arsenic): Pipet 1.00 mL of the 1000 ppm stock arsenic solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Arsenic Standard | Dilute to |
|---|---|---|
| 0 ug/L | 0 mL of 1000 ug/L As | 100 mL |
| 5 ug/L | 1/2 mL of 1000 ug/L As | 100 mL |
| 10 ug/L | 1 mL of 1000 ug/L As | 100 mL |
| 20 ug/L | 2 mL of 1000 ug/L As | 100 mL |
| 50 ug/L | 5 mL of 1000 ug/L As | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Nickel nitrate is added as a matrix modifier to minimize volatilization losses during the drying and charring steps.

4. The use of the background correction is required.

5. High concentrations of phosphorus interfere with this procedure. The gaseous hydride method for arsenic should be used in these cases.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Prior to Analysis: To 5 mL of digested sample or standard, add 0.1 mL of 5% nickel nitrate solution. Mix well.

If Arsenic is to be analyzed in concentration mode, use the 20 and 50 ug/L arsenic standards and the procedures for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. A digested duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# BARIUM

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 208.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

**Detection Limit:** 0.20 mg/L

**Optimum Concentration Range:** 0.20 - 10.0 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Barium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 553.6 nm
3. Slit Width: 0.2
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Barium Solution (100 mg/L Barium): Pipet 10 mL of the 1000 ppm stock barium solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$ and dilute to the mark with Milli-Q water.

2. Standards (Prepare fresh every 1 month.):

| Concentration of Standard | Volume of Barium Standard | Dilute to |
|---|---|---|
| 1.00 mg/L | 1 mL of 100 mg/L Ba | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Ba | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Ba | 100 mL |
| 10.0 mg/L | 10 mL of 100 mg/L Ba | 100 mL |

3. Potassium chloride solution: In a 1 liter volumetric flask, dissolve 95g KCl in Milli-Q water and dilute to the mark.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Barium is easily ionized in the nitrous oxide-acetylene flame. This can be controlled by the addition of potassium. Add 2 mL of 1000 ppm potassium to 100 mL sample and standards.

4. High calcium can cause an extremely noisy signal and high false positive values.

5. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

Potassium chloride solution is added as a matrix modifier to the samples and standards at a ratio of 0.2 mL KCL to 10 mL of sample or standard.

If barium is to be run in concentration mode, use the 5.00 and 10.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

# BERYLLIUM

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 210.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.02 mg/L

**Optimum Concentration Range:** 0.02 - 2.00 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Beryllium hollow cathode lamp with lamp energy set at 30.
2. Wavelength: 234.9 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 0.20, 0.50, 1.00, 2.00 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Beryllium Solution (10.0 mg/L Beryllium): Pipet 10 mL of the 1000 ppm stock beryllium solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Beryllium Standard | Dilute to |
|---|---|---|
| 0.20 mg/L | 2 mL of 10.0 mg/L Be | 100 mL |
| 0.50 mg/L | 5 mL of 10.0 mg/L Be | 100 mL |
| 1.00 mg/L | 10 mL of 10.0 mg/L Be | 100 mL |
| 2.00 mg/L | 20 mL of 10.0 mg/L Be | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Sodium and silicon in excess of 1000 mg/L severely depress the absorbance for beryllium. The addition of oxine (8-hydroxyquinoline) as a matrix modifier will control these interferences.

5. Aluminum of concentrations of 500 ug/L will depress the sensitivity.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If beryllium is to be run in concentration mode, use the 1.00 and 2.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression.

3. Calculate using the concentration mode.

[ALM-10-2]

# CADMIUM

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 213.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.01 mg/L

**Optimum Concentration Range:** 0.01 - 1.00 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Cadmium hollow cathode lamp with lamp energy set at 4.
2. Wavelength: 228.8 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.10, 0.20, 0.50, 1.00 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Cadmium Solution (10.0 mg/L Cadmium): Pipet 1 mL of the 1000 ppm stock cadmium solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$ and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Cadmium Standard | Dilute to |
|---|---|---|
| 0.10 mg/L | 1 mL of 10.0 mg/L Cd | 100 mL |
| 0.20 mg/L | 2 mL of 10.0 mg/L Cd | 100 mL |
| 0.50 mg/L | 5 mL of 10.0 mg/L Cd | 100 mL |
| 1.00 mg/L | 10 mL of 10.0 mg/L Cd | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples, or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If cadmium is to be run in the concentration mode, use the 0.50 and 1.00 standards and follow the procedure for analyzing in concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.10 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

[ALM8-10]

# CADMIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 213.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

Detection Limit: 0.0002 mg/L

Optimum Concentration Range: 0.0002 - 0.0020 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. All samples must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Cadmium hollow cathode lamp with lamp energy set at 4.

2. Wavelength: 228.8 nm

3. Slit Width: 0.7 Alternate

4. Mode: Peak area

5. HGA Furnace Programming:

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1: | 120 | (dry temp) | 10 | (ramp time) | 20 | (hold time) |
| Step 2: | 250 | (char temp) | 10 | (ramp time) | 20 | (hold time) |
| Step 3: | 2100 | (atom temp) | 2 | (ramp time) | 3 | (hold time) |

* Also press the read, record and stop flow buttons; enter t = 5 sec

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 4: | 2700 | (max temp) | 1 | (ramp time) | 5 | (hold time) |

Press record button.

6. Sample Volume: 20 uL

7. Standards to use for curve set-up: 0.50, 1.00, 2.00, ug/L

8. Pyrolytic tubes must be used.

Reagent Preparation:

1. Standard Cadmium Solution (1000 ug/L Cadmium): Pipet 1.00 mL of the 1000 ppm stock cadmium solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Working Cadmium Solution (100 ug/l Cadmium): Pipet 10 mL of the 1000 ug/l cadmium into a 100 mL volumetric flask and dilute to the mark with Milli-Q water. Prepare fresh every month.

3. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Cadmium Standard | Dilute to |
|---|---|---|
| 0.00 ug/L | 0 mL of 100 ug/L Cd | 100 mL |
| 0.50 ug/L | 0.5 mL of 100 ug/L Cd | 100 mL |
| 1.00 ug/L | 1 mL of 100 ug/L Cd | 100 mL |
| 2.00 ug/L | 2 mL of 100 ug/L Cd | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The cadmium flame procedure is recommended where concentrations of greater than 0.10 mg/L are expected.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use of peak area is required.

If cadmium is to be analyzed in concentration mode, use the 1.00 and 2.00 ug/L cadmium standards and follow the procedures for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 1.00 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. A digested duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. peak area on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

Revision Dates

9/25/87

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

Kim Finner
Kim D. Finner
Analytical Laboratory QA Officer

Lawrence D. Andersen
Lawrence D. Andersen
Vice President, Technical Services

# CALCIUM

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 215.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.05 mg/L

**Optimum Concentration Range:** 0.05 - 25.0 mg/L

**Sampling Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. The Ca-Mg combination hollow cathode lamp is used. Set lamp energy to 25.
2. Wavelength: 422.7 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 2.00, 5.00, 10.00, 25.0 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Calcium Solution (100 mg/L Calcium): Pipet 10 mL of the 1000 ppm stock calcium solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every 2 months.):

| Concentration of Standard | Volume of Calcium Standard | Dilute to |
|---|---|---|
| 2.00 mg/L | 2 mL of 100 mg/L Ca | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Ca | 100 mL |
| 10.0 mg/L | 10 mL of 100 mg/L Ca | 100 mL |
| 25.0 mg/L | 25 mL of 100 mg/L Ca | 100 mL |

3. Lanthanum Chloride Solution: In a 500 mL volumetric flask, dissolve 29g of $La_2O_3$ slowly and in small portions, in 250 mL conc. HCL (CAUTION: Reaction is violent!) and dilute to 500 mL with Milli-Q water.

**Notes:**

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Silicon, aluminum, phosphate and sulfate depress the signal for calcium. Lanthanum chloride is added as a matrix modifier to control these interferences.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual but make the following changes:

1. Turn the burner head counter clockwise as far as it will go (approximately a 45° angle).

2. Lanthanum chloride solution is added as a matrix modifier to the samples and standards in a ratio of 1.0 mL lanthanum chloride solution to 10 mL samples, blanks and standards.

3. If calcium is to be run in the concentration mode, use the 5.00 and 25.0 standards and follow the procedure for analyzing in concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 10.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

**Calculations:**

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression.

3. Calculate using the concentration mode.

| | Revision Date |
|---|---|
| Michael Linskens 1/4/88<br>Michael J. Linskens<br>Laboratory Manager | 11-14-86 |
| | 4-13-87 |
| Kim Finner 1/6/88<br>Kim D. Finner<br>Analytical Laboratory QA/QC Officer | 1-6-88 |
| Lawrence D. Andersen 1/6/88<br>Lawrence D. Andersen<br>Vice President, Technical Services | |

[ALM-8-7]

# CHROMIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 218.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH $< 2$. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Chromium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 357.9 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Reducing, rich, yellow
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.

1. Standard chromium solution (100 mg/L Chromiumn): Pipet 10 mL of the 1000 ppm stock chromium solution into a 100 mL volumetric flask, add 1/2 mL $HNO^3$, and dilute to the mark with DI water.

[V-600-99A]

2. Standards (Prepare fresh every 2 months.):

| Concentration of Standard | Volume of Chromium Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 0.5 mL of 100 mg/L Cr | 100 mL |
| 1.00 mg/L | 1 mL of 100 mg/L Cr | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Cr | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Cr | 100 mL |

3. Ammonium bifluoride (10%): Dissolve 10g of ammonium bifluoride and 2g of sodium sulfate in DI water. Dilute to 100 mL.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. A solution of ammonium bifluoride and sodium sulfate is added as a matrix modifier to control interferences from iron, nickel and other metals.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not requi$d.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

Add 1 ml of ammonium bifluoride solution to 10 ml of samples, blanks, and standards.

If chromium is to be run in the concentration mode, use the 2.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

[V-600-99A]

2. A quality control calibration standard of 2.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

# CHROMIUM

**Method:** AA - Furnace; Direct Injection

**Reference:** EPA 1983, Method 218.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July, 1985

**Detection Limit:** 0.0002 mg/L

**Optimum Concentration Range:** 0.0002 - 0.010 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Chromium hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 357.9 nm
3. Slit Width: 0.7 Alternate
4. Mode: Peak height
5. HGA Furnace Programming:

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1: | 130 | (dry temp) | 15 | (ramp time) | 15 | (hold time |
| Step 2: | 1000 | (char temp) | 10 | (ramp time) | 15 | (hold time |
| Step 3: | 2300 | (atom temp) | 0 | (ramp time) | 3 | (hold time |

* Also press the read, record and stop flow buttons; enter t = 3

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 4: | 2300 | (max temp) | 0 | (ramp time) | 3 | (hold tim |

Press the record button.

6. Sample Volume: 20 uL
7. Standards to use for curve set-up: 1.00, 5.00, 10.0 ug/L.

Reagent Preparation:

1. Standard Chromium Solution (1000 ug/L Chromium): Pipet 1.00 mL of the 1000 ppm stock Chromium solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Working Chromium Standard (100 ug/L Chromium): Pipet 10 mL of the 1000 ug/L chromium into a 100 mL volumetrick flask and dilute to the mark with Milli-Q water. Prepare fresh every month.

3. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Chromium Standard | Dilute to |
|---|---|---|
| 1.00 ug/L | 1.0 mL of 100 ug/L Cr | 100 mL |
| 5.00 ug/L | 5.0 mL of 100 ug/L Cr | 100 mL |
| 10.0 ug/L | 10.0 mL of 100 ug/L Cr | 100 mL |

4. Calcium Nitrate: 11.8g $Ca(NO_3)_2$, dilute to 100 mL a volumetric flask.

5. Hydrogen Peroxide: 30% $H_2O_2$, purchased.

6. Mixed $Ca(NO_3)$ + $H_2O_2$ Solution: 10 mL $Ca(NO_3)_2$ mL in a volumetric flask solution + 10 mL $H_2O_2$, dilute to 100 mL.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Low concentrations of calcium may cause interferences, yet at concentrations above 200 mg/L calcium, the effect is constant. To ensure a constant effect, calcium is added as a matrix modifier.

4. 30% hydrogen peroxide is added (1 mL of 30% $H_2O_2$ to 100 mL sample and standards) to convert all chromium to the trivalent state.

5. Be careful when reporting units!

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

To 10 mL of samples, standards, and blanks add 1 mL of the $Ca(NO_3)$ + $H_2O_2$ solution.

If chromium is to be analyzed in concentration mode, use the 5.00 and 10.0 ug/L chromium standards and follows the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 5.0 ug/l is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Digest a duplicate and spike; a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85-115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

| | Revision Date |
|---|---|
| Michael Linskens 1/4/88<br>Michael J. Linskens<br>Laboratory Manager | 11-14-86<br>4-13-87 |
| Kim Finner 1/6/88<br>Kim D. Finner<br>Analytical Laboratory QA/QC Officer | 1-6-88 |
| Lawrence D. Andersen 1/6/88<br>Lawrence D. Andersen<br>Vice President, Technical Services | |

# COBALT

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 219.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.05 mg/L

**Optimum Concentration Range:** 0.05 - 5.00 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Cobalt hollow cathode lamp with lamp energy set at 7.
2. Wavelength: 240.7 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

**Reagent Preparation:** Prepare fresh every 6 months unless otherwise noted.

1. Standard Cobalt Solution (10.0 mg/L Cobalt): Pipet 1.0 mL of the 1000 ppm stock cobalt solution into a 100 mL volumetric flask, add 1/2 ml $HNO_3$ and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Cobalt Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 5 mL of 10.0 mg/L Co | 100 mL |
| 1.00 mg/L | 10 mL of 10.0 mg/L Co | 100 mL |
| 2.00 mg/L | 20 mL of 10.0 mg/L Co | 100 mL |
| 5.00 mg/L | 50 mL of 10.0 mg/L Co | 100 mL |

**Notes:**

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where high concentrations of cobalt (concentrations greater than 0.50 mg/L) are expected and low detection limits are not required.

**Procedure:** For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If cobalt is to be analyzed in concentration mode, use the 2.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

**Quality Control:**

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

[ALM-8-14]

# COPPER

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 220.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.02 mg/L

**Optimum Concentration Range:** 0.02 - 5.00 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestions procedures). Analyze within 6 months.

**Instrument Conditions:**

1. The Copper hollow cathode lamp is used. Set lamp energy to 18.
2. Wavelength: 324.7 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Copper Solution (100 mg/L Copper): Pipet 10 mL of the 1000 ppm stock copper solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Copper Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 0.5 mL of 100 mg/L Cu | 100 mL |
| 1.00 mg/L | 1 mL of 100 mg/L Cu | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Cu | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Cu | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If copper is to be run in the concentration mode, use the 2.00, and 5.00 mg/L copper standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# IRON

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 236.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.05 mg/L

**Optimum Concentration Range:** 0.05 - 5.00 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. The Iron hollow cathode lamp is used. Set lamp energy to 18.
2. Wavelength: 248.3 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

**Reagent Preparation:** (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Iron Solution (100 mg/L Iron): Pipet 10 mLs of the 1000 ppm stock iron solution into a 100 mL volumetric flask, add 1/2mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Iron Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 1/2 mL of 100 mg/L Fe | 100 mL |
| 1.00 mg/L | 1 mL of 100 mg/L Fe | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Fe | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Fe | 100 mL |
| 10.0 mg/L | 10 mL of 100 mg/L Fe | 100 mL |
| 25.0 mg/L | 25 mL of 100 mg/L Fe | 100 mL |
| 50.0 mg/L | 50 mL of 100 mg/L Fe | 100 mL |
| 75.0 mg/L | 75 mL of 100 mg/L Fe | 100 mL |

Notes:

1. Be very careful when scaling in wavelength, a nearby one exists.

2. Samples must be diluted to obtain concentrations within the optimum concentration range.

3. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

4. The use of background correction is required.

5. An alternate wavelength of 373.7 nm can be used for high iron concentrations (concentrations greater than 5.00 mg/L). The optimum concentration range at this wavelength is 1.00 - 100 mg/L iron. Standards to use are: 1.00, 10.0, 25.0, 50.0 mg/L. The quality control calibration standard is the 10.0 mg/L iron standard. All other instrument conditions remain the same as those at the 248.3 nm wavelength.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If iron is to be run in the concentration mode, use the 2.00 and 5.00 mg/L iron standards (use the 25.0 and 75.0 mg/L iron standards if using the 373.7 nm wavelength) and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

[ALM-8-3]

# LEAD

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 239.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.10 mg/L

**Optimum Concentration Range:** 0.10 - 10.0 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

**Instrument Conditions:**

1. Lead electrodeless dishcarge lamp with lamp energy set at 10.
2. Wavelength: 283.3 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

**Reagent Preparation:** Prepare fresh every 6 months unless otherwise noted.

1. Standard Lead Solution (100 mg/L Lead): Pipet 10 mL of the 1000 ppm stock lead solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.

2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Lead Standard | Dilute to |
|---|---|---|
| 1.00 mg/L | 1 mL of 100 mg/L Pb | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Pb | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Pb | 100 mL |
| 10.0 mg/L | 10 mL of 100 mg/L Pb | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If lead is to be analyzed by the concentration mode, use the 5.00 and 10.00 mg/L lead standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates must be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

# LEAD

**Method:** AA - Furnace; Direct Injection

**Reference:** EPA 1983, Method 239.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Contract Laboratory Program, "Statement of Work", July 1985

**Detection Limit:** 0.003 mg/L

**Optimum Concentration Range:** 0.003 - 0.050 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Lead electrodeless discharge lamp with lamp energy set at 10.
2. Wavelength: 283.3 nm
3. Slit Width 0.7 Alternate
4. Mode: Peak height
5. HGA Furnace Programming:

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1: | 130 | (dry temp) | 10 | (ramp time) | 20 | (hold time) |
| Step 2: | 500 | (char temp) | 15 | (ramp time) | 10 | (hold time) |
| Step 3: | 2400 | (atom temp) | 2 | (ramp time) | 2 | (hold time) |

* Also press the read, record and stop flow buttons; enter t = 4 sec.

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 4: | 2400 | (max temp) | 2 | (ramp time) | 2 | (hold time) |

Press record button.

6. Sample Volume: 20 uL
7. Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.

Reagent Preparation:

1. Standard Lead Solution (1000 ug/L Lead): Pipet 1.00 mL of the 1000 ppm stock lead solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Lead Standard | Dilute to |
|---|---|---|
| 5.0 ug/L | 1/2 mL of 1000 ug/L Pb | 100 mL |
| 10.0 ug/L | 1 mL of 1000 ug/L Pb | 100 mL |
| 20.0 ug/L | 2 mL of 1000 ug/L Pb | 100 mL |
| 50.0 ug/L | 5 mL of 1000 ug/L Pb | 100 mL |

3. Lanthanum Nitrate Solution: Dissolve 58.64g of $La_2O_3$ in 100 mL concentrated nitric acid and dilute to 1000 mL with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Sulfate is a negative interference for lead. Lanthanum nitrate solution is added as a matrix modifier in a 1:10 ratio of lanthanum nitrate to sample and standards prior to analysis.

5. Be careful when reporting units!

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

To 10 mL samples, blanks and standards, add 1 mL of $La(NO_3)_2$ solution.

If lead is to be analyzed in concentration mode, use the 20.0 and 50.0 ug/L lead standard and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/l is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Digest a duplicate and spike; a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a digested duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution, or method of standard additions is to be applied to reduce the interferences.

4. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85-115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required.

5. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

| | Revision Date |
|---|---|
| Michael Linskens 1/4/87<br>Michael J. Linskens<br>Laboratory Manager | 11-14-86 |
| | 4-13-87 |
| Kim Finner 1/6/88<br>Kim D. Finner<br>Analytical Laboratory QA/QC Officer | 1-6-88 |
| Lawrence Andersen 1/6/88<br>Lawrence D. Andersen<br>Vice President, Technical Services | |

# MAGNESIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 242.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.05 mg/L

Optimum Concentration Range: 0.05 - 10.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. The Ca-Mg combination hollow cathode lamp is used. Set lamp energy to 25.
2. Wavelength: 285.2 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Magnesium Solution (100 mg/L Magnesium): Pipet 10 mL of the 1000 ppm stock magnesium solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Magnesium Standard | Dilute to |
|---|---|---|
| 1.0 mg/L | 1 mL of 100 mg/L Mg | 100 mL |
| 2.0 mg/L | 2 mL of 100 mg/L Mg | 100 mL |
| 5.0 mg/L | 5 mL of 100 mg/L Mg | 100 mL |
| 10.0 mg/L | 10 mL of 100 mg/L Mg | 100 mL |

3. Lanthanum Chloride Solution: In a 500 mL volumetric flask, dissolve 29 g $La_2O_3$, in small portions, in 250 mL of concentrated HCL (CAUTION-Reaction is violent!), and dilute to mark with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Silicon and aluminium depress the signal for magnesium. Lanthanum chloride is added as a matrix modifier to control these interferences.

5. Sodium, POtassium and Calcium can interfere if above concentrations of 400 mg/L.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual but make the following changes:

1. Turn the burner head counter clockwise as far as it will go (approximately a 45° angle).

2. Lanthanum chloride solution is added as a matrix modifier to the samples, standards, and blanks, in a ratio of 1 mL Lanthanum chloride solution to 10 mL sample or standard.

3. If magnesium is to be analyzed in concentration mode, use the 5.0 and 10.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

**Calculations:**

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression.

3. Calculate using concentration mode.

[ALM-8-6]

# MANGANESE

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 243.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.02 mg/L

**Optimum Concentration Range:** 0.02 - 2.50 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. The Manganese hollow cathode lamp is used. Set lamp energy to 18.
2. Wavelength: 279.5 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.25, 0.50, 1.00, 2.50 mg/L.

**Reagent Preparation:** Prepare fresh every 6 months unless otherwise noted.

1. Standard Manganese Solution (100 mg/L Manganese): Pipet 10 mL of the 1000 ppm stock manganese solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$ and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Manganese Standard | Dilute to |
|---|---|---|
| 0.25 mg/L | 1/2 mL of 1.00 mg/L Mn | 100 mL |
| 0.50 mg/L | 1 mL of 50 mg/L Mn | 100 mL |
| 1.00 mg/L | 2 mL of 50 mg/L Mn | 100 mL |
| 2.50 mg/L | 5 mL of 50 mg/L Mn | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If manganese is to be run in the concentration mode, use the 1.00, and 2.50 mg/L manganese standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in a run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# TOTAL MERCURY
## Liquid Samples

Scope and Application: This method is applicable to drinking, surface, groundwater, domestic, and industrial wastewaters.

Method: Manual Cold Vapor

Reference: EPA 1983, Method 245.1

Detection Limits: 0.0002 mg/L (in 100 mL sample)

Optimum Range: 0.0002-0.010 mg/L

Sample Handling: Preserve with concentrated $HNO_3$ to pH <2. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Mercury cold-vapor Analyzer System
2. Water bath set @ 95*C
3. BOD bottles; 300 mL
4. Class A volumetric glassware
5. Instra-Analyzed sulfuric acid
6. Instra-analyzed nitric acid
7. Potassium persulfate
8. Potassium permanganate
9. Sodium chloride
10. Hydroxylamine hydrochloride solution
11. Stannous chloride
12. Various Class A volumetric pipettes
13. Mercury lamp
14. Mercury stock and standard solutions
15. Drierite
16. Activated charcoal
17. Glass wool
18. Tygon tubing

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Sulfuric acid (0.5 N): Pipet 14.0 mL of conc. $H_2SO_3$ to 500 mL D.I. water in a 1 liter volumetric flask, dilute to the mark. PREPARE IN THE HOOD!

2. Stannous chloride (10% w/v): Add 100.0 g stannous chloride to 1 liter of 0.5 N sulfuric acid.

[C-600-82]

3. Sodium chloride-hydrdoxylamine hydrochloride solution: Dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.

4. Potassium permanganate (5% solution, w/v): Dissolve 50.0 g of potassium permanganate in D.I. water, dilute to 1 liter.

5. Potassium persulfate (5% solution, w/v): Dissolve 50.0 g of potassium persulfate in D.I. water, dilute to 1 liter.

6. Intermediate mercury standard (10.0 mg/L): Transfer 1.0 mL stock mercury (1000 mg/L) solution, plus 1/2 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

7. Working mercury standard (0.100 mg/L): Transfer 1.0 mL of the 10.0 mg/L intermediate standard, plus 1/2 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

Notes:

1. The mercury standards are volatile and unstable. Standards must be prepared daily.

2. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.

3. A 10% solution of stannous sulfate may be substituted for stannous chloride.

4. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.

5. Standard additions must be used for all EP extracts and delisting petitions.

6. The calibration check standard is a 0.005 mg/L standard.

7. Interferences:

   a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.

   b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. during the oxidation step, chlorides are converted to free chlorine which also absorbs at the same wavelength as mercury. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. this may be accomplished by using an excess of hydroxylamine chloride reagent. In addition, the dead air space in the BOD bottle must be purged before adding the stannous sulfate.

d. Certain volatile organic materials that absorb at this wavelength may also cause an interference. A preliminary run without reagents should determine if this type of interference is present.

Instrument Conditions:

1. Mercury electrodeless discharge lamp with lamp energy set at 6.
2. Wavelength: 253.6 nm. Background is required.
3. Slit Width: 0.7
4. Mode: Peak height
5. Time = 25 seconds
6. Standards to use for curve set-up: 2.0, 5.0, 10.0 ug/L.

Cold Vapor System Set-up:

Cell Alignment:

1. Insert quart cell in burner chamber. (Replace the burner head in the burner chamber.)
2. Align cell in light path (use 0.5 sec t, adjust to the lowest abs. reading).
3. Check drying tube and charcoal tube - replace if necessary (see attached page).
4. Insert aerator into a BOD bottle filled with 100 mLs D.I. water.
5. Turn on pump. Turn on strip recorder.
6. Let warm-up a few minutes.
7. Zero machine.

Procedure:

All glassware is to be washed with soap and water, rinsed with tap water, acid rinsed with 10% $HNO_3$, and final rinsed with D.I. water.

A. Standard Preparation

1. The standard curve is to consist of the following standards:

| Standard Concentration |
|---|
| 0.00 ug/L |
| 2.00 ug/L |
| 5.00 ug/L |
| 10.0 ug/L |

2. Pipet 0, 2.0, 5.0, and 10.0 mL aliquots of 0.10 ug/mL working stock mercury solution to 300 mL BOD bottles.

3. Add D.I. water to bring volume to 100 mL and continue with the digestion procedure.

B. Sample Preparation:

1. Transfer 100 mL, or an aliquot diluted to 100 mL, to a 300 mL BOD bottle.

   To Spike: Pipette 5.0 mL of 0.10 mg/L standard into the sample bottle. Proceed as written.

C. Digestion:

1. Add 5 mL conc. sulfuric acid and 2.5 mL conc. nitric acid to each bottle. Mix by swirling.

2. Add 15 mL potassium permanganate solution to each bottle, mix by swirling. Allow to stand for at least 15 minutes. If the bottle does not remain purple in color, additional potassium permanganate is required.

3. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 hours in a water bath maintained at 95°C. Check the bottles periodically throughout the 2 hours to insure the samples remain purple. Add potassium permanganate if needed.

4. Cool to room temperature.

D. Sample Analysis:

1. Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce excess permanganate. If necessary, additional amounts of sodium chloride hydroxylamine hydrochloride may be required to discharge the purple color. Swirl.

2. Add 5 mL of stannous chloride solution and immediately insert the aerator, making sure that the stopper provides a good seal.

3. Press the read button.

4. Record the absorbance value on the bench sheet.

5. Remove the aerator, rinse aerator, and place it in the D.I. blank bottle.

6. Allow strip recorder to return to baseline.

7. Repeat for additional samples.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, tubing, lamp alignment, pump, etc.)

2. A quality control calibration standard of 0.005 mg/L is to be analyzed initially, and after every 10 samples. This standard is to be carried through the digestion procedure. If less than 10 samples are analyzed, a calibration standard is still required. The last sample must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike recoveries and duplicate results are to be within acceptable ranges or the use of matrix modifiers, dilution, or method of standard additions is to be applied to reduce the interferences.

Calculation:

1. Average the standard readings, subtract the absorbance of the blank standard from all readings.

2. Calculate using linear regression.

   Calculate the spike recovery as follows:

$$\% \text{ Recovery} = \frac{\text{ug (spike)} - \text{ug (sample)}}{0.5 \text{ ug}}$$

# NICKEL

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 249.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.04 mg/L

Optimum Concentration Range: 0.04 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. Nickel hollow cathode lamp with lamp energy set at 25.
2. Wavelength: 232.0 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standard Nickel Solution (100 mg/L Nickel): Pipet 10 mL of the 1000 ppm stock nickel solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepared fresh every month.):

| Concentration of Standard | Volume of Nickel Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 1/2 mL of 100 mg/L Ni | 100 mL |
| 1.00 mg/L | 1 mL of 100 mg/L Ni | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Ni | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Ni | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. A nearby wavelength is present. Take care in selection of this wavelength.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If nickel is to be run in the concentration mode, use the 2.00, 5.00 mg/L nickel standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate results are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# POTASSIUM

Method: Flame Emission; Direct Aspiration

Reference: "Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.10 mg/L

Optimum Concentration Range: 0.10 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Set signal to emission. (No lamp is required.)
2. Wavelength: 766.5 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Potassium Solution (100 mg/L Potassium): Pipet 10 mL of the 1000 ppm stock potassium solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Potassium Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 0.5 mL of 100 mg/L | 100 mL |
| 1.00 mg/L | 1 mL of 100 mg/L | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If potassium is to be analyzed in concentration mode, use the 2.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the check standard in the absorbance check book. The emission readings should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# SELENIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 270.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Instrument Conditions:

1. Selenium electrodeless discharge lamp with lamp energy set at 6.
2. Wavelength: 196.0 nm
3. Slit Width: 0.7 Alternate
4. Mode: Peak height
5. HGA Furnace Programming:

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1: | 130 | (dry temp) | 10 | (ramp time) | 20 | (hold time) |
| Step 2: | 850 | (char temp) | 10 | (ramp time) | 20 | (hold time) |
| Step 3: | 2200 | (atom temp) | 0 | (ramp time) | 3 | (hold time) |

* Also press the read, record and stop flow buttons

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 4: | 2500 | (max temp) | 2 | (ramp time) | 3 | (hold time) |

Press record button.

6. Sample Volume: 20 uL
7. Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.
8. Platform is required.

Sample Handling: Acidify with nitric acid to pH < 2. Analyze within 6 months.

Reagent Preparation:

1. Standard Selenium Solution (1000 ug/L Selenium): Pipet 1.00 mL of the 1000 ppm stock selenium solution into a 1000 mL volumetric flask, add 1/2 $HNO_3$, and dilute to the mark with Milli-Q water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Selenium Standard | Dilute to |
|---|---|---|
| 0 ug/L | 0 mL of 1000 ug/L Se | 100 mL |
| 5 ug/L | 1/2 mL of 1000 ug/L Se | 100 mL |
| 10.0 ug/L | 1 mL of 1000 ug/L Se | 100 mL |
| 20.0 ug/L | 2 mL of 1000 ug/L Se | 100 mL |
| 50.0 ug/L | 5 mL of 1000 ug/L Se | 100 mL |

3. Nickel Nitrate 5% Solution: Dissolve 25.0 grms of Nickel nitrate to 100 mLs of D.I. water

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards and samples are to be digested prior to analysis. (See AsSedig for aqueous samples and SoilDig for non-aqueous samples.)

3. Chloride (> 800 mg/L) and sulfate (> 200 mg/L) interfere with this selenium procedure. Nickel nitrate is added as a matrix modifier to minimize these interferences.

4. Background correction is required.

5. Selenium may also be analyzed by the gaseous hydride technique.

6. Platform technique is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For concentration mode, use the 20.0 and 50.0 standards and follow the procedure for analyzing using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standards. Spike recoveries and duplicates are to be within acceptable ranges or the use of matrix modifiers, dilution, or method of standard additions is to be applied to reduce the interferences.

4. An EPA reference standard will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

# SILVER

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 272.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.01 mg/L

Optimum Concentration Range: 0.01 - 2.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedure). Analyze within 6 months.

Instrument Conditions:

1. Silver hollow cathode lamp with lamp energy set at 12.
2. Wavelength: 328.1 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Silver Solution (100 mg/L Silver): Pipet 10 mL of the 1000 ppm stock silver solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Silver Standard | Dilute to |
|---|---|---|
| 0.50 mg/L | 0.5 mL of 100 mg/L Ag | 100 mL |
| 1.00 mg/L | 1 mL of 100 mg/L Ag | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Ag | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

5. Any groundwater samples which silver is detected, must be verified by furnace. (Detection limit is at the WI PAL limit.)

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If silver is to be run in the concentation mode, use the 1.00 and 2.00 mg/L silver standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.50 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph or

2. Calculate using linear regression or

3. Calculate using the concentration mode.

# THALLIUM

**Method:** AA - Flame; Direct Aspiration

**Reference:** EPA 1983, Method 279.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

**Detection Limit:** 0.50 mg/L

**Optimum Concentration Range:** 0.50 - 10.0 mg/L

**Sample Handling:** Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

**Instrument Conditions:**

1. Thallium electrodeless discharge lamp with lamp energy set at 9.
2. Wavelength: 276.8 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.00, 2.00, 5.00, 10.0 mg/L.

**Reagent Preparation:** Prepare fresh every 6 months unless otherwise noted.

1. Standard Thallium Solution (10.0 mg/L Thallium): Pipet 1.0 mL of the 1000 ppm stock thallium solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Thallium Standard | Dilute to |
|---|---|---|
| 1.00 mg/L | 1 mL of 100 mg/L Tl | 100 mL |
| 2.00 mg/L | 2 mL of 100 mg/L Tl | 100 mL |
| 5.00 mg/L | 5 mL of 100 mg/L Tl | 100 mL |
| 10.00 mg/L | 10 mL of 100 mg/L Tl | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. This flame procedure can be used for digested samples, EP Toxicity samples or any other samples where low detection limits are not required. EP Toxicity samples must be spiked to verify that standard additions are not required.

5. The use of halide acids is to be avoided.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If thallium is to be run in concentration mode, use the 5.00 and 10.0 standards and follow the procedure for analyzing in concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 5.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

[ALM-8-13]

# THALLIUM

Method: AA - Furnace; Direct Injection

Reference: EPA 1983, Method 279.2

"Analytical Methods for Furnace Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation.

"Techniques in Graphite Furnace Atomic Absorption Spectrophotometry", 1985, Perkin-Elmer Corporation.

Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.050 mg/L

Instrument Conditions:

1. Thallium electrodeless discharge lamp with lamp energy set at 9.
2. Wavelength: 276.8 nm
3. Slit Width: 0.7 Alternate
4. HGA Furnace Programming:

   Step 1: 130 (dry temp) 10 (ramp time) 20 (hold time)
   Step 2: 500 (char temp) 10 (ramp time) 20 (hold time)
   Step 3: 1400 (atom temp) 0 (ramp time) 3 (hold time)

   * Also press the read, record and stop flow buttons; t = 3 sec.

   Step 4: 2500 (max temp) 0 (ramp time) 3 (hold time)

   Press the record button.

5. Sample Volume: 20 uL
6. Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.
7. Platform is required.

Sample Handling: Acidify with nitric acid to pH <2. Analyze within 6 months.

[C-600-97a]

Reagent Preparation:

1. Standard Thallium Solution (1000 ug/L Thallium): Pipet 1.00 mL of the 1000 ppm stock thallium solution into a 1000 mL volumetric flask, add 1/2 mL $HNO_3$ and dilute to the mark with D.I. water. Prepare fresh every month.

2. Standards (Prepare fresh every week.):

| Concentration of Standard | Volume of Thallium Standard | Dilute to |
|---|---|---|
| 10.0 ug/L | 1 mL of 1000 ug/L Tl | 100 mL |
| 20.0 ug/L | 2 mL of 1000 ug/L Tl | 100 mL |
| 50.0 ug/L | 5 mL of 1000 ug/L Tl | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Be careful when reporting the units.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For the use of the concentration mode, use the 20.0 and 50.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These

standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed. Record the calibration standard in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ration of sample to standards. Spike recoveries and duplicates are to be within an acceptable range or the use of matrix modifiers, dilution, or method of standard additions is to be applied to reduce the interferences.

4. An EPA reference standard will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance (or peak height) on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using concentration mode.

# VANADIUM

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 286.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 1.00 mg/L

Optimum Concentration Range: 1.00 - 50.0 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyzed within 6 months.

Instrument Conditions:

1. Vanadium hollow cathode lamp.
2. Wavelength: 318.4 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Red
7. Standards to use for curve set-up: 5.00, 10.0, 20.0, 50.0 mg/L.

Reagent Preparation: Prepare fresh every 6 months unless otherwise noted.

1. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Vanadium Standard | Dilute to |
|---|---|---|
| 5.00 mg/L | 0.5 of 1000 mg/L V | 100 mL |
| 10.0 mg/L | 1 of 1000 mg/L V | 100 mL |
| 20.0 mg/L | 2 of 1000 mg/L V | 100 mL |
| 50.0 mg/L | 5 of 1000 mg/L V | 100 mL |

2. Aluminum nitrate solution: In a 200 mL volumetric flask, dissolve 139g $Al(NO_3)_3$ in 150 mL of Milli-Q water. Heat to dissolve into solution. Allow to cool. Dilute to 200 mL with Milli-Q water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. High concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum to both samples and standards (2 mL of aluminum nitrate solution to 100 mL samples and standards).

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

Add 0.2 mL of $AlNO_3$ to 10 mL of samples, blanks and standards.

If vanadium is to be run in the concentration mode, use the 20.0 and 50.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 20.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicate to be within an acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# ZINC

Method: AA - Flame; Direct Aspiration

Reference: EPA 1983, Method 289.1

"Analytical Methods for Atomic Absorption Spectrophotometry", 1982, Perkin-Elmer Corporation

Detection Limit: 0.01 mg/L

Optimum Concentration Range: 0.01 - 1.00 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. The Zinc hollow cathode lamp with lamp energy set at 27.
2. Wavelength: 213.9 nm
3. Slit Width: 0.7 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.10, 0.20, 0.40, 1.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Zinc Solution (20.0 mg/L Zinc): Pipet 2 mLs of the 1000 ppm stock zinc solution into a 100 mL volumetric flask, add 1/2 mL $HNO_3$, and dilute to the mark with Milli-Q water.
2. Standards (Prepare fresh every month.):

| Concentration of Standard | Volume of Zinc Standard | Dilute to |
|---|---|---|
| 0.10 mg/L | 0.5 mL of 20.0 mg/L Zn | 100 mL |
| 0.20 mg/L | 1 mL of 20.0 mg/L Zn | 100 mL |
| 0.40 mg/L | 2 mL of 20.0 mg/L Zn | 100 mL |
| 1.00 mg/L | 5 mL of 20.0 mg/L Zn | 100 mL |

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Zinc's may be run at a 30° angle for high level samples. High standards are made accordingly.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If zinc is to be run in the concentration mode, use the 0.40 and 1.00 mg/L zinc standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.).

2. A quality control calibration standard of 0.20 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of twice the concentration of the sample in a 1:1 ratio of sample to standard. Spike recoveries and duplicates results are to be within acceptable ranges or the use of dilution or method of standard additions is to be applied to reduce the interferences.

Calculations:

1. Plot concentration vs absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

# TOTAL VOLATILE SOLIDS

Scope and Application: This method determines the weight of solid material combustible at 550°C, and is applicable to sewage, sludge, industrial wastes, soils and sediments.

Method: Gravimetric, ignition at 550°C

Reference: EPA 1983, Method 160.4
Standard Methods, 16th Edition, 1985, Method 209F. (Pages 99-100)

Sample Handling: Refrigerate at 4°C and analyze within 7 days of collection.

Reagents and Apparatus:

1. Porcelain evaporating dishes
2. Muffle furnace, set at 550°C
3. Dessicator
4. Analytical balance

Notes:

1. This is not an accurate measure of organic carbon.

2. The most common error is failure to obtain a representative sample. Make sure the sample is thoroughly mixed or composited prior to analysis.

3. The muffle furnace is slow to heat to 550°C. Turn muffle furnace on early in the day.

4. When opening and closing the muffle, remember to stay to the side of the compartment.

5. Use tongs when placing dishes in/out of the muffle furnace. The temperature is very high!

6. Take weighings quickly - wet samples tend to lose weight by evaporation. Dried samples can be hygroscopic and rapidly absorb atmospheric moisture.

Procedure:

Preparation of Evaporation Dish

1. All glassware is to be soap and water washed, tap rinsed, and deionized water rinsed prior to analysis.

2. Ash a clean evaporating dish at 550 ±50°C for one hour in muffle furnace.

3. Cool in dessicator for at least one hour and weigh. Dishes may be prepared and stored in desiccator until ready for use.

Sample Analysis

4. Fluid samples - Stir to mix.

   - Place 25 to 50g of sample in the prepared evaporating dish and weigh.

   - Evaporate to dryness on a water bath.

   - Dry at 103 - 105°C overnight.

   - Place in desiccator and cool to room temperature.

   - Weigh.

   Solid Samples - If sample contains pieces of solid material, pulverize the sample coarsely.

   - Place 25 to 50g of sample into prepared evaporating dish and weigh.

   - Place in oven at 103 - 105°C overnight.

   - Place in desiccator and cool to room temperature.

   - Weigh.

5. After the total solids have been determined, ignite the residue left in the evaporating dish at 550°C in the muffle furnace.

   Note: If residue for step 4 contains large amounts of organic matter, first ignite the residue over a gas burner in an exhaust hood; then proceed with step 5.

6. Let dish cool partially by the air. Then, cool in a dessicator for at least one hour and weigh. Repeat the ashing cycle (igniting, cooling, dessicating, and weighing) until a weight loss of <0.4% is obtained.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates should be within acceptable ranges. The duplicate results are to be averaged.

2. A blank dish is carried throughout the entire procedure, as a check on contamination (glassware, oven, muffle furnace, etc.)

Calculations:

$$\text{TVS, mg/kg} = \frac{\text{wt. dried residue (g)} - \text{wt. residue after ignition (g)}}{\text{wt. dried residue (g)}} \times 1000000$$

$$\text{TVS, \%} = \frac{\text{wt. dried residue (g)} - \text{wt. residue after ignition (g)}}{\text{wt. dried residue (g)}} \times 100$$

Revision Date

Michael Linskens 10/19/87
Michael J. Linskens
Laboratory Manger — 7-23-86

Kim Finner
Kim D. Finner
Analytical Laboratory QA/QC Officer — 5-21-87

Lawrence D. Andersen
Lawrence D. Andersen
Vice President, Technical Services

# ACID DIGESTIONS FOR SEDIMENTS, SLUDGES AND SOILS -

Scope and Application: This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectropscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

| | | |
|---|---|---|
| Aluminum | Chromium | Nickel |
| Antimony | Cobalt | Potassium |
| Arsenic | Copper | Silver |
| Barium | Iron | Selenium |
| Beryllium | Lead | Thallium |
| Cadmium | Magnesium | Vanadium |
| Calcium | Manganese | Zinc |

Method: Nitric acid, hydrogen peroxide and hydrochloric acid digestion for flame work and antimony by furnace; nitric acid/hydrogen peroxide digestion for furnace work.

Reference: EPA SW-846, "Test Methods for Evaluating Solid Waste", July, 1982. Methods 3020 and 3050.

Contract Laboratory Program - "Statement of Work", July, 1985.

Sample Handling: Set up digestion as soon as possible; digested sample must be analyzed within 6 months.

Reagents and Apparatus:

1. Hot plate
2. Mortar and Pestle
3. 250 mL beakers
4. Class A volumetric glassware
5. Milli-Q water
6. 30% hydrogen peroxide
7. Instra-analyzed nitric acid
8. Instra-analyzed HCL acid
9. Stock and standard metal solutions
10. Whatman #42 filter paper
11. Glass or plastic funnels
12. Watch glasses

Reagent Preparation:

1. Intermediate and Working Metal Solutions: Refer to the specific metal SOP for instructions on preparation.

2. 1:1 Nitric Acid: Using a 250 mL volumetric cylinder, add 250 mL Milli-Q water. Cautiously add 250 mL concentrated nitric acid. Mix.

3. 1:1 HCL: Using a 250 mL volumetric cylinder, add 250 mL Milli-Q water. Cautiously add, 250 mL concentrated hydrochloric acid. Mix.

Notes:

1. Arsenic and selenium by the AA-furnace techniques follow this digestion procedure and nickel nitrate is added prior to analysis.

2. Mercury by the AA-Cold Vapor technique has a separate digestion procedure.

3. All blanks, duplicates and spikes must be carried through the digestion procedure along with a digestion check standard.

4. If elevated levels are expected, increase the spike concentration accordingly.

Procedure:

A. Digestion for Flame Work and Furnace Analysis of Antimony:

1. All glassware used must be acid rinsed with 1:1 nitric prior to use.

2. Pulverize and thoroughly mix the sample.

3. Weigh out approximately 1.000 g - 1.500 g of the sample into a 250 mL beaker on analytical balance. Record the weight of the sample used on the digestion sheet.

4. Add 10 mL of 1:1 $HNO_3$. Mix and cover with a watchglass. Place samples on the hot plate and heat at medium heat (95° C). Reflux for 10 minutes.

5. Take sample off hot plate and allow to cool. Add 5 mL concentrated $HNO_3$. Return to hot plate and reflux for 30 minutes.

6. Cool. Add 2 mL Milli-Q water and 3 mL 30% $H_2O_2$.

7. Heat until effervesence subsides. Cool.

8. Continue the addition of 30% $H_2O_2$ in 1 mL aliquots with warming until the effervesence is minimal or appearance of sample is unchanged. DO NOT add more than a total of 10 mL 30% $H_2O_2$.

9. Cool. Add 5 mL 1:1 HCL and 10 mL Milli-Q water.

10. Cover and heat for 10 minutes.

11. Cool. Quantitatively transfer to 100 mL volumetric flasks while filtering through a Whatman #42 filter to remove sediment. Rinse beaker and filter paper 3 times and dilute to 100 mL with Milli-Q water. The final acid concentration is approximately 2.5% HCL and 5.0% $HNO_3$. Dilute the digestate 1:1 with deionized water. (200 mL final volume.)

B. Digestion for Furnace Work, except for Antimony:

1. Follow the digestion procedure above for flame work through Step 8.

2. Continue to heat until the volume is reduced to approximately 2 mL. (Watch closely; bumping and spattering may occur.)

3. Cool. Add 10 mL Milli-Q water and warm on hot plate.

4. Cool. Quantitatively transfer to 100 mL volumetric flasks while filtering through a Whatman #42 filter to remove sediment. Rinse the beakers and filter paper 3 times and dilute to 100 mL with Milli-Q water. The final acid concentration is approximately 2.0% $HNO_3$. Dilute the digestate 1:1 with deionized water (200 mL final volume).

Quality Control:

1. Refer to each specific metal SOP for quality control requirements.

2. If a digested spike is diluted out of the working concentration (too low to detect) run a manual spike. The data is acceptable if the manual spike is within acceptable ranges. If the manual spike is outside the QC ranges, the sample and spike must be re-digested.

Revision Date

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

9/25/87

Kim Finner
Kim D. Finner
Analytical Laboratory QA/QC Officer

Lawrence D. Andersen
Lawrence D. Andersen
Vice President, Technical Services

## ACID DIGESTION FOR WASTEWATER, GROUNDWATER AND EP TOXICITY SAMPLES -

Scope and Application: This acid digestion is applicable to all aqueous sample matrices. A nitric/hydrochloric acid digestion is used for all metals which are to be analyzed by the AA-flame technique and for the furnace analysis of antimony. Metals which are to be analyzed by the AA-furnace technique will follow the nitric acid/ hydrogen peroxide digestion.

Method: Nitric and nitric/hydrochloric acid digestions.

Reference: EPA SW-846, "Test Methods for Evaluating Solid Wastes", July, 1982. Methods 3010 and 3020.

Contract Laboratory Program, "Statement of Work", July, 1985.

Sample Handling: Aqueous samples must be acidified with concentrated nitric acid to pH < 2. Set up digestion as soon as possible; digested sample must be analyzed within 6 months.

Reagents and Apparatus:

1. Hot Plate
2. 250 mL beakers
3. 100 mL graduated cylinders
4. Class A volumetric glassware
5. Milli-Q water
6. Instra-analyzed nitric acid
7. Instra-analyzed HCL acid
8. Stock and standard metal solutions
9. Whatman #42 filter paper
10. Glass funnels
11. Watch glasses
12. 30% hydrogen peroxide

Reagent Preparation:

1. Intermediate and Working Metal Solutions: Refer to the specific metal SOP for instructions on preparation.

Notes:

1. All blanks, duplicates, and spikes, as well as a digested check standard must be carried through this digestion procedure.

Procedure:

A. Digestion For AA-Flame and Antimony by Furnace:

1. All glassware must be acid-washed with 1:1 nitric acid and thoroughly rinsed with Milli-Q water prior to use.

2. Measure out 100 mL aliquots of samples, blanks, and standards into 250 mL beakers using a graduated cylinder.

3. Add 2 mL of 1:1 $HNO_3$ and 10 mL of 1:1 HCL.

4. Cover with a watch glass and heat on the hot plate until the volume has been reduced to between 25 and 50 mL. Make certain that the sample does not boil.

5. Quantitatively transfer digested samples, blanks, and standards into 100 mL volumetric flasks. Filter samples through Whatman #42 filters, rinse beakers and filters with Milli-Q water and dilute to 100 mL. Alternatively, samples can be transfered to 100 mL volumetric flasks, without filtering. Dilute to volume and let any insoluble material settle overnight.

6. Samples are now ready for analysis using the AA-flame procedure.

B. Digestion For AA-Furnace (except Antimony):

1. All glassware must be acid-washed with 1:1 nitric acid and thoroughly rinsed with Milli-Q water prior to use.

2. Measure 100 mL aliquots of samples, blanks, and standards into 250 mL beakers using a graduated cylinder.

3. Add 1.0 mL of 1:1 $HNO_3$ and 2 mL of 30% $H_2O_2$.

4. Cover with a watch glass and heat on the hot plate at 95°C for 2 hours or until the volume is reduced to between 25 and 50 mL. Make certain that the sample does not boil.

5. Quantitatively transfer digested samples, blanks, and standards into 100 mL volumetric flasks. Filter samples through Whatman #42 filters, rinse beakers and filters with Milli-Q water and dilute to 100 mL. Alternatively, samples can be transfered to 100 mL volumetric flask without filtering. Dilute to volume and let any insoluble material settle overnight.

6. Samples are now ready for analysis using the AA furnace procedures.

## Quality Control

1. Refer to each specific metal SOP for quality control requirements.

2. If a digested spike is diluted out of the working concentration range (too low to detect) run a manual spike. The data is acceptable if the manual spike is within acceptable ranges. If the manual spike is outside the QC ranges, the sample and spike must be re-digested at a dilution.

Revision Date

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

9/25/87

Kim Finner
Kim D. Finner
Analytical Laboratory QA/QC Officer

Lawrence D. Andersen
Lawrence D. Andersen
Vice President, Technical Services

# AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalzyer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Appartus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

4. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

   a. Use correct sample loop length to connect. Lines 1, 4.

   b. Line 2 is carrier line.

   c. Line 3 goes to manifold.

   d. Line 5 goes to waste container.

   e. Line 6 comes from sample probe.

   f. Connect manifold to flow through cell.

   Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

5. Insert correct filter.

6. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

7. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

8. Put lines into reagents and/or degassed Milli-Q water.

9. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

10. Select appropriate method. Press <enter>.

11. Printer should be set at FONT 0.

12. Pump reagents until a steady baseline is achieved.

13. When using a method with a column ($SO_4$ or $NO_3$), the column may be inserted at this point. See method SOP's for more details.

14. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

15. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

    d. Adjust gain knob on detector so that peak reading on the colorimeter is 1.700-1.950.

    e. Repeat until gain is properly adjusted.

    f. Wipe probe and replace the autosampler probe into the sampler.

16. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <Enter>.

    b. Press <Enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

17. Put tray with samples in appropriate cup locations on autosampler. Position tray to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

18. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

19. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)

    - select "display calibration graph" (Press <enter>)

    - review the data

    - return to the background (Press Alt, Esc keys)

      - press "G" for good calibration. Analysis will continue.

      - press "R" for re-calibration. Remember to refill standard cups and reposition sample tray <u>before</u> pressing "R"!

B. <u>Instrument Shut-Down</u>

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (see section C )

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
   After everything is copied - remove disc.

4. At C> Type: del *.*. Press <enter>

5. Are you sure (Y/N)? Type: Y. Press <enter>

6. At C> Type: cd\ Press <enter>

7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

Michael Linskens 9/25/87
Michael J. Linskens
Laboratory Manager

Kim Finner
Kim D. Finner
Analytical Laboratory QA/QC Officer

Lawrence D. Anderson
Lawrence D. Anderson
Vice President, Technical Services

Revision Date

8-18-87

9-25-87

# ALKALINITY - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 310.2
Lachat Instruments 1986, Method 10-303-31-1-C

Sample Handling: Refrigerate at 4°C and analyze within 14 days of collection.

Detection Limit: 5.0 mg/L as $CaCO_3$

Optimum Concentration Range: 5.0 - 500 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 60 seconds
3. Load period: 30 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 10 seconds
6. Inject to end of peak period: 56 seconds
7. Gain: 150 x 10
8. Zero: 180
9. Interference filter: 410 nm
10. Sample loop: 90 cm
11. Standards for curve set-up: 0, 20.0, 50.0, 100, 250, 500 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.

2. Stock alkalinity standard (1000 mg/L as $Na_2CO_3$): In a 1 liter volumetric flask, dissolve 1.060 g of anhydrous primary standard grade sodium carbonate ($Na_2CO_3$-dried at 140°C for 4 hours) in approximately 900 mL of helium purged Milli-Q water, and dilute to mark.

3. Standards: (Prepare fresh every 2 months.)

| Concentration of Standard | Letter Identifier | Volume of Alk. Standard | Dilute to |
|---|---|---|---|
| 0 mg/L | A | 0 | 200 mL |
| 20.0 mg/L | B | 4.0 | 200 mL |
| 50.0 mg/L | C | 10.0 | 200 mL |
| 100 mg/L | D | 50.0 | 500 mL |
| 250 mg/L | E | 125.0 | 500 mL |
| 500 mg/L | F | 100.0 | 200 mL |

NOTE: Final volumes are not the same!
Computer refers to standards by letter.

4. Sodium hydroxide (0.1M): In a 1 liter flask, dissolve 4.0 g sodium hydroxide (NaOH) and dilute to the mark with Milli-Q water.

5. Hydrochloric acid (0.1M): In a 1 liter flask, dilute 8.3 mL of concentrated HCL in Milli-Q water and dilute to the mark.

6. KHP buffer (25.0 mM, pH 3.1): In a 1 liter flask, dissolve 5.10 g of potassium acid phthalate (KHP) ($KHC_3H_4O_4$) in approximately 500 mL of helium purged Milli-Q water. Add 87.6 mL of 0.1M HCL and dilute to the mark. Adjust the pH of the buffer to 3.1 with 0.1M HCL or 0.1M NaOH. STORE IN GLASS AND PREPARE MONTHLY!

7. Methyl orange reagent: In a 1 liter volumetric flask, dissolve 0.125 g of methyl orange indicator in about 700 mL of helium-purged Milli-Q water and dilute to the mark. Store in glass!

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be adjusted each day to optimize.

3. The alkalinity standards can be combined with chloride and sulfate standards for use with the 3 channel method.

4. Turbidity will interfere. Samples must be filtered prior to analysis. (Use Whatman #1 or #4.)

5. Color will interfere, dilute the sample and also spike this sample to confirm the quality of the result.

System Operation:

A. Refer to "Auto Analyzer Operation start-up procedure." (IOP# LAA-section A)

B. Analyze a blank and an EPA check standard at the beginning of each run.

C. Use 125 mg/L for the spike level.

D. The calibration check standard is 100 mg/L (D).

E. Refer to "Auto Analyzer shut-down procedure". (IOP# LAA-section B)

Quality Control:

1. Establish a standard curve with the standards listed above. Record the check standard in the check standard book. The concentration should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check reagents, pump tubing, valves, etc.).

2. A quality control calibration standard of 100 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The acceptable limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

Revision Dates

8-18-87

9-25-87

Michael Linksens 9/25/87
Michael J. Linksens
Laboratory Manager

Kim Finner
Kim D. Finner
Analytical Laboratory QA/QC Officer

Lawrence D. Andersen
Lawrence D. Andersen
Vice President, Technical Services

# CHLORIDE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater, and wastewater.

References: EPA 1983, Method 325.2
Lachat Instruments 1986, Method 10-117-07-1-B

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Detection Limit: 1.0 mg/L.

Optimum Concentration Range: 1.0 - 100 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle speed: 30 seconds
3. Load period: 15 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 8 seconds
6. Inject to end of peak period: 35 seconds
7. Gain: 200
8. Zero: 250
9. Interference filter; 480 nm
10. Sample loop: 20 cm
11. Standards for curve set-up: 0, 10.0, 20.0, 50.0, 80.0, 100.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Degassed Milli-Q water - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. (15 min/20 L.) Store in cubitainer.

2. Stock chloride standard (1000 mg/L Cl): In a 1 liter volumetric flask, dissolve 1.648 g of primary grade sodium chloride (NaCl), previously dried at 103°C, in 500 mL Milli-Q water. Dilute to the mark and invert to mix.

3. Standards: (Prepare fresh every 2 months.)

| Concentration of Standard | Letter Identifier | Volume of Cl Standard | Dilute to |
|---|---|---|---|
| 0 mg/L | A | 0 | 200 |
| 10.0 mg/L | B | 2.0 | 200 |
| 20.0 mg/L | C | 4.0 | 200 |
| 50.0 mg/L | D | 25.0 | 500 |
| 80.0 mg/L | E | 40.0 | 500 |
| 100 mg/L | F | 20.0 | 200 |

Note: Final volumes are not the same!
Computer refers to standards by letter.

4. Stock mercuric thiocyanate reagent: In a 1 liter volumetric flask, dissolve 4.17g of mercuric thiocyanate ($Hg(SCN)_2$) in one liter of methanol. Invert to mix. Store in amber glass.

CAUTION: Mercury is a very toxic metal. WEAR GLOVES!

5. Stock ferric nitrate reagent (0.5M): In a 1 liter volumetric flask, dissolve 202.0g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in approximately 800 mL of deionized water. Add 25 mL of concentrated nitric acid and dilute to one liter. Invert to mix.

6. Combined color reagent: Mix 150 mL of stock mercuric thiocyanate solution with 150 mL of stock ferric nitrate reagent and dilute to 1000 mL with deionized water. Vacuum filter through a 0.45 micron membrane filter.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be adjusted each day to optimize.

3. The chloride standards may be combined with alkalinity and sulfate standards for use with the 3 channel method.

4. Any sample with turbidity must be filtered prior to analysis. (Use Whatman #1 or #4.)

5. Color is an interference, dilute the sample and also spike this sample to confirm the quality of the result.

System Operation:

A. Refer to "Auto Analyzer Operation Start-up procedure". (IOP# LAA-section A)

B. Analyze a blank and an EPA check standard at the beginning of each run.

C. Use a 40 ppm Cl for the spike level.

D. The calibration check standard is 50 mg/L (D).

E. Refer to "Auto Analyzer Shut-down procedure". (IOP# LAA-section B)

Quality Control:

1. Establish a standard curve with the standards listed above. Record the check standard in the check standard book. The concentration should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check reagent, pump tubing, valves, etc.).

2. A quality control calibration standard of 50.0 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The acceptable limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

| | Revision Date |
|---|---|
| Michael Linskens 9/25/87 | 8-18-87 |
| Michael J. Linskens<br>Laboratory Manager | 9-25-87 |
| Kim Finner<br>Kim D. Finner<br>Analytical Laboratory QA/QC Officer | |
| Lawrence D. Andersen<br>Lawrence D. Andersen<br>Vice President, Technical Services | |

# NITRATE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 353.2
Lachat Instruments, 1986

Detection Limit: 0.02 mg/L

Optimum Range: 0.02 - 2.00 mg/L $NO_3$.

Sample Handling: Analyze within 48 hours of collection. If this is not possible, preserve the sample with 2 mL concentrated $H_2SO_4$/1 liter and analyze within 14 days.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 20 seconds
5. Inject to start of peak period: 22 seconds
6. Inject to end of peak period: 68 seconds
7. Gain: 450
8. Zero: 400
9. Interference filter: 520 nm
10. Sample loop: 17 cm
11. Standards for curve set-up: 0, 0.20, 0.50, 1.00, 2.00
12. Column: (see reagents 7-10)

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water (2 options):

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in a cubitainer, or

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. Store in a cubitainer. (15 min/20 L)

2. Stock nitrate standard (100 mg/L $NO_3$): In a 1 liter volumetric flask, dissolve 0.7218 potassium nitrate ($KNO_3$) in about 600 mL of Milli-Q water. Add 2 mL of chloroform, as a preservative. Dilute to the mark. Store in a dark glass bottle.

3. Working stock nitrate standard (10 mg/L $NO_3$): In a 100 mL volumetric flask, pipet 10.0 mL of the stock nitrate standard and dilute to the mark with Milli-Q water. Standard is good for 2 weeks if $H_2SO_4$ preserved.

4. Standards: (Prepare fresh every 2 weeks.) Preserve with 0.2 mL $H_2SO_4$.

| Concentration of Standard | Letter Identifier | Volume of $NO_3$ Standard | Dilute to |
|---|---|---|---|
| 0 mg/L | A | 0 | 100 mLs |
| 0.20 mg/L | B | 2.0 | 100 mLs |
| 0.50 mg/L | C | 5.0 | 100 mLs |
| 1.00 mg/L | D | 10.0 | 100 mLs |
| 2.00 mg/L | E | 20.0 | 100 mLs |

Note: Computer refers to standards by letter.

5. Sodium hydroxide (15M): To 250 mL of Milli-Q water, add 150.0g NaOH. SLOWLY! This solution will get very HOT! Swirl to dissolve. Store in a plastic bottle.

6. Ammonium chloride buffer solution: In a 1 liter volumetric flask, dissolve 85.0g of ammonium chloride ($NH_4Cl$) and 1.0g of disodium ethylenediamine tetracetate dihydrate (EDTA) in approximately 800 mL Milli-Q water. Adjust the pH to 8.5 with the 15M NaOH. Dilute to the mark.

7. Sulfanilamide color reagent: In a 1 liter volumetric flask, add approximately 800 mL of Milli-Q water. Then add 100 mL concentrated phosphoric acid ($H_3PO_4$). Add 40.0g sulfanilamide and dissolve completely. Dissolve 1.0g N-1-naphthlethylenediamine dihydrochloride (NED) and dilute to one liter. Store in dark bottle at 4°C. Stable for 2 months when refrigerated.

8. Column Preparation:

   a. Cadmium preparation: Place 10-20g of coarse cadmium powder (granules) in a 250 mL beaker and wash with 50 mL of acetone, then distilled water, then two 50 mL portions of 1 M hydrochloric acid (8 mL concentrated hydrochloric acid plus 92 mL deionized water). Then rinse thoroughly with deionized water. If using cadmium for second time, rinse with 1 M hydrochloric acid before beginning process. CAUTION: Collect and store all waste cadmium. Wear gloves!

   b. Copperization: Prepare a 2% copper sulfate solution (20g $CuSO_4 \cdot 5H_2O$) per liter of deionized water) and add a 100 mL portion to the cadmium prepared in "a" above. Swirl gently for about 5 minutes, then decant the liquid and repeat with a fresh 100 mL portion of 2% copper sulfate. Continue this process until colloidal copper is visible in the supernatant (a red-brown precipitate) and solution remains blue in color. Decant and wash with at least 5 portions of ammonium chloride solution (Reagent #6) to remove the colloidal copper. The cadmium should be black or dark gray. The cadmium granules may be stored in a stoppered bottle in ammonium chloride solution (Reagent 6).

c. Packing the column (wear gloves!): Place a small piece of polyurethane foam (or glass wool) loosely in the end of the glass tube. Insert the plugged end of the glass tube into the column end fitting. Cut a length of 0.032" id teflon tubing 3 to 4 inches longer than the column.

Insert the teflon tube in the end fitting and fill the whole tube with water, holding the flexible tube in a U-shape so that the ends are level. Place the second end fitting on the other end of the teflon tubing. (Placing a small funnel onto the end fitting may aid filling.) Taking care that no air bubbles are introduced, place the copperized cadmium granules in the column. Tap the column gently, every 1-2 cm, to pack the granules. When the column is packed to within about 5 mm of the end of the glass column, insert another foam plug, then the column end fitting. Store the column with the ends connected with a length of teflon tubing, as air pockets or having the column dry out will necessitate repacking. If air remains in the column, connect the column to the manifold and turn the pump on maximum. Tap column firmly until all air is removed.

d. Column activation: The column must be activated before use or it will not reduce nitrate. This may be accomplished by pumping the 10 mg/L nitrate standard through the sampler line. When the solution is injected, a brilliant pink color will be visible in the coil. The cadmium column effeciency should be above 80%, if less, the column must be repacked.

Notes:

1. Interferences:

   - Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample must be pre-filtered.

   - Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate these interferences.

   - Samples that contain large concentrations of oil and grease will coat the surface of the column. This interference is eliminated by pre-extracting the sample with an organic solvent.

2. Samples must be diluted to obtain concentrations within the optimum working range.

3. The gain and zero settings are guidelines and must be adjusted each day to optimize.

4. Color will intefere; dilute the sample and also spike this sample to confirm the quality of the result.

5. ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination, so an alternative preparation for the ammonium chloride buffer (Reagent 6) is as follows:

   In the hood, add 126 mL concentrated HCl to a 1 liter volumetric flask containing 500 mL degassed Milli-Q water. Mix. Add 95 mL ammonium hydroxide and 1.0 gm disodium EDTA. Dissolve and dilute to the mark. The pH should be 8.5 $\pm$ .1, adjust pH if necessary.

System Operation:

1. Refer to Auto Analyzer Operation - Start-up Procedure (IOP# LAA-section A).

2. After pumping reagents through the lines, turn off the pump and insert column, making sure that air bubbles are not introduced into the column.

3. Activate column. (See #8d. above.)

4. Analyze a blank and EPA check standard at the beginning of each run.

5. Use 0.5 ppm spike levels. The calibration check standard is 1.00 mg/L $NO_3$ (D).

6. If only nitrate is requested, nitrites must be analyzed and subtracted from the nitrate + nitrite value.

7. However, since this method analyzes both forms of nitrogen, if the nitrate + nitrite result is <0.02, nitrite does not need to be run for that sample.

8. After use, turn off the pump and remove the column from the manifold.

9. Refer to Auto Analyzer Shut-down Procedure. (IOP# LAA-section B.)

Quality Control:

1. Establish a standard curve with the standards listed above. Record the check standard in the check standard book. The concentration should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check reagents, pump tubing, valves, etc.).

2. A quality control calibration standard of 1.00 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalzyed. Record the calibration standards in the quality control book. The acceptable limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard in a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

Revision Dates

8-18-87

Michael Linskens 8/20/87
Michael J. Linskens
Laboratory Manager

Kim Finner
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Analytical Laboratory QA/QC Officer

Lawrence D. Andersen 8/20/87
Lawrence D. Andersen
Vice President, Technical Services

# SULFATE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater, and wastewaters.

Reference: EPA, 1983, Method 375.2
Lachat Instruments, 1986, QuikChem Method 10-116-10-2-B

Detection Limit: 5.0 mg/L

Optimum Concentration Range: 5.0 - 200 mg/L

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Instrument Condition:

1. Load time: 20 seconds
2. Inject Period: 30 seconds
3. Inject to peak start period: 9 seconds
4. Inject to peak end period: 54 seconds
5. Cycle time: 50 seconds
6. Gain: 200
7. Zero: 700
8. Interference filter: 460 nm
9. Sample loop: 10 cm
10. Standards to use for curve set-up: 0, 25.0, 50.0, 100, 150, 200 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Degassing with helium - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. (15 min/20 L.) Store in cubitainer.

2. Carrier (0.3 ppm $SO_4^{=}$): In a 1 liter volumetric flask, add 0.3 mL of 1000 ppm stock sulfate solution and dilute to mark with degassed Milli-Q water.

3. Barium chloride solution (6.24M): In a 1 liter volumetric flask, dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 mL of degassed Milli-Q water and dilute to 1 liter.

4. Hydrochloric acid (1.0N): In a 100 mL volumetric flask, containing approximately 80 mL of Milli-Q water, add 8.3 mL of concentrated hydrochloric acid and dilute to the mark with Milli-Q water.

5. Barium - MTB color reagent: (The purity of the methylthymol blue and the alcohol can be critical. USE THE SOURCES STATED BELOW.)

   In a dry 1000 mL volumetric flask, place 0.2364 g of methylthymol blue (3', 3"bis-N,N-bis carboxymethyl)-amino methylthymolsulfonephthalein pentasodium salt (Kodak No. 8068). Add 50 mL of barium chloride solution ("3" above). The solution may be used to aid in the transfer of the dye. Swirl to dissolve. Add 8.0 mL of the 1.0 N HCl solution ("4" above) and mix - solution should turn orange. Add 142 mL deionized water and dilute to 1000 mL with ethanol (Aldrich 24.511.9) Mix. The pH of this solution should be 2.5. Prepare this solution the day before use and store it refrigerated in an amber bottle.

6. Sodium hydroxide (50% stock solution): Cautiously dissolve 500 g of sodium hydroxide (NaOH) in 600 mL of Milli-Q water. Cool and dilute to 1 liter. Store in plastic bottle. CAUTION: The solution will become very hot!

7. Sodium hydroxide (0.18 N): In a 1 liter volumetric flask, add 14.4 mL of 50% sodium hydroxide ("6" above) to degassed Milli-Q water, and dilute to the mark.

8. Buffered EDTA (for cleaning manifold): In a 1 liter volumetric flask, dissolve 6.75 g ammonium chloride ($NH_4Cl$) in 500 mL Milli-Q water. Add 57 mL concentrated ammonium hydroxide and 40.0 g tetrasodium EDTA dihydrate. Dissolve by swirling; dilute to the mark with Milli-Q water.

9. Sulfate stock (1000 mg/L): Dry approximately 2 g of sodium sulfate ($Na_2SO_4$) at 105°C for 2 hours. Cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.479 g of the dried sodium sulfate in Milli-Q water and dilute to 1 liter. (1.0 mL = 1.0 mg $SO_4^{=}$).

10. Working standard: (Prepare fresh every 2 months)

| Concentration of Standard | Letter Identifier | Volume of Stock Sulfate Standard | Dilute to |
|---|---|---|---|
| 0 mg/L | A | 0 | 200 mL |
| 25.0 mg/L | B | 5.0 | 200 mL |
| 50.0 mg/L | C | 10.0 | 200 mL |
| 100 mg/L | D | 50.0 | 500 mL |
| 150 mg/L | E | 75.0 | 500 mL |
| 200 mg/L | F | 40.0 | 200 mL |

Note: Final volumes are not the same.
Computer refers to standards by letter.

Preparation of Ion Exchange Column:

1. Make a slurry of approximately 0.5 g of BioRex 70, 50-100 mesh ion exchange resin in Milli-Q water.

2. Remove one column end from the glass column. Fill the column with water, then aspirate the slurry or allow it to settle by gravity to pack the column. Take care to avoid trapping air bubbles in the column and its fittings at this point and all subsequent operations.

3. After the resin has settled, replace the end fitting. To ensure a good seal, remove any resin particles from the threads of the glass, the column end and the end fittings. To store the column, the ends of the Teflon tubing may be joined with a union.

4. To test the effectiveness of the column, make up a standard of pure sodium sulfate and compare its peak height to an identical standard with hardness typical of the samples added. If the column is being depleted, the standard with hardness will read lower because the divalent cations are complexing the free MTB. The concentration of the standard should be mid-range. If depletion has occured, repack the column with fresh resin.

5. Regenerating Resin: Batch regeneration is recommended because the hydrogen form of BioRex 70 can swell considerably more than the sodium form. Collect the used resin in a small beaker or flask. Wash with dilute HCl until the wash tests free of calcium and/or magnesium. This procedure removes the divalent cations by converting the carboxylate exchange group to the protonated form - COOH. Convert the resin back to the sodium form by neutralizing with washes of 0.5M NaOH until the wash has a pH of 9 or greater. Rinse with deionized water for storage or repacking. A column may be used for 3-4 trays (approximately 150 samples) before it needs to be replaced.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. Sulfate standards may be combined with alkalinity and chloride standards for use with the 3-channel method.

3. The gain and zero settings are guidelines and must be adjusted each day to optimize.

4. Inteferences:

- The cation exchange column removes multivalent cations. Run a mid-range sulfate standard containing a typical concentration of $CaCO_3$ periodically to check performance. Any decrease in peak height should indicate the need to regenerate or replace the resin. (At 600 ppm $CaCO_3$, the column is good for 80 + injections.)

- Samples with pH less <2 should be neutralized. High acid concentrations can displace multivalent cations from the column.

- Color will interfere. Dilute the sample and also spike this sample to confirm the quality of the result.

- Turbidity - turbid samples may be filtered (use Whatman #1 or #4) prior to analysis on Lachat.

- Orthophosphate also forms a precipitate with barium at high pH. Check the response of pure orthophosphate standards, if samples are known to be high in $PO_4^{=}$.

5. Troubleshooting:

A. Baseline noise with reagents pumping.

1. Noise with column in line but good baseline without column.

a. Repack column, air bubbles may be causing pulsing.

b. Check flow fit connectors and end fittings on column for blockage or leaks.

2. Noise with and without column in line.

a. Degas carrier and/or reagents. Fine bubbles cause sharp spikes on baseline.

b. Place a longer piece of manifold tubing on the outlet of the flow cell leading to the waste container. This method requires the use of the screw type flow cell.

c. Replace the pump tubes. The silicone tube, used for the color reagent, wears faster than the PVC pump tubes.

d. With water pumping in the lines, check all hydraulic connections for blockages, leaks, etc.

B. Baseline drift.

1. Clean the manifold with the buffered EDTA.

2. Turn the gain high and use the shortest sample loop possible. This improves the linearity of the calibration curve, prolongs the useful life of the column, and minimizes the build up of $BaSO_4$ on the manifold tubing.

System Operation:

1. Refer to "Auto Analyzer Operation Start-up procedure" (SOP# LAA-section A).

2. Pump reagents through lines until baseline is stable. Then turn off pump and insert column.

3. Pump reagents through the lines before inserting the column. Use a short piece of manifold tubing in place of the column. When all air has passed and the baseline is steady, turn off the pump and insert the column. The column should be placed in a vertical position with flow in the top and out the bottom. In this configuration, the column will operate effectively even if the resin packs down more to leave a gap at the top. Resume pumping.

4. Analyze a blank and an EPA check standard at the beginning of each run.

5. Use a 75 ppm spike level. The calibration check standard is 100 mg/L (D).

6. To shut down, turn off pump and remove the column.

   To remove the column:

   a. Turn off the pump.
   b. Remove the column.
   c. Join ends of the column with a union.
   d. Replace the column on the manifold with the short teflon tubing piece.
   e. Rinse manifold with Milli-Q water.
   f. Rinse manifold with EDTA cleaning solution.
   g. Rinse manifold again with Milli-Q water.
   h. Pump dry.
   Follow "Auto Analyzer Shut-down procedures" (SOP# LAA-Section B).

Quality Control:

2. A quality control calibration standard of 100 mg/L is to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike samples with a standard of a 1:1 ratio of sample to standard. Spike recoveries and duplicates are to be within acceptable ranges or troubleshooting must be performed.

Calculations:

1. Calculate with the Lachat QuikChem software, in the concentration mode, using the IBM-XT computer.

Revision Date

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8-18-87

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9-25-87

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# AMMONIA NITROGEN

Scope and Application: This method is applicable to the determination of ammonia-nitrogen in drinking water, surface water, groundwater, sludges, soils, and industrial wastes.

Method: Micro-distillation, Colorimetric

Reference: EPA, 1983, Method 350.2

Detection Limit: 0.10 mg/L for aqueous samples
5.00 mg/kg for soils and sludges

Optimum Range: 0.10 - 2.00 mg/L for aqueous samples
5.00 - 100 mg/kg for soils and sludges

Sample Handling: Acidify aqueous samples with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Refrigerate soils ans sludges at 4°C. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Kjeldahl flasks, 100 mL
2. Keeney distillation apparatus
3. Spectrophotometer, set at 425nm with sipper cell
4. Erlenmeyer flasks, 50 mL
5. Sulfuric acid, concentrated
6. Milli-Q water
7. pH meter, 0.1 pH unit sensitivity
8. Volumetric glassware, Class A (pipets and flasks)
9. Top loading balance, 0.01g sensitivity
10. Graduated cylinders, 50 mL
11. Mixing cylinders, 50 mL
12. Ammonium chloride ($NH_4Cl$)
13. Boric acid ($H_3BO_3$)
14. Mercuric iodide ($HgI_2$)
15. Potassium iodide (KI)
16. Sodium hydroxide (NaOH)
17. Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)
18. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)
19. Analytical balance, 0.0001g sensitivity
20. 150 mL beaker
21. Stir bars and stir plate

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated).

1. Ammonium chloride stock solution(1000 mg/L): In a 1 liter volumetric flask, dissolve 3.819g $NH_4Cl$ in approximately 300 mL Milli-Q water and bring to volume.

[C-600-92]

2. Ammonium chloride standard solution (10 mg/L): Dilute 10.0 mL of the ammonium chloride stock solution to 1 liter with Milli-Q water in a volumetric flask.

3. Boric acid solution: Dissolve 20.0g $H_3BO_3$ in Milli-Q water and dilute to 1 liter in a volumetric flask.

4. Nessler reagent: Dissolve 100g of mercuric iodide and 70g of potassium iodide in about 200 mL of Mill-Q water. Add this mixture slowly, while stirring to a COOLED solution of 160g NaOH in 500 mL Milli-Q water. Dilute the mixture to 1 liter. Store in a Pyrex bottle and keep out of direct sunlight.

5. Sodium hydroxide (1N): Dissolve 40g of NaOH in Milli-Q water and dilute to 1 liter.

6. Sodium hydroxide (0.1N): Dilute 100 mL of 1N NaOH to 1 liter with Milli-Q water.

7. Sodium tetraborate solution (0.025M): Dissolve 9.5g of $Na_2B_4O_7 \cdot 10H_2O$ or 5.0g anhydrous $Na_2B_4O_7$ in Milli-Q water and dilute to 1 liter.

8. Borate buffer: Add 88 mL of 0.1N NaOH solution to 500 mL of 0.025M sodium tetraborate solution. Dilute to 1 liter.

9. Sodium thiosulfate (1/70N): Dissolve 3.5g $Na_2S_2O_3 \cdot 5H_2O$ in Milli-Q water and dilute to 1 liter. (1 mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample).

NOTES:

1. Residual chlorine must be removed prior to distillation by pretreating the sample with sodium thiosulfate solution.

2. Pre-steam the distillation apparatus with 10% NaOH before use for each batch analyzed.

3. Cyanate and some volatile alkaline compounds may cause an offcolo. nesslerization. This off-color can be eliminated by boiling the sample at a low pH (pH 2-3) to drive off the compound. This should be done prior to the distillation step.

Procedure: Sample must be homogenized prior to analysis to ensure a representative sample aliquot.

Distillation:

1. All glassware is to be soap and wate washed, tap water rinsed, and Milli-Q water rinsed prior to use.

2. The reservoir should be 2/3 full with Milli-Q water. Add a few boiling chips. Add sulfuric acid to reservoir to bring to a pH <2. Turn on the heater. Set heater control to about 6. Allow the steam reservoir to heat up. This unit will take about 45 minutes to heat-up. Turn the heater control to about a setting of 9 and bring to boiling. Analysis can begin once boiling begins.

3. Prepare the distillation apparatus as follows: Steam out the distillation apparatus with a 10% NaOH solution. Analyze a blank to confirm no trace of ammonia exists (no color change with the addition of the Nessler reagent to the distillate).

4. Aqueous samples:

   Place 40 mL or an aliquot of sample diluted to 50 mL in a 150 mL beaker. Record the volume used. Add 1N NaOH while stirring very slowly until the pH is 9.5 using pH paper.

   To spike: Place 45 mL sample and 5 mL of the 10 mg/L ammonia standard to the Kjeldahl flask and continue with procedure.

   Non-aqueous samples:

   Place approximately 1.0g in a 150 mL beaker. Record weight used. Add 50 mL Milli-Q water and adjust the pH with 1N NaOH, while stirring slowly, to pH 9.5 using pH paper.

   To spike: Place 1.0g sample, 1 mL of the 1000 mg/L ammonia standard in the Kjeldahl flask. Add 50 mL Milli-Q water and continue with procedure.

5. Transfer the pH-adjusted sample to a 100 mL Kjeldahl flask. Add 2.5 mL of borate buffer.

6. Add 5 mL of boric acid to a 50 mL Erlenmeyer flask and place flask at the condenser outlet with the tip of the condenser immersed in the boric acid.

7. Connect the Kjeldahl flask to the distillation apparatus and secure with springs.

8. Open the stopcock to the still on the condensation chamber. Close the drain stopcock. The steam will now pass through the Kjeldahl flask.

9. Steam distill 30-40 mL at a rate of 4-5 mL/min.

10. Remove the Erlenmeyer flask.

11. Rinse the tip of the condenser and steam outlet into a waste beaker.

12. Continue distilling remaining samples, blanks and standards. When all samples, blanks and standards are distilled, the colorimetric determination can be performed.

Colorimetric Determination:

1. Prepare the following series of blanks and standards in 50 mL mixing cylinders (These do not need to be taken through the distillation step).

| mL of 10 mg/L ammonium chloride solution | Dilute to | Concentration (mg/L |
|---|---|---|
| 0 | 50 mL | BLANK |
| 0.5 | 50 mL | 0.10 |
| 1.0 | 50 mL | 0.20 |
| 2.0 | 50 mL | 0.40 |
| 5.0 | 50 mL | 1.00 |
| 10.0 | 50 mL | 2.00 |

2. Add 2.0 mL of Nessler reagent to the blank and standards. Stopper and mix by inverting several times.

3. After 20 minutes, read the absorbances on the spectrophotometer set at 425nm using the sipper cell. Zero the spectrophotometer to the distilled reagent blank.

4. Transfer distilled samples to 50 mL volumetric flasks and dilute to 50 mL with Milli-Q water. Mix.

5. Determine the ammonia in the distillate as follows:

   - Transfer 25 mL of distillate, or an aliquot diluted to 25 mL, to a mixing cylinder.

   - Add 1 mL of Nessler reagent and mix by inverting several times.

   - After 20 minutes, read the absorbance as described in Step 3.

Calculations:

1. Aqueous Samples:

   a. Calculate using linear regression.

   b. Multiply in any dilution factors performed in the distillation and colorimetric steps to obtain the final result in mg/L.

2. Non-Aqueous Samples:

   a. Calculate using regression to obtain a mg/L value.

   b. Multiply in any dilution factor performed in the colorimetric step (mg/L).

   c. Multiply result obtained from "Step b" by 50 and divide by grams of sample used to obtain the final result in mg/kg.

3. Spike calculation:

$$\% \text{ Recovery} = \frac{\begin{bmatrix}\text{Total mL}\\ \text{SA + STD}\end{bmatrix}\begin{bmatrix}\text{Conc. of}\\ \text{spike}\end{bmatrix} - \begin{bmatrix}\text{mL}\\ \text{SA used}\end{bmatrix}\begin{bmatrix}\text{Conc. of}\\ \text{SA}\end{bmatrix}}{(\text{mL STD used})\ (\text{Conc. STD})}$$

Where SA = sample
STD = standard

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. The standard curve must be carried through the distillation process. Record the absorbance check standards (1.00 mg/L) in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrometer bulb, solutions, etc.).

2. A distilled blank and standard (1.00 mg/L) is to be analyzed initially and at the end of the analytical run. The standard must be within acceptable ranges (± 10% of true value), or troubleshooting must be performed.

3. A quality control calibration standard of 1.00 mg/L is to be analyzed, initially and after every 10 samples. This standard does not need be carried through the distillation procedure. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges (± 10% of the true value) or the samples run after the last acceptable check standard are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike recoveries and duplicate results are to be within acceptable ranges.

# CHEMICAL OXYGEN DEMAND

Scope and Application: This method is applicable to surfacewater, sewages, wastewater, and groundwater.

Method: Dichromate reflux, Colorimetric

Reference: EPA 1983, Method 410.4.

Detection Limit: 20 mg/L

Optimum Range: 20-700 mg/L

Sample Handling: Preserve with sulfuric acid to a pH <2 and refrigerate at 4°C. Analyze within 28 days.

Reagents and Apparatus:

1. Dichromate - mercuric sulfate-sulfuric acid digestion solution
2. Silver sulfate - sulfuric acid catalyst solution
3. COD standard solutions
4. Block digestor, set at 150°C
5. 16 x 100 mm culture tubes with teflon lined screw caps
6. Eppendorf macropipeter, 0-5 mL
7. Spectrophotometer, set at 600 nm wavelength with sipper cell
8. Eppendorf microliter pipeter, 10-100 ul
9. 2 Repipette Dispensers, 1000 mL
10. Milli-Q water

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Digestion Solution: Add 10.2 g of dried potassium dichromate ($K_2Cr_2O_7$), 33.3 g of mercuric sulfate ($HgSO_4$) and 167 mL of concentrated $H_2SO_4$ to about 500 mL of Milli-Q water; dilute to 1000 mL in a volumetric flask and stir until dissolved. Store in a dark place.

2. Silver Sulfate-Sulfuric Acid Catalyst Solution: Add 22.0 g of silver sulfate ($Ag_2SO_4$) to a 2.5L bottle of conc. $H_2SO_4$. Stir to dissolve.

3. COD Stock Standard, 1000 mg/L: Carefully weigh 0.8500g of dried potassium acid phthalate (KHP), dissolve in Mill-Q water and dilute to 1 liter in a volumetric flask. Refrigerate.

4. Working COD Standards: (Prepare fresh monthly and refrigerate.)

   A. 700 mg/L COD Standard: To a 100 mL volumetric flask, add 70 mL of 1000 mg/L COD Stock Standard and dilute to the mark with Milli-Q water.

B. 300 mg/L COD Standard: To a 100 mL volumetric flask, add 30 mL of 1000 mg/L stock standard and dilute to the mark with Milli-Q water.

C. 100 mg/L COD Standard: To a 100 mL volumetric flask, add 10 mL of 1000 mg/L COD Stock Standard and dilute to the mark with Milli-Q water.

D. 50 mg/L COD Standard: To a 100 mL volumetric flask, add 5 mL of 1000 mg/L COD Stock Standard and dilute to the mark with Milli-Q water.

E. 20 mg/L COD Standard: To a 100 mL volumetric flask, add 2 mL of 1000 mg/L COD Intermediate Standard and dilute to the mark with Milli-Q water.

Notes:

1. If a dark green or turquoise color occurs when sample is added or when the tube is being heated; it is over the upper limit of the curve and must be diluted.

2. Interference: Chlorides represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chloride. Mercuric sulfate can complex up to 2,000 mg/L chloride before reacting with dichromate in the sample. If chloride exceeds 2,000 mg/L, dilute the sample.

3. Reagents are corrosive and toxic. Avoid skin contact.

4. Store standards in the refrigerator.

5. Store the dichromate solution and prepared tubes in the dark.

6. To clean the tubes, rinse several times in Milli-Q water.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and Milli-Q water rinsed prior to analysis. Rinse digestion tubes and caps with Milli-Q water prior to use. Caps deterioriate over time. Discard caps after 3 uses.

2. Into each tube, pipet exactly 1.5 mL of COD digestion solution, using repipetter dispenser.

3. Into each tube, pipet exactly 3.5 mL of the silver sulfate-sulfuric acid solution, using the repipetter dispenser, down the side of the tube. These tubes may be stored, with caps having teflon liners, indefinitely. Store in the dark!

4. The standard curve consists of the following standards:

   3 Milli-Q water blanks
   2-20 mg/L
   2-50 mg/L
   1-100 mg/L
   1-300 mg/L
   1-700 mg/L

   The standards are carried through the digestion step.

5. To Spike: In a disposable cup, place 2.5 mL sample, add 2.5 mL of the 300 mg/L standard. Mix well. Take 2.5 mL of this mixture, proceed as follows.

   Using the Oxford 0-5 mL pipet, add 2.5 mL of sample, standard, blank or spike to the tube. Be careful to avoid air bubbles in the pipet tip and to eject all of the sample. Cap tubes tightly and mix by inverting 10-12 times.

6. Place tubes in a block heater at 150°C for 2 hours. Block heater should be preheated at least 1 hour prior to use.

7. Remove tubes from block heater. Cool to room temperature. Read the absorbance on spectrophotometer, set at 600 nm, using the sipper cell. Samples can be stored in refrigerator overnight and read the next day. Do not shake tubes. Be very careful not to aspirate any of the precipitate in the bottom of the tube. Initially zero with the blank standard, and after 20 samples rezero.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistant from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrophotometer bulb, solution, etc.)

2. A quality control calibration standard of 100 mg/L COD is to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard is still required. The last sample analyzed in the run is to be the calibration standard. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the quality control book. The confidence limits are noted in the quality control book.

3. Duplicate and spike a miniumum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Duplicates are to be averaged. Spike recoveries and duplicate results are to be within acceptable ranges.

Calculation:

1. Calculate using linear regression.

To Calculate Spike:

$$\% \text{ Recovery} = \frac{(\text{spike value}) - (0.5)(\text{sample value})}{150} \times 100$$

| | Revision Date |
|---|---|
| Michael Linskens<br>Michael J. Linskens<br>Laboratory Manager | 7-23-86 |
| Kim Finner<br>Kim D. Finner<br>Analytical Laboratory QA/QC Officer | 4-27-87 |
| Thomas J. Lynch<br>Thomas J. Lynch<br>QA Officer | |

[AL-1-13]

# TOTAL ORGANIC CARBON

Scope and Application: This method is applicable to surface water, sewage, wastewater, and groundwater.

Method: Wet oxidation, non-dispersive infra-red detection

Reference: EPA 1983, Method 415.1 and OI Model 524C Total Carbon System Manual

Detection Limit: 1.0 mg/L

Optimum Range: 1.0-25 mg/L

Sample Handling: Acidify with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Analyze within 28 days.

Reagents and Apparatus:

1. OI Model 524C Total Carbon System
2. 10 mL sealed ampules
3. Commercial grade $O_2$ gas
4. Disposable propane gas cylinder
5. Commercial-grade $N_2$ gas
6. Eppendorf microliter pipet, 100-1000 uL
7. Eppendorf macropipet, 0-5 mL
8. Silicone grease
9. Saturated potassium persulfate solution
10. Organic carbon standard solutions
11. Phosphoric acid solution, 10%
12. Milli-Q water

Reagent Preparation:

1. Total Organic Carbon (TOC) Stock Solution, 1000 mg/L: Dry potassium biphthalate (KHP) at 105°C for 2 hours. Cool in a dessicator. Weigh exactly 2.1254 g KHP and dilute with Milli-Q water to 1000 mL in a volumetric flask.

2. Standard Carbon Solutions:

   25 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 25.0 mL stock carbon solution, and dilute to the mark with Milli-Q water.

   10 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 10.0 mL stock cabron solution, and dilute to the mark with Milli-Q water.

   5 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 5.0 mL stock carbon solution, and dilute to the mark with Milli-Q water.

   3 mg/L TOC Standard: To a 1000 mL volumetric flask, pipet 3.0 mL stock carbon solution, and dilute to the mark with Milli-Q water.

1 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 10.0 mL of a 10.0 mg/L work carbon solution, and dilute to the mark with Milli-Q water.

3. Potassium Persulfate Solution, Saturated: Fill a 1 liter glass stoppered bottle 3/4 full with Milli-Q water. Add potassium persulfate until no more crystals will dissolve.

4. Phosphoric acid solution, 10% (v/v): Add 100 mL of phosphoric acid to 900 mL Milli-Q water.

Notes:

1. Contamination can be a problem. Keep ampules covered with aluminum foil after opening.

2. Purge and seal the ampules believed to contain the lowest carbon content first.

3. Always use clean purge tubes and purge cones. Clean with Milli-Q water, or a 10% HCL solution followed by Milli-Q water rinse.

4. The flow rate of $N_2$ must remain constant.

5. Changes in flow rate may be due to:

   a. Exhausted primary drying tube
   b. Leaky ampule seal
   c. Glass lodged in purge tube

6. Check zero and span settings monthly.

7. Change secondary drying tube daily.

8. Leave IR power on.

9. High suspended solids can give variable results. It is important that the sample is well mixed prior to measuring out the sample.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and Milli-Q rinsed prior to analysis.

2. Snap open an ampule along scoring.

3. Using Eppendorf 1000 microliter pipet, pipet 1000 uL of saturated potassium persulfate solution into ampule.

4. Using calibrated Oxford macropipet, carefully pipet 5.0 mL of sample into ampule.

5. Using Eppendorf 1000 microliter pipet, pipet 200 uL of 10% phosphoric acid solution into ampule.

# TOTAL SUSPENDED SOLIDS

Scope and Application: This method is applicable to drinking water, surface water, groundwater, domestic and industrial wastewaters.

Method: Gravimetric, dried at 103-105°C

Reference: EPA 1983, Method 160.2

Detection Limit: 2 mg/L (using a 500 mL sample volume)

Sample Handling: Refrigerate at 4°C and analyze within 7 days of sampling.

Reagents and Apparatus:

1. Glass fiber filters, Whatman GF/C
2. Gelman filtration funnel and support
3. Suction flask, 1000 mL.
4. Aluminum foil weighing dishes
5. Graduated cylinder, 100 mL
6. Drying oven set at 103-105°C
7. Dessicator
8. Analytical balance
9. Deionized water

Notes:

1. Interferences: Samples with high dissolved solids may have a positive interference, and the filter should therefore be rinsed well with deionized water under suction after the sample has gone through the filter.

2. Select a sample volume that will filter without overloading the filter. The amount of vacuum applied to filter the sample should not be excessive. Excessive vacuum will cause the filter to breakdown and lose weight.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed, and deionized rinsed prior to analysis.

2. Prepare the glass fiber filter by placing it on the filter support, applying vacuum, and rinsing with three-20 mL portions of deionized water through it.

3. Place the filter in an aluminum weighing dish and dry at 103-105°C for one hour.

4. Place in a dessicator, and cool before weighing (at least one hour). Repeat this cycle until a constant weight ($\pm$ 0.5 mg) is obtained. Filters may be prepared ahead of time and stored in the dessicator until ready to use.

6. Place ampule on purging rack and place a purge tube into ampule to the bottom of the ampule. (There is room to purge 10 samples at a time.)

7. Purge each sample for at least 6 minutes with nitrogen ($N_2$) gas.

8. Light microburner. Place ampule into clamping assembly, leaving purge tube in-place in ampule. Base of ampule should be snug with base of clamping assembly.

9. Swing microburner into place and seal ampule.

10. Continue purging while sealing the tube being careful not to fuse the purging tube while sealing. Do this by raising the purge tube just above the sealing point of the ampule.

11. Swing microburner back as soon as ampule is sealed.

12. Remove sealed ampule from holder. Open clamping assembly and drop hot ampule tip into a beaker partially filled with water.

13. Continue with steps 8-11 for the remaining samples.

14. Place ampules in an oven set at 95°C for 2 hours. Cool.

15. Place plastic stress adaptor and gum rubber seal on neck of ampule. (Silicon grease may be necessary.)

16. Place ampule in breaking assembly and turn clamping screw until ampule is firmly in-place. Check seals to make sure these are no air leaks.

17. Lower purge tube until it is level with the tip of the ampule.

18. Open zero gas valve ($N_2$). Adjust flow to 13 (200 mL/min.) on flowmeter. Purge air from top of ampule until integrator stops. Clear integrator.

19. Close zero gas valve ($N_2$). Wait for flow to drop to zero.

20. Raise purge tube clear of plunger cutters.

21. Break ampule with a downward, twisting motion.

22. Check ampule for cracks or leaks.

23. Put purge tube down into solution in ampule, about 1/8" from bottom.

24. Open zero gas valve ($N_2$). Flow rate should be 13 (200 mL/min.).

25. Allow ampule to purge until integrator stops.

26. Record the reading and clear the integrator.

27. Remove ampule from assembly and discard.

Daily Instrument Set-Up:

1. Check to make sure the IR detector is on (red light should be on). If not left on, allow warm-up time of at least one hour.

2. Place standardization vial with plastic adapter and gum rubber seal in ampule-breaking assembly.

3. Turn valves on front panel to "Ampule Mode" and "I.R. Flow".

4. Open $N_2$ valve on top of tank (pressure regulator set at 20 PSI).

5. Open zero gas ($N_2$) valve by lifting handle straight out.

6. Adjust flow rate to a flow meter reading of 13 (200 mL/min).

7. Turn integrator unit on clear and zero.

8. Check purging and sealing unit to ensure that a disposable propane gas cylinder is connected to adapter.

9. Open $O_2$ valve on top of tank (pressure regulator set at 20 PSI).

10. Turn on catalyst heater on front panel of purge and seal unit. Allow unit to purge at 500°C for one hour.

11. Check the ascarite in the tubes in the sides of the units. It should be brown to light tan in color. If white, it is $CO_2$ saturated and must be replaced.

12. Check drying tubes on front of ampule panel. If they appear wet or "clumpy", replace with fresh dessicant (magnesium perchlorate).

13. Change secondary drying tube.

Daily Instrument Shut-Down:

1. Turn integrator power switch off.

2. Close $O_2$, propane, and $N_2$ cylinder valves.

3. Close $O_2$ and $N_2$ toggle valves.

4. Remove and clean cutter plunger and barrel with Milli-Q water. Wipe dry.

5. Lubricate O-rings with silicone grease and re-install cutter plunger and barrel.

6. Re-install standardization vial.

7. Turn catalyst heater switch off.

8. Leave I.R. power on.

Quality Control:

1. Standard curve is to consist of the following standards; set in duplicate:

   Milli-Q water blank
   1.0 mg/L
   3.0 mg/L
   5.0 mg/L
   10.0 mg/L
   20.0 mg/L

2. The quality control check standard is to be analyzed before and after every 10 samples. The 10 mg/L check standard must be within the critical levels or the samples analyzed prior to the last check standard are to be reanalyzed. Before the samples are reanalyzed, the analyst must diagnose the problem and consult with the laboratory supervisor until the problem has been resolved and approved. Record the result of the check standard in the quality control check standard book.

3. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Average the results.

4. Spike 1 out of 10 samples. If less than 10 samples are analyzed, a spike is still required. For spikes, pipet 4 mL of sample and 1 mL of 20 mg/L organic carbon standard. Spike recoveries and duplicate results are to be within acceptable calculated ranges.

Calculation:

1. Plot a standard curve from a series of standards. Calculate directly from graph.

2. Calculate using linear regression.

Revision Date

7-23-86

9-25-87

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Vice President, Technical Services

[ALM-1A-1]

5. Weigh the aluminum dish containing the prepared filter on the analytical balance and record the weight.

6. Assemble the filtering apparatus. Begin applying vacuum. Wet the filter with a little D.I. water.

7. Shake the sample well and pour an appropriate volume using a graduated cylinder. The use of pipets is required for volumes of 25 mL and less. Record the volume.

8. With the vacuum still on, rinse the apparatus with 3-10 mL portions of D.I. water. Continue the vacuum until filtration is complete.

9. With forceps, carefully remove the filter from the support and place in the <u>same</u> aluminum dish.

10. Place in the drying oven and dry at 103-105°C for one hour.

11. Cool in a dessicator for one hour and weigh. Record the weight.

12. Repeat drying cycle until weight change is $\leq$0.5 mg. Record the final weight.

<u>Quality Control</u>:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates should be within acceptable ranges. Duplicates are to be averaged.

2. A blank dish and filter are carried through the entire procedure, as a check on contamination (cleanliness of dishes, oven, pipettes, etc.)

<u>Calculations</u>:

$$\text{TSS, mg/L} = \frac{(A-B)}{C} \times 1000000$$

Where A = weight of filter, aluminum pan and residue (g)
B = weight of filter and aluminum pan (g)
C = sample volume (mL)

| | Revision Date |
|---|---|
| Michael Linskens<br>Michael J. Linskens<br>Laboratory Manager | 7-23-86 |
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| Thomas J. Lynch<br>Thomas J. Lynch<br>QA Officer | |

# TOTAL DISSOLVED SOLIDS

Scope and Application: This method is applicable to drinking water, surface water, groundwater, and domestic and industrial wastewaters.

Method: Gravimetric, dried at 180°C

Reference: EPA 1983, Method 160.1

Detection Limit: 10 mg/L (using a 100 mL sample volume)

Sample Handling: Refrigerate at 4°C and analyze sample within 7 days of sampling.

Reagents and Apparatus:

1. Glass fiber filters, Whatman GF/C
2. Gelman filtration funnel and support
3. Suction flask, 1000 mL
4. Porcelain evaporating dishes
5. Graduated cylinder, 100 mL
6. Drying oven at 180°C ± 2°C
7. Dessicator
8. Analytical balance
9. Deionized water

Notes:

1. Interferences: Samples with high concentrations of bicarbonate, Ca, Mg, Cl, and $SO_4$ will require prolonged drying, dessication, and rapid weighing.

2. Total residue should be < 200 mg. Excessive residue (>200 mg) is difficult to dry thoroughly. Use a smaller volume if TDS is suspected to be high; likewise use a larger volume if TDS is suspected to low.

3. Groundwater samples which have already been filtered through a 0.45 micron membrane filter do not need to be carried through the filtration step of the procedure.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and deionized rinsed prior to analysis.

2. Evaporating Dish Preparation: If volatile dissolved solids is also to be analyzed, prepare the evaporating dishes by ashing at 550 ±50°C for one hour in a muffle furnace.

   Otherwise, heat the dishes at 180 ± 2°C for one hour. Cool in dessicator. Weigh. Record the weight. The dishes must be cool before being weighed (about one hour). Repeat this cycle until a constant weight is obtained (± 0.5 mg). Weigh just before use.

3. Filter Preparation: Place the glass fiber filter on the filtration support, place the funnel on top, and wash the filter with three-20 mL portions of deionized water while vacuum is applied. Discard the washings. The filters may be prepared ahead of time. If this is the case, dry them for 1 hour at 103 - 105°C and store in the dessicator until needed.

4. Assemble the filtering apparatus, place a prepared filter on the support and begin suction. Shake the sample and measure out 100 mL in graduated cylinder.

5. Filter the sample, then rinse the cylinder and funnel with a small amount of deionized water. Apply vacuum until all the sample has been filtered. Rinse with 3 - 10 mL portions of D.I. water and continue the vacuum until filtration is complete.

6. Pipet 50 mL of the filtrate (less, if the sample is expected to have a high dissolved solids content) into a prepared evaporating dish.

7. Evaporate the sample to dryness in the oven at 180 ±2°C. Cool in a dessicator for at least one hour and weigh. Repeat the drying cycle until the weight loss is ≤0.5 mg.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates should be within acceptable ranges. Duplicate results are to be averaged.

2. A blank must be analyzed with each run. (This is a check on contamination, cleanliness of dishes, oven, pipettes, etc.).

Calculation:

$$\text{TDS, mg/L} = \frac{(A-B)}{C} \times 1000000$$

Where A = weight of dish plus residue (g)
B = weight of dish (g)
C = volume of filtered sample used (mL)

| | Revision Date |
|---|---|
| Michael Linskens<br>Michael J. Linskens<br>Laboratory Manager | 7-23-86 |
| Kim Finner<br>Kim D. Finner<br>Analytical Laboaratory QA/QC Officer | 5-21-87 |
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# CATION EXCHANGE CAPACITY OF SOILS

Scope of Application: This method is applicable to soil samples collected as part of the American Chemical Services RI/FS. A total of 20 soil samples are anticipated.

Method: Cation exchange capacity of soils.

Reference: ASA-SSSA, 1982. Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties. Agronomy Monograph No. 9 (2nd Edition).

Sample Handling: Samples will be air dried at 60°C upon receipt. A separate sample aliquot will be oven dried to determine moisture content. Samples will be stored until analysis.

Interference - Corrective Action: If the soil is initially high in salts (EC ≥ 4 mmho/cm) wash the soil with one 33-ml increment of water before beginning saturation (avoid excessive washing to prevent loss of particles during decantation).

Quality Control

1. Laboratory duplicates should be run at a frequency of one per ten investigative samples and at least one per sample set. Duplicates should agree within 20 percent.

Apparatus:

1. Atomic absorption spectrometer
2. Centrifuge
3. Round-bottom, narrow-neck centrifuge tubes, 50 ml
4. Ultrasonic disperser with microtip focusing horn
5. Reciprocating shaker
6. Balance (.01 g sensitivity)
7. Automatic coulometric/amperometric $Cl^-$ titrator

Reagents:

1. Saturating solution, 0.4N NaOAc-0.1N, NaCl, 60% ethanol, pH 8.2 solution: Combine 544.32 g of sodium acetate (NaOAc), 58.44 g of sodium chloride (NACl), and 6 liters of ethanol, and dilute to 10 liters with distilled water. Adjust the pH by stirring and dropwise addition of 6N sodium hydroxide (NaOH). Determine the Na/Cl ratio of this solution.

2. Extracting solution, 0.5N magnesium nitrate [$Mg(NO_3)$]: Weigh out 641.1 g of $Mg(NO_3)_2 \cdot 6H_2O$, and dilute to 10 liters.

3. Suppresant solution for Na+: Add 6.358 g of lithium chloride (LiCl) and make to 1 liter in distilled water (0.15N).

4. Nitric acid-acetic acid/polyvinyl alcohol (PVA): Dissolve 1.8 g of powdered PVA in 100 ml of demineralized water with heating and stirring, cool to room temperature. Add 6.4 ml of conc nitric acid ($HNO_3$) and 100 ml of glacial acetic acid to a 1-liter volumetric flask containing 600 ml of demineralized water, and mix thoroughly. Add the cooled PVA solution to the nitric acid-acetic acid solution, mix, cool, and make to volume with demineralized water. Store this nitric acid-acetic acid/PVA reagent in a tightly stoppered container at room temperature. This reagent is stable for at least 12 months.

Procedure:

Sample Preparation

1. Weigh out samples of 4 to 5 g of air-dry soil (correct to oven-dry moisture content as determined using a separate subsample), and place in centrifuge tube.

2. Add 33 ml of saturating solution, stopper the tube, and shake for 5 min. Unstopper, and centrifuge at relative centrigual force of 1,000 until the supernatant liquid is clear (about 5 min). Decan the supernatant liquid and discard. Add fresh saturating, solution, insert sonifier tip, and "sonify" for 10 to 30 sec to disperse sediment, then continue as above. Make four successive "equilibrations," discarding the supernatant liquid each time.

3. Add 33 ml of extracting solution, shake for 5 min, centrifuge until the supernatant liquid is clear, and decant the extracted solution into a 100-ml volumetric flask. Repeat the extraction steps two more times with fresh extracting solution, and make to volume.

4. Determine $Na^+$ ($Na_t$) and $Cl^-$($Cl_t$) in dilutions of this extracted solution using standards made up in the same batch of extracting solution. Chloride is determined so that the soluble $Na^+$ ($Na_{sol}$) carried over from the saturation step to the extraction step can be deducted from the total Na to obtain exchangeable $Na^+$ ($Na_{exch}$):

$$CEC = (Na_t - Na_{sol}) = Na_t - (Cl_t)\ (Na/Cl)sat\ sol$$

Chloride Determination:

5. Add 4 ml of nitric acid-acetic acid/PVA reagent together with a sample aliquot (<3 ml) to a titration vial.

6. Position vial in the coulometric/amperometric titrator, immersing the electrode assembly into the solution.

7. Zero the timer, and initiate automatic titration at low, medium, or high current setting. Note the titration times of blank, standards, and samples.

Sodium Determination

8. Add enough lithium chloride suppressant solution to sample, blank and standard aliquots to give 10% (by volume) in the final solution.

9. Adjust the atomic absorption spectrometer controls and settings for sodium as recommended by the manufacturer.

10. Calibrate the instrument with at least 4 Na standard solutions ranging from 0 to 1 meq/liter.

11. Any dilutions should be made in such a way that the standards and unknowns have the same final $Mg(NO_3)_2$ concentration.

12. Record results in meq $Na^+$/liter of aspirated solution.

Calculations:

Cloride

$Cl^-$ in meq/liter
= (K) (Titration time of sample minus titration time of blank)/aliquot

where K is a standardization factor and aliquot is sample size in ml.

K = (Volume of $Cl^-$ standard in ml) (Conc of $Cl^-$ standard in meq/liter/(titration time of standard minus blank).

Sodium:

$Na^+$ meq/liter original sample

= (meq $Na^+$/liter in aspirated sample) x (analytical dilution factor)

Cation Exchange Capacity:

CEC in meq/100 g = (10/weight soil sample in g)

[(Na concentration in meq/liter) $(DF_{Na})$ - (Cl concentration in meq/liter)

$(DF_{Cl})$ $(NaCl)_{sat\ sol}$]

where DF represents the dilution factor, i.e., (final analytical volume in milliliters)/(aliquot volume in milliliters).

# GRAIN SIZE ANALYSIS OF SOIL

**Scope and Application:** This method is applicable to soil samples collected as part of the Muskego Sanitary Landfill RI/FS. The Muskego site RI/FS is a PRP lead investigation.

**Method:** Particle size analysis of soil.

**Reference:** ASTM Methods D421, and D422 and D2217 (see attached).

**Detection Limit:** 2 percent by weight.

**Sample Handling:** Samples will be air dried at 60°C upon receipt. After drying, the sample, or a representative portion of the sample, will be separated into fractions passing and retained on a 2mm sieve per ASTM Method D421 or D2217. The fractions will then be stored until analysis.

**Reagents and Apparatus:**

1. Balance (0.01 g sensitivity)
2. Dispersion cup
3. Hydrometer
4. Sedimentation cylinder
5. Thermometer (0.5°C sensitivity)
6. Sieves (see ASTM D422 Section 3.6)
7. Temperature controlled room (±1°C)
8. 4% Sodium hexametaphosphate solution

**Reagent Preparation:**

The sodium hexametaphosphate solution is to have been prepared within 30 days of use.

**Procedures:**

1. The sample fraction greater than 2mm is fractioned by sieving using sieves and procedures as outlined in Section 6 of ASTM D422. The sum of the masses of the sieved fractions should be within ± 2 g of the original fraction mass.

2. Determine the hygroscopic moisture content of the less than 2mm fraction by drying a minimum 10 to 15 g subsample to constant weight at 110 plus or minus 5 degree C.

3. Disperse a 50 g sample if the sample is primarily silt and clay or a 100 g sample is primarily sand for one minute using a dispersion cup as outlined in Section 9 of ASTM D422.

4. Transfer the dispersed sample to a sedimentation cylinder, suspend the sample by successive inversions and record hydrometer readings after sedimentation times of 1, 2, 3, 6, 15, 60, 120, 300, 420 and 1440 minutes.

5. After hydrometer readings are complete, the hydrometer and hygroscopic moisture specimens are combined with the remaining P10 and R10 material for sieving.

Reportables:

1. Submit all raw data including container tare weights, hydrometer readings (along with any correction factor associated with the hydrometer used) and temperatures.

2. A data summary will be provided as described in Sections 17 and 18 of ASTM Method D422.

Quality Control:

1. Laboratory Duplicates will be run at a frequency of one per ten investigative samples and at least one per sample set. Duplicates should agree within 10 percent.

2. If performance criteria for duplicates is exceeded, the Warzyn project manager (Mike Radcliffe, 608-273-0440) should be notified as soon as possible so a determination regarding reanalysis can be made.

NOTE 9—Other *in situ* test procedures are being prepared by ASTM Committee D-18.

9.2 The soil and rock investigation should consist of the following steps.

9.2.1 A review of all available information on the geologic history and formation of rock, or soil, or both, and ground-water conditions occurring at the proposed location and in the immediate vicinity.

9.2.2 On-site investigation of the surface and subsurface materials by either wash borings, hand- or power-auger borings, test pits, rotary or cable-tool (churn) drilling, and geophysical methods.

9.2.2.1 A determination of the depths to water table and firm foundation material, either bedrock or satisfactory load-bearing soils.

9.2.2.2 Field identification of soil and rock types with depth records of their occurrence, and location of their structural discontinuities.

9.2.2.3 The recovery of representative disturbed samples for laboratory classification tests of soil, rock, and local construction material. These should be supplemented by undisturbed specimens suitable for the determination of those engineering properties pertinent to the investigation.

9.2.3 An evaluation of performance of existing installations in the immediate vicinity of the proposed site, relative to their foundation material and environment.

## 10. Classification of Material

10.1 Treat samples of soils and rock submitted to the laboratory for identification and classification tests in accordance with one of the following:

10.1.1 Test Method D 2487.

10.1.2 Practice D 3282.

10.1.3 Descriptive Nomenclature C 294. This is a brief, useful description of the more common minerals and rocks as they occur in nature.

## 11. Interpretation of Results

11.1 Interpret the results of an investigation only in terms of actual findings and make every effort to collect and include all field and laboratory data from previous investigations in the same area. Extrapolation of data into local areas not surveyed and tested can be done only where geologically uniform subsurface disposition of soil and rock are known to exist. Engineering properties of the soils and rocks encountered on important projects should not be predicted wholly on field identifications or classification but should be checked by laboratory and field tests made on samples collected in accordance with 8.1 and 9.1.

11.2 The recommendations for design parameters can be made only by professional engineers or geologists who have specialized in the field of soils and foundations or highway engineering, and who are familiar with the problems for which the study is being made. Soil mechanics, rock mechanics, and geomorphological concepts must be combined with a knowledge of structural or pavement engineering in order to make a complete application of the results of the soil and rock survey. A more detailed study than that envisioned by this recommended practice may be necessary before design recommendations can be made.

## 12. Report

12.1 A subsurface investigation report should:

12.1.1 Locate the area investigated in terms pertinent to the project. This may include sketch maps or aerial photos on which the test holes, pits, and sample areas are located, as well as topographic items relevant to the determination of the various soil and rock types such as contours, streambeds, pot holes, cliffs, etc. Where feasible, include a geologic map of the area investigated in the report.

12.1.2 Include copies of all borings and test-hole logs and of all laboratory test results.

12.1.3 Describe and relate the findings obtained under Sections 3, 4, 5, and 6, using the subhead titles for the respective sections.

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Designation: D 421 – 85

# Standard Practice for DRY PREPARATION OF SOIL SAMPLES FOR PARTICLE-SIZE ANALYSIS AND DETERMINATION OF SOIL CONSTANTS[1]

This standard is issued under the fixed designation D 421; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice covers the dry preparation of soil samples as received from the field for particle-size analysis and the determination of the soil constants.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Applicable Documents

2.1 *ASTM Standards:*

D2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

## 3. Significance and Use

3.1 This practice can be used to prepare samples for particle-size and plasticity tests where it is desired to determine test values on air-dried samples, or where it is known that air drying does not have an effect on test results relative to samples prepared in accordance with Practice D 2217.

## 4. Apparatus

4.1 *Balance*, sensitive to 0.1 g.

4.2 *Mortar and Rubber-Covered Pestle*, suitable for breaking up the aggregations of soil particles.

4.3 *Sieves*—A series of sieves, of square mesh woven wire cloth, conforming to Specification E 11. The sieves required are as follows:

No. 4 (4.75-mm)
No. 10 (2.00-mm)
No. 40 (425-μm)

4.4 *Sampler*—A riffle sampler or sample splitter, for quartering the samples.

## 5. Sampling

5.1 Expose the soil sample as received from the field to the air at room temperature until dried thoroughly. Break up the aggregations thoroughly in the mortar with a rubber-covered pestle. Select a representative sample of the amount required to perform the desired tests by the method of quartering or by the use of a sampler. The amounts of material required to perform the individual tests are as follows:

5.1.1 *Particle-Size Analysis*—For the particle-size analysis, material passing a No. 10 (2.00-mm) sieve is required in amounts equal to 115 g of sandy soils and 65 g of either silt or clay soils.

5.1.2 *Tests for Soil Constants*—For the tests for soil constants, material passing the No. 40

[1] This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

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[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

(425-μm) sieve is required in total amount of 220 g, allocated as follows:

| Test | Grams |
|---|---|
| Liquid limit | 100 |
| Plastic limit | 15 |
| Centrifuge moisture equivalent | 10 |
| Volumetric shrinkage | 30 |
| Check tests | 65 |

## 6. Preparation of Test Sample

6.1 Select that portion of the air-dried sample selected for purpose of tests and record the mass as the mass of the total test sample uncorrected for hygroscopic moisture. Separate the test sample by sieving with a No. 10 (2.00-mm) sieve. Grind that fraction retained on the No. 10 sieve in a mortar with a rubber-covered pestle until the aggregations of soil particles are broken up into the separate grains. Then separate the ground soil into two fractions by sieving with a No. 10 sieve.

6.2 Wash that fraction retained after the second sieving free of all fine material, dry, and weigh. Record this mass as the mass of coarse material. Sieve the coarse material, after being washed and dried, on the No. 4 (4.75-mm) sieve and record the mass retained on the No. 4 sieve.

## 7. Test Sample for Particle-Size Analysis

7.1 Thoroughly mix together the fractions passing the No. 10 (2.00-mm) sieve in both sieving operations, and by the method of quartering or the use of a sampler, select a portion weighing approximately 115 g for sandy soils and approximately 65 g for silt and clay soil for particle-size analysis.

## 8. Test Sample for Soil Constants

8.1 Separate the remaining portion of the material passing the No. 10 (2.00-mm) sieve into two parts by means of a No. 40 (425-μm) sieve. Discard the fraction retained on the No. 40 sieve. Use the fraction passing the No. 40 sieve for the determination of the soil constants.

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*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.*

Designation: D 422 – 63 (Reapproved 1972)[1]

# Standard Method for PARTICLE-SIZE ANALYSIS OF SOILS[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[1] NOTE—Section 2 was added editorially and subsequent sections renumbered in July 1984.

## 1. Scope

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (1) a high-speed mechanical stirrer, and (2) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

## 2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

## 3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft³/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

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[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.

drometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

## 8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

## 9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

| Plasticity Index | Dispersion Period, min |
|---|---|
| Under 5 | 5 |
| 6 to 20 | 10 |
| Over 20 | 15 |

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

## 10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.



10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

## 11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-µm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

## CALCULATIONS AND REPORT

## 12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

## 13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

## 14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight $W$ in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

$a$ = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

$P$ = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

$R$ = hydrometer reading with composite correction applied (Section 7),

$W$ = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

$G$ = specific gravity of the soil particles, and

$G_1$ = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for $R$ is based on a value of one for $G_1$.

## 15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is

results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

| | |
|---|---|
| 3-in. (75-mm) | No. 10 (2.00-mm) |
| 2-in. (50-mm) | No. 20 (850-µm) |
| 1½-in. (37.5-mm) | No. 40 (425-µm) |
| 1-in. (25.0-mm) | No. 60 (250-µm) |
| ¾-in. (19.0-mm) | No. 140 (106-µm) |
| ⅜-in. (9.5-mm) | No. 200 (75-µm) |
| No. 4 (4.75-mm) | |

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

| | |
|---|---|
| 3-in. (75-mm) | No. 16 (1.18-mm) |
| 1½-in. (37.5-mm) | No. 30 (600-µm) |
| ¾-in. (19.0-mm) | No. 50 (300-µm) |
| ⅜-in. (9.5-mm) | No. 100 (150-µm) |
| No. 4 (4.75-mm) | No. 200 (75-µm) |
| No. 8 (2.36-mm) | |

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.

## 4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

## 5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

| Nominal Diameter of Largest Particles, in. (mm) | Approximate Minimum Mass of Portion, g |
|---|---|
| ⅜ (9.5) | 500 |
| ¾ (19.0) | 1000 |
| 1 (25.4) | 2000 |
| 1½ (38.1) | 3000 |
| 2 (50.8) | 4000 |
| 3 (76.2) | 5000 |

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

# SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

## 6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, 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 in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

# HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

## 7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cyclinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hy-

ing to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)] \times L/T}$$

where:

$D$ = diameter of particle, mm,

$n$ = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

$L$ = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

$T$ = interval of time from beginning of sedimentation to the taking of the reading, min,

$G$ = specific gravity of soil particles, and

$G_1$ = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal elocity of a single sphere falling in an infinity of liquid, he sizes calculated represent the diameter of spheres hat would fall at the same rate as the soil particles.

15.2 For convenience in calculations the bove equation may be written as follows:

$$D = K\sqrt{L/T}$$

here:

$K$ = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of $K$ for a range of temperatures and specific gravities are given in Table 3. The value of $K$ does not change for a series of readings constituting a test, while values of $L$ and $T$ do vary.

15.3 Values of $D$ may be computed with sufcient accuracy, using an ordinary 10-in. slide ule.

NOTE 15—The value of $L$ is divided by $T$ using the - and $B$-scales, the square root being indicated on the -scale. Without ascertaining the value of the square ot it may be multiplied by $K$, using either the $C$- or $D$-scale.

## 16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the rious sieves used in sieving the portion of the mple from the hydrometer test involves several eps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2) and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

## 17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting 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. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

## 18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.



NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(*i*) Gravel, passing 3-in. and retained on No. 4 sieve ..... %

(*j*) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %

(*a*) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %

(*b*) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %

(*c*) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %

(*k*) Silt size, 0.074 to 0.005 mm ..... %

(*l*) Clay size, smaller than 0.005 mm ..... %

Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

| Sieve Size | Percentage Passing |
|---|---|
| 3-in. | ..... |
| 2-in. | ..... |
| 1½-in. | ..... |
| 1-in. | ..... |
| ¾-in. | ..... |
| ⅜-in. | ..... |
| No. 4 (4.75-mm) | ..... |
| No. 10 (2.00-mm) | ..... |
| No. 40 (425-μm) | ..... |
| No. 200 (75-μm) | ..... |

HYDROMETER ANALYSIS

| | |
|---|---|
| 0.074 mm | ..... |
| 0.005 mm | ..... |
| 0.001 mm | ..... |

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

TABLE 1 Values of Correction Factor, $a$, for Different Specific Gravities of Soil Particles[A]

| Specific Gravity | Correction Factor[A] |
|---|---|
| 2.95 | 0.94 |
| 2.90 | 0.95 |
| 2.85 | 0.96 |
| 2.80 | 0.97 |
| 2.75 | 0.98 |
| 2.70 | 0.99 |
| 2.65 | 1.00 |
| 2.60 | 1.01 |
| 2.55 | 1.02 |
| 2.50 | 1.03 |
| 2.45 | 1.05 |

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

| Hydrometer 151H | | Hydrometer 152H | | | |
|---|---|---|---|---|---|
| Actual Hydrometer Reading | Effective Depth, $L$, cm | Actual Hydrometer Reading | Effective Depth, $L$, cm | Actual Hydrometer Reading | Effective Depth, $L$, cm |
| 1.000 | 16.3 | 0 | 16.3 | 31 | 11.2 |
| 1.001 | 16.0 | 1 | 16.1 | 32 | 11.1 |
| 1.002 | 15.8 | 2 | 16.0 | 33 | 10.9 |
| 1.003 | 15.5 | 3 | 15.8 | 34 | 10.7 |
| 1.004 | 15.2 | 4 | 15.6 | 35 | 10.6 |
| 1.005 | 15.0 | 5 | 15.5 | | |
| 1.006 | 14.7 | 6 | 15.3 | 36 | 10.4 |
| 1.007 | 14.4 | 7 | 15.2 | 37 | 10.2 |
| 1.008 | 14.2 | 8 | 15.0 | 38 | 10.1 |
| 1.009 | 13.9 | 9 | 14.8 | 39 | 9.9 |
| 1.010 | 13.7 | 10 | 14.7 | 40 | 9.7 |
| 1.011 | 13.4 | 11 | 14.5 | 41 | 9.6 |
| 1.012 | 13.1 | 12 | 14.3 | 42 | 9.4 |
| 1.013 | 12.9 | 13 | 14.2 | 43 | 9.2 |
| 1.014 | 12.6 | 14 | 14.0 | 44 | 9.1 |
| 1.015 | 12.3 | 15 | 13.8 | 45 | 8.9 |
| 1.016 | 12.1 | 16 | 13.7 | 46 | 8.8 |
| 1.017 | 11.8 | 17 | 13.5 | 47 | 8.6 |
| 1.018 | 11.5 | 18 | 13.3 | 48 | 8.4 |
| 1.019 | 11.3 | 19 | 13.2 | 49 | 8.3 |
| 1.020 | 11.0 | 20 | 13.0 | 50 | 8.1 |
| 1.021 | 10.7 | 21 | 12.9 | 51 | 7.9 |
| 1.022 | 10.5 | 22 | 12.7 | 52 | 7.8 |
| 1.023 | 10.2 | 23 | 12.5 | 53 | 7.6 |
| 1.024 | 10.0 | 24 | 12.4 | 54 | 7.4 |
| 1.025 | 9.7 | 25 | 12.2 | 55 | 7.3 |
| 1.026 | 9.4 | 26 | 12.0 | 56 | 7.1 |
| 1.027 | 9.2 | 27 | 11.9 | 57 | 7.0 |
| 1.028 | 8.9 | 28 | 11.7 | 58 | 6.8 |
| 1.029 | 8.6 | 29 | 11.5 | 59 | 6.6 |
| 1.030 | 8.4 | 30 | 11.4 | 60 | 6.5 |
| 1.031 | 8.1 | | | | |
| 1.032 | 7.8 | | | | |
| 1.033 | 7.6 | | | | |
| 1.034 | 7.3 | | | | |
| 1.035 | 7.0 | | | | |
| 1.036 | 6.8 | | | | |
| 1.037 | 6.5 | | | | |
| 1.038 | 6.2 | | | | |

[A] Values of effective depth are calculated from the equation

$$L = L_1 + \tfrac{1}{2}\,[L_2 - (V_b/A)]$$

where:

$L$ = effective depth, cm,
$L_1$ = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,
$L_2$ = overall length of the hydrometer bulb, cm,
$V_b$ = volume of hydrometer bulb, cm³, and
$A$ = cross-sectional area of sedimentation cylinder, cm².

Values used in calculating the values in Table 2 are as follows:

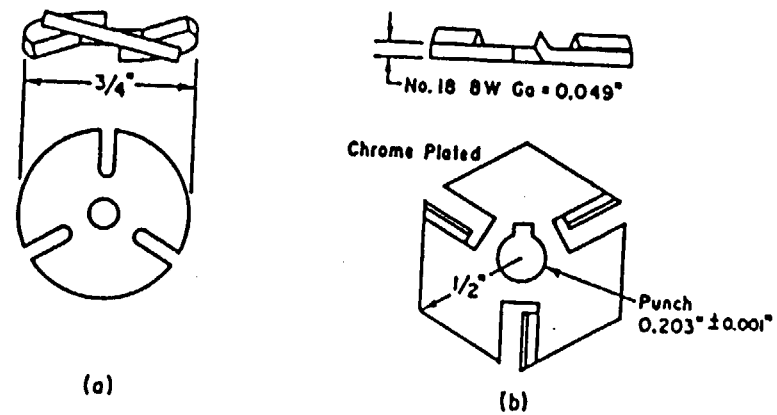
For both hydrometers, 151H and 152H:
$L_2$ = 14.0 cm
$V_b$ = 67.0 cm³
$A$ = 27.8 cm²

For hydrometer 151H:
$L_1$ = 10.5 cm for a reading of 1.000
= 2.3 cm for a reading of 1.031

For hydrometer 152H:
$L_1$ = 10.5 cm for a reading of 0 g/litre
= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of $K$ for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

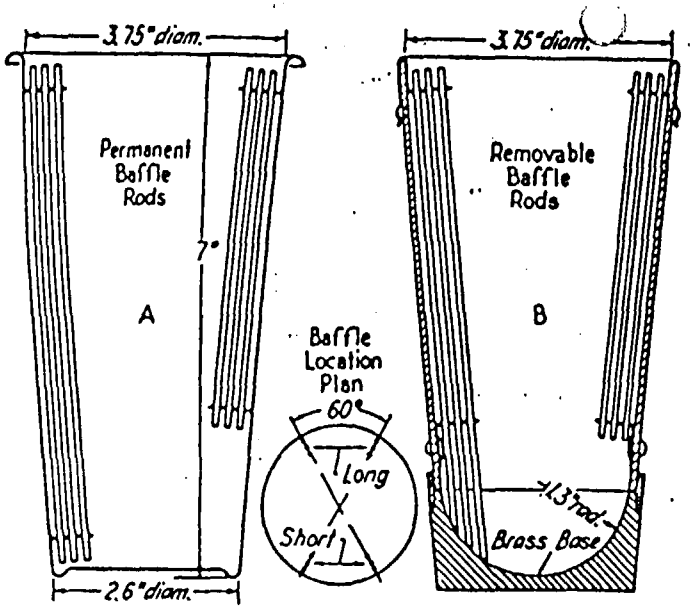
| Temperature, °C | Specific Gravity of Soil Particles | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2.45 | 2.50 | 2.55 | 2.60 | 2.65 | 2.70 | 2.75 | 2.80 | 2.85 |
| 16 | 0.01510 | 0.01505 | 0.01481 | 0.01457 | 0.01435 | 0.01414 | 0.01394 | 0.01374 | 0.01356 |
| 17 | 0.01511 | 0.01486 | 0.01462 | 0.01439 | 0.01417 | 0.01396 | 0.01376 | 0.01356 | 0.01338 |
| 18 | 0.01492 | 0.01467 | 0.01443 | 0.01421 | 0.01399 | 0.01378 | 0.01359 | 0.01339 | 0.01321 |
| 19 | 0.01474 | 0.01449 | 0.01425 | 0.01403 | 0.01382 | 0.01361 | 0.01342 | 0.1323 | 0.01305 |
| 20 | 0.01456 | 0.01431 | 0.01408 | 0.01386 | 0.01365 | 0.01344 | 0.01325 | 0.01307 | 0.01289 |
| 21 | 0.01438 | 0.01414 | 0.01391 | 0.01369 | 0.01348 | 0.01328 | 0.01309 | 0.01291 | 0.01273 |
| 22 | 0.01421 | 0.01397 | 0.01374 | 0.01353 | 0.01332 | 0.01312 | 0.01294 | 0.01276 | 0.01258 |
| 23 | 0.01404 | 0.01381 | 0.01358 | 0.01337 | 0.01317 | 0.01297 | 0.01279 | 0.01261 | 0.01243 |
| 24 | 0.01388 | 0.01365 | 0.01342 | 0.01321 | 0.01301 | 0.01282 | 0.01264 | 0.01246 | 0.01229 |
| 25 | 0.01372 | 0.01349 | 0.01327 | 0.01306 | 0.01286 | 0.01267 | 0.01249 | 0.01232 | 0.01215 |
| 26 | 0.01357 | 0.01334 | 0.01312 | 0.01291 | 0.01272 | 0.01253 | 0.01235 | 0.01218 | 0.01201 |
| 27 | 0.01342 | 0.01319 | 0.01297 | 0.01277 | 0.01258 | 0.01239 | 0.01221 | 0.01204 | 0.01188 |
| 28 | 0.01327 | 0.01304 | 0.01283 | 0.01264 | 0.01244 | 0.01255 | 0.01208 | 0.01191 | 0.01175 |
| 29 | 0.01312 | 0.01290 | 0.01269 | 0.01249 | 0.01230 | 0.01212 | 0.01195 | 0.01178 | 0.01162 |
| 30 | 0.01298 | 0.01276 | 0.01256 | 0.01236 | 0.01217 | 0.01199 | 0.01182 | 0.01165 | 0.01149 |




Metric Equivalents

| | | | | | |
|---|---|---|---|---|---|
| in. | 0.001 | 0.049 | 0.203 | ½ | ¾ |
| mm | 0.03 | 1.24 | 5.16 | 12.7 | 19.0 |

FIG. 1 Detail of Stirring Paddles




Metric Equivalents

| | | | |
|---|---|---|---|
| in. | 1.3 | 2.6 | 3.75 |
| mm | 33 | 66 | 95.2 |

FIG. 2 Dispersion Cups of Apparatus

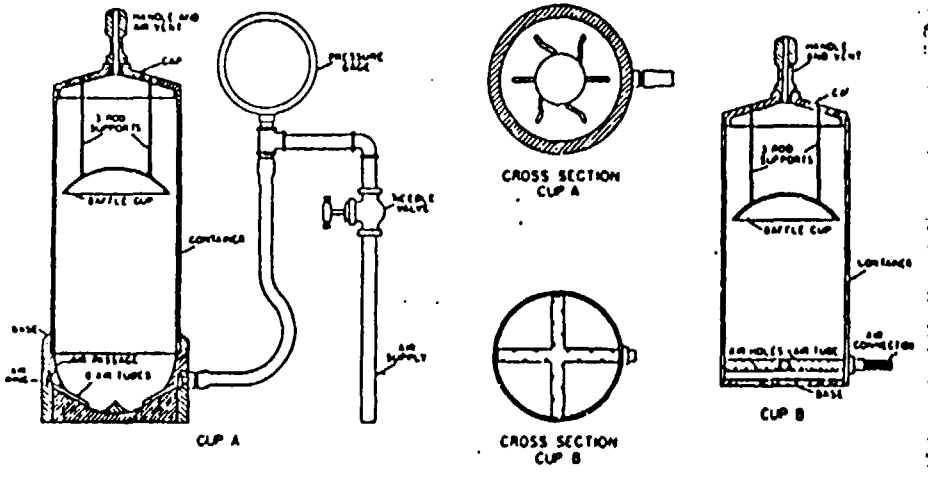
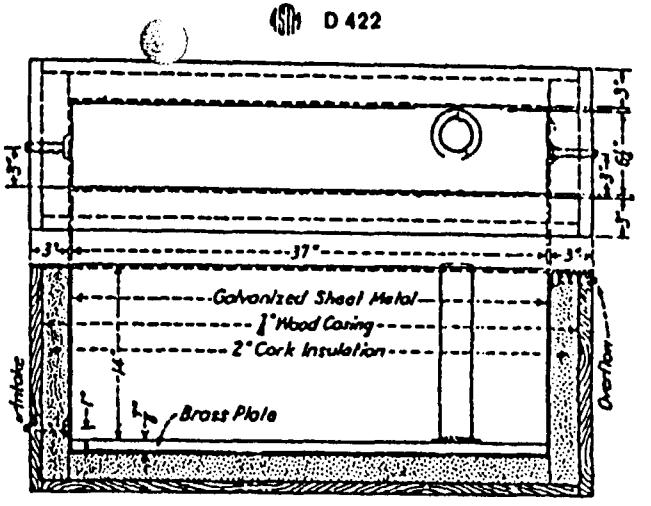



FIG. 3 Air-Jet Dispersion Cups of Apparatus B






Metric Equivalents

| | | | | | | |
|---|---|---|---|---|---|---|
| in. | ½ | 1 | 3 | 6¼ | 14 | 37 |
| mm | 22.2 | 25.4 | 76.2 | 158.2 | 356 | 940 |

FIG. 4 Insulated Water Bath

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content. Reduction of moisture content may be accomplished as follows: by exposure to air at ordinary room temperature, by heating in an oven at a temperature not exceeding 230°F (110°C), by boiling, by filtering on a Büchner funnel, or by use of filter candles. During evaporation and cooling, stir the sample often enough to prevent overdrying of the fringes and soil pinnacles on the fac[illegible]ool the heated samp[illegible] to normal room temperature before testing. F[illegible] soil samples containing soluble salts, us[illegible] method of water reduction that will not elimin[illegible] the soluble salts from the test sample. Protect [illegible] prepared sample in a suitable container fro[illegible] further drying until all required tests have be[illegible] performed.

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ASTM Designation: D 2325 – [illegible] (Reapproved 1981)[1]

# Standard Test Method for CAPILLARY-MOISTURE RELATIONSHIPS FOR COARSE- AND MEDIUM-TEXTURED SOILS BY POROUS-PLATE APPARATUS[1]

This standard is issued under the fixed designation D 2325; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[1] Note—Section 2 was added editorially and editorial changes were made throughout in October 1984.

## 1. Scope

1.1 This test method covers the determination of capillary-moisture relationships for coarse- and medium-textured soils as indicated by the soil-moisture tension relations for tensions between 10 and 101 kPa (0.1 and 1 atm). Under equilibrium conditions, moisture tension is defined as the equivalent negative gage pressure, or suction, corresponding to a soil moisture content. This test method determines the equilibrium moisture content retained in a soil subjected to a given soil-water tension. This test method is not suitable for very fine-textured soils.

NOTE 1—For determination of capillary-moisture relationships for fine-textured soils, refer to Test Method D 3152.

## 2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

D698 Test Methods for Moisture-Density Relations of Soils and Soil-Aggregate Mixtures Using 5.5-lb (2.49-kg) Rammer and 12-in. (305-mm) Drop[2]

D3152 Test Method for Capillary Moisture Relationships for Fine-Textured Soils by Pressure-Membrane Apparatus[2]

## 3. Summary of Method

3.1 Saturated soil samples are placed in contact with a saturated porous plate installed within a pressure chamber. The bottom of each plate is covered by a rubber membrane, or otherwise sealed to be airtight. The bottom of each plate is maintained at atmospheric pressure by means of a small drain tube or opening through the side of the pressure chamber. A desired air pressure admitted to the pressure chamber, and consequently to the top of the porous plate, creates a pressure drop across the porous plate. The saturated soil samples on the plates establish equilibrium with the water in the plate. The water, held at a tension less than the pressure drop across the porous plate, will then move out of the soil, through the plate, and out through the drain tube. When water has ceased to flow from the sample and porous plate, (indicating equilibrium for that particular tension), the moisture content of each sample is determined. A series of these tests at various tensions is required to prepare a complete curve of the capillary-moisture relationship for any particular soil.

## 4. Apparatus

4.1 An assembly of the apparatus is shown in Fig. 1.

4.1.1 *Porous Plate Apparatus*, consisting of the following:

4.1.1.1 *Pressure Container*, (such as a pressure cooker), of approximately 15-L (16-qt) capacity.

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.04 on Hydrologic Properties of Soils and Rocks.

Current edition approved Sept. 13, 1968. Originally issued as D 2325 – 64 T. Last previous edition D 2325 – 64 T.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

4. *Apparatus*

4.1 *Balance*, sensitive to 0.1 g.

4.2 *Mortar and Rubber-Covered Pestle*, suitable for breaking up the aggregations of soil particles.

4.3 *Sieves*, No. 10 (2.00-mm) and No. 40 (425-µm), of square mesh woven-wire cloth, conforming to Specification E 11.

4.4 *Sampler*—A riffle sampler or sample splitter for quartering the samples.

4.5 *Drying Apparatus*—Thermostatically controlled drying oven for use at 140°F (60°C) or below and at 230°F (110°C), infrared lamps; air drier; or other suitable device for drying samples.

4.6 *Filter Funnels or Candles*—Büchner funnels 10 in. (254 mm) in diameter and filter paper or filter candles.

4.7 *Miscellaneous Equipment*—Pans 12 in. (304.8 mm) in diameter and 3 in. (76.2 mm) in depth; a suitable container that will prevent loss of moisture during storage of the moist test sample prepared in Procedure B.

## PROCEDURE A

5. Sampling

5.1 Dry the soil sample as received from the field, using one of the following methods: (*1*) in air at room temperature, (*2*) in a drying oven at a temperature not exceeding 140°F (60°C), or (*3*) using any warming device that will not raise the temperature of the sample above 140°F. Break up thoroughly any aggregations of particles using the mortar and rubber-covered pestle or other suitable device (Note 1). Select a representative portion by the method of quartering or by use of the sampler. This portion must be sufficient to provide samples for particle-size analyses of material retained on and passing the No. 10 (2.00-mm) sieve, and to provide an adequate amount of material passing the No. 40 (425-µm) sieve for the tests to determine soil constants. The amounts of material required to perform the individual tests are as follows:

| | |
|---|---|
| Particle-Size Analysis of Material Retained on No. 10 (2.00-mm) Sieve: | |
| Gravelly soils, g | 4 000 to 10 000 |
| Sandy soils, g | 1 500 |
| Silty or clayey soils, g | 400 |
| Particle-Size Analysis of Material Passing No. 10 (2.00-mm) Sieve: | |
| Sandy soils, g | 115 |
| Silty or clayey soils, g | [illegible] |
| Tests for Determination of Soil Constants: | |
| Liquid limit, g | 100 |
| Plastic limit, g | 15 |
| Centrifuge moisture equivalent, g | 10 |
| Shrinkage factors, g | 30 |
| Check tests, g | 65 |

NOTE 1—When the sample contains particles of shale or sandstone or similar weak material, proper care must be exercised to avoid excessive reduction in the size of the particles.

6. Preparation of Test Samples

6.1 *For Particle-Size Analysis:*

6.1.1 Weigh the portion of the test sample selected for particle-size analysis and record the weight of test sample uncorrected for hygroscopic moisture. Separate this material into two portions using the No. 10 (2.00-mm) sieve. Set aside the portion passing for later recombination with additional material washed from the portion retained on the No. 10 (2.00-mm) sieve.

6.1.2 Place the material retained on the No. 10 (2.00-mm) sieve in a pan, cover with water and allow to soak until the particle aggregations become soft. After soaking, wash the material on a No. 10 (2.00-mm) sieve in the following manner: Place an empty No. 10 (2.00-mm) sieve on the bottom of a clean pan and pour the water from the soaked sample into the sieve. Add sufficient water to bring the level approximately ½ in. (12.7 mm) above the mesh of the sieve. Transfer the soaked material to the sieve in increments not exceeding 1 lb (0.45 kg), stirring each increment with the fingers while agitating the sieve up and down. Crumble or mash any lumps that have not slaked, using the thumb and fingers. Raise the sieve above the water in the pan and complete the washing operation using a small amount of clean water. Transfer the washed material on the sieve to a clean pan before placing another increment of soaked material on the sieve.

6.1.3 Dry the material retained on the No. 10 (2.00-mm) sieve at a temperature of 230 ± 9°F (110 ± 5°C), sieve on the No. 10 (2.00-mm) sieve, and add the material passing the sieve to similar material obtained in 6.1.1. Set aside the material retained on the sieve for use in the particle-size analysis.

6.1.4 Set aside the pan containing the washings for a period of several hours or until the water above the particles is clear. Decant, pipet, or siphon off as much of the clear water as



can at a temperature not exceeding 140°F (60°C). Grind the dried soil in the mortar with the rubber-covered pestle or other suitable device, and combine with similar material obtained in 6.1.1.

6.1.5 Alternatively, after all the soaked material has been washed, remove most of the water by filtering the wash water on one or more Büchner funnels fitted with filter paper or by using filter candles. Remove the moist soil from the filter paper or filter candles, combine with any sediment remaining in the pan, and dry at a temperature not exceeding 140°F (60°C). Grind the dried soil in the mortar with a rubber-covered pestle or other suitable device and combine with similar material obtained in 6.1.1.

NOTE 2—In some instances, the wash water will not become clear in a reasonable length of time; in this case the entire volume must be evaporated.

6.2 *For Determination of Soil Constants*—Proceed in accordance with 6.1, substituting a No. 40 (425-µm) sieve for the No. 10 (2.00-mm) sieve.

NOTE 3—In some areas it is possible that the cations of salts present in the tap water may exchange with the natural cations in the soil and alter significantly the values of the soil constants should tap water be used in the soaking and washing operations. Unless it is known that such cations are not present in the tap water, distilled or demineralized water should be used. The soaking and washing operation will remove soluble salts contained in the soil. When soluble salts are present in the soil, the wash water should be saved and evaporated, and the salts returned to the soil sample.

7. Test Samples

7.1 Keeping each portion separate from the other portion, mix thoroughly the portions of the soil sample passing the No. 10 (2.00-mm) sieve and the No. 40 (425-µm) sieve. By the method of quartering or by the use of the sampler, select and weigh out test samples of the weights indicated in Section 5, as may be needed to make the required tests.

## PROCEDURE B

8. Samples

8.1 Samples prepared in accordance with this procedure must be shipped from the field to the laboratory in sealed containers and must contain all their natural moisture. Samples obviously containing only particles passing the No. 10 (2.00-mm) sieve may be tested in the particle-size analysis without first washing on the No. 10 (2.00-mm) sieve. Samples obviously containing only particles passing the No. 40 (425-µm) sieve may be used in the tests to determine soil constants without first washing on the No. 40 (425-µm) sieve.

9. Preparation of Test Samples

9.1 *For Particle-Size Analysis:*

9.1.1 Select and weigh a representative portion of the moist sample estimated to contain 50 g of particles passing the No. 10 (2.00-mm) sieve for silty and clayey soil, or 100 g for sandy soil. For samples containing particles not passing the No. 10 (2.00-mm) sieve for which a particle-size analysis is required, select and weigh a representative sample estimated to contain the required amounts of particles both passing and not passing the No. 10 (2.00-mm) sieve. Determine the moisture content at 230 ± 9°F (110 ± 5°C) using an auxiliary sample, for use in Method D 422.

9.1.2 Soak the moist sample and wash on a No. 10 (2.00-mm) sieve as described in 6.1.2. After washing, dry the material retained on the No. 10 (2.00-mm) sieve in an oven at a temperature of 230 ± 9°F (110 ± 5°C), weigh, and retain for the particle-size analysis. If the volume of the wash water and soil is too large for use in the sedimentation procedure of the test for particle-size analysis, evaporate excess water by exposure to air at room temperature, by heating in an oven at a temperature not exceeding 230°F (110°C), or by boiling. Regardless of the method of evaporation used, the following precautions must be taken: (*1*) stir the slurry from time to time to prevent a dry soil ring from forming on the walls of the evaporation vessel, and (*2*) return the temperature of the sample to room temperature before testing.

9.2 *For Determination of Soil Constants*—Select a representative portion of the moist sample estimated to contain sufficient particles passing the No. 40 (425-µm) sieve to make the required tests for determination of soil constants. Soak this selected portion of the moist sample and wash on the No. 40 (425-µm) sieve as described in 6.2 (Note 2). Reduce the moisture content of the material passing the No. 40 (425-µm) sieve until the mass reaches a putty-like consistency (such as 30 to 35 drops of the cup in the liquid limit test) but never below the natural moisture

10.1 Requirements for the precision and accuracy of this method have not yet been developed.

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# Standard Practice for WET PREPARATION OF SOIL SAMPLES FOR PARTICLE-SIZE ANALYSIS AND DETERMINATION OF SOIL CONSTANTS[1]

This standard is issued under the fixed designation D 2217; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

*This practice has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.*

## 1. Scope

1.1 This practice covers the wet preparation of soil samples as received from the field for particle-size analysis and determination of soil constants.

1.2 Procedure A provides for drying the field sample at a temperature not exceeding 140°F (60°C), making a wet separation on the No. 10 (2.00-mm) sieve, or No. 40 (425-µm) sieve, or both, as needed, and finally drying at a temperature not exceeding 140°F. Procedure B provides that the sample shall be kept at a moisture content equal to or greater than the natural water content. The procedure to be used should be indicated in the specification for the material being tested. If no procedure is specified, the provisions of Procedure B shall govern.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

D422 Method for Particle-Size Analysis of Soils[2]

E 11 Specification for Wire Cloth Sieves for Testing Purposes[3]

## 3. Significance and Use

3.1 Procedure A is used to prepare soil samples for plasticity tests and particle-size analysis when the coarse-grained particles of a sample are soft and pulverize readily, as in Practice D 421, or when the fine particles are very cohesive and tend to resist removal from the coarse particles.

3.2 Some soils never dry out in nature and may change their characteristics greatly when dried. If the true natural gradation and plasticity characteristics of such soils are desired, these soils should be shipped to the laboratory in sealed containers and processed in accordance with Procedure B of this practice.

3.3 Liquid limit and plasticity index values derived from samples containing their natural moisture are usually, but not always, equal to or higher than values derived from similar samples of the dried soil. In the case of fine-grained organic soil, there is a radical drop in plasticity due to oven drying.

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[1] This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved July 26, 1985. Published September 1985. Originally published as D 2217 – 63 T. Last previous edition D 2217 – 66 (1978)ε[1].

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.03.

# PERMEABILITY OF SOIL

Scope and Application: This method is applicable to soil samples collected as part of the Muskego Sanitary Landfill RI/FS.

Method: Permeability Test with Back Pressure (Flexible Wall permeability).

Reference: Appendix VII, Section 7, Engineer Manual EM 1110-2-1906 (30 November 1970), Headquarters, Department of the Army, Office of the Chief of Engineers (see Attachment One).

Precision: The method is applicable to soil having a saturated permeability of less than 1 x 10-3 cm/sec. Overall precision is expected to be less than 50 relative percent difference (RPD).

Sample Handling: Samples will be collected in 3 inch diameter Shelby tubes, capped and store at 4 degrees centigrade until analyzed.

Reagents and Equipment:

1. 0.005N CaSO4 in dearied, deionized water (boiled).
2. Pressure chamber for permeability testing.
3. Scale capable of weighing to the nearest 0.01 gram.
4. Sample extruder capable of extruding the soil core from the Shelby tube in the same direction of travel that it entered.
5. Specimen trimming equipment, which may include soil lathe, wire saw, spatulas, knives, steel rasp or steel straight edge.
6. Flexible membrane which shall encase the lateral boundaries of the specimen and prevent leakage.
7. Drying oven (105° C).

Procedure:

1. Extrude sample from the Shelby tube in the same direction the sample entered the tube.
2. Select and trim a minimum 6 inch length of undistrubed core for use. Avoid smearing of the sample ends while trimming samples.
3. Retain a separate section of core for determination of specific gravity (ASTM D854-83, see Attachment Two).

4. Measure and record the length and diameter of the trimmed specimen to the nearest 0.01 inch and the wet weight to the nearest 0.1%.

5. Performance of the test shall follow that described under paragraph 7a, page VII-17 of EM 1110-2-1906 (attached).

6. After permeability testing is completed, determine the dry weight of the sample by drying at 105 degree centigrade.

Results:

1. Conductivity will be calculated using the falling head method (See Attachment three).
2. Results will be presented in the format shown on Attachment Three.

Quality Control:

1. Samples analysed for quality control purposes will be limited to field duplicates. As samples for permeability testing are taken from intact cores (ie. not measured on homogenized, repacked samples), it is not possible to obtain what could be considered a laboratory duplicate. Results of field duplicates are expected to agree within 50 relative percent difference (RPD).

KDF/CAW/DLN
[KAW-7-28]

ATTACHMENT TABLE

WARZYN ENGINEERING INC

# FLEXIBLE WALL
## FALLING HEAD/RISING HEAD
## PERMEABILITY TEST RESULTS

PROJECT:

LOCATION:

Test No. _____
Job No. _____
Date _____
Sheet _____ of _____

1409 EMIL STREET • P.O. BOX 9538, MADISON, WIS. 53715 • TEL. (608) 257-4848

| | | | | | | |
|---|---|---|---|---|---|---|
| SAMPLE | | | | | | |
| DEPTH | | | | | | |
| SOIL DESCRIPTION | | | | | | |
| | INITIAL | FINAL | INITIAL | FINAL | INITIAL | FINAL |
| SAMPLE DIAMETER (cm) | | | | | | |
| SAMPLE AREA, A ($cm^2$) | | | | | | |
| SAMPLE LENGTH, L (cm) | | | | | | |
| MOISTURE CONTENT, % | | | | | | |
| DRY DENSITY (PCF) | | | | | | |
| MAXIMUM GRADIENT | | | | | | |
| NET CONFINING PRESSURE (PSI) | | | | | | |

COEFFICIENT OF PERMEABILITY, k (cm/sec)

| | | | |
|---|---|---|---|
| RUN NO. 1 | | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| 8 | | | |
| 9 | | | |
| 10 | | | |
| AVERAGE k, (cm/sec) | | | |

FORMULA: $k = \frac{2.3\ a\ L}{2\ At} \log_{10} \frac{h_0}{h_1}$ Where a = cross-sectional area of standpipe,
t = time for water level to fall from initial height, $h_0$, to final height, $h_1$
(All other terms are defined above)

REMARKS:

# ATTERBERG LIMITS

Scope and Application: This method determines the liquid limit, plastic limit and plasticity index of soil samples from Shelby tubes after permeability testing.

Method: Standard Test Method for Liquid Limit, Plastic Limit and Plasticity Index of Soils ASTM D-4318 (Liquid Limit by One-Point Test) with minor modifications.

Sample Handling: Samples will remain in Shelby tubes and be shipped daily by overnight carrier.

Reference: Annual Book of ASTM Standards, 1987, Soil and Rock; Building Stones; Geotextiles, Vol. 04.08, Section 4, Construction.

Apparatus:

1. Brass cup
2. Grooving tools
3. Liquid limit drop device
4. Soil sieves
5. Height Gage
6. Balance
7. Drying oven & moisture containers
8. Hard rubber base

Notes:

1. The liquid and plastic limits of many soils that have been allowed to dry before testing may be considerably different from values obtained on undried samples. If the liquid and plastic limits of soils are used to correlate or estimate the engineering behavior of soils in their moist state, samples should not be permitted to dry before testing unless data on dried samples are specifically desired.

2. The composition and concentration of soluble salts in a soil affect the values of the liquid and plastic limits, as well as the water content values of the soil (see Method D 2216). Special consideration should therefore be given to soils from a marine environment or other sources where high soluble salt concentrations may be present. The degree to which the salts present in these soils are diluted or concentrated must be given consideration if meaningful results are to be obtained.

3. Since the tests described herein are performed only on that portion of a soil which passes the 425-um (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate the properties of a soil.

Procedure:

Sample Preparation: One-point Liquid Limit

1. Samples for One-point Liquid Limit analysis will be prepared according to ASTM D4318 procedure, Section 10.1 (wet preparation) or 10.2 (dry preparation).

2. Samples for Plastic Limit analysis will be prepared according to ASTM D4318 procedure, Section 16.1.

Sample Analysis:

1. The sample will be processed to remove any material retained on a 425-um (No. 40) sieve. The liquid limit will be determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the blows caused by repeatedly dropping the cup in a standard mechanical device. ASTM D4318, Sections 13 and 14. indicate the one-point liquid limit test can be used when the number of blows is between 20 and 30. A minimum of two trials are performed. If the number of blows differ by no more than 1 blow, then the moisture content is determined. If the number of blows differs by more than 1 blow, then the test is repeated until two consecutive trails agree within 1 blow.

2. The plastic limit will be determined by alternately pressing together and rolling into a 3.2 mm (1/8 in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and is no longer able to be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

3. The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

Calculations:

1. The "K" factor for liguid limit in Table 1 of ASTM D4318 is applied to the moisture content from the liquid limt trials to determine the liquid limit value.

2. Threads of soil will be rolled to the targeted diameter until a total specimen weight of 50 grams or more is obtained. The moisture content of the specimen is the plastic limit value.

3. The plasticity index is equal to the liquid limit minus the plastic limit.

Quality Control:

1. Duplicate 2 out of 10 for sets of less than or equal to 10 samples and 1 out of 10 for sets greater than 10. Duplicates should be less than or equal to 10%.

# Standard Test Method for LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS[1]

This standard is issued under the fixed designation D 4318; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

*This test method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.*

## 1. Scope

1.1 This test method covers the determination of the liquid limit, plastic limit, and the plasticity index of soils as defined in Section 3.

1.1.1 Two procedures for preparing test specimens and two procedures for performing the liquid limit are provided as follows:

*A* Multipoint test using a wet preparation procedure, described in Sections 10.1, 11, and 12.

*B* Multipoint test using a dry preparation procedure, described in Sections 10.2, 11, and 12.

*C* One-point test using a wet preparation procedure, described in Sections 13, 14, and 15.

*D* One-point test using a dry preparation procedure, described in Sections 13, 14, and 15.

The procedure to be used shall be specified by the requesting authority. If no procedure is specified, Procedure A shall be used.

NOTE 1—Prior to the adoption of this test method, a curved grooving tool was specified as part of the apparatus for performing the liquid limit test. The curved tool is not considered to be as accurate as the flat tool described in 6.2 since it does not control the depth of the soil in the liquid limit cup. However, there are some data which indicate that typically the liquid limit is slightly increased when the flat tool is used instead of the curved tool.

1.1.2 The plastic limit test procedure is described in Sections 16, 17, and 18. The plastic limit test is performed on material prepared for the liquid limit test. In effect, there are two procedures for preparing test specimens for the plastic limit test.

1.1.3 The procedure for calculating the plasticity index is given in Section 19.

1.2 The liquid limit and plastic limit of soils (along with the shrinkage limit) are often collectively referred to as the Atterberg limits in recognition of their formation by Swedish soil scientist, A. Atterberg. These limits distinguish the boundaries of the several consistency states of plastic soils.

1.3 As used in this test method, soil is any natural aggregation of mineral or organic materials, mixtures of such materials, or artificial mixtures of aggregates and natural mineral and organic particles.

1.4 The multipoint liquid limit procedure is somewhat more time consuming than the one-point procedure when both are performed by experienced operators. However, the one-point procedure requires the operator to judge when the test specimen is approximately at its liquid limit. In cases where this is not done reliably, the multipoint procedure is as fast as the one-point procedure and provides additional precision due to the information obtained from additional trials. It is particularly recommended that the multipoint procedure be used by inexperienced operators.

1.5 The correlations on which the calculations of the one-point procedure are based may not be valid for certain soils, such as organic soils or

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

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soils from a marine environment. The liquid limit of these soils should therefore be determined by the multipoint procedure (Procedure A).

1.6 The liquid and plastic limits of many soils that have been allowed to dry before testing may be considerably different from values obtained on undried samples. If the liquid and plastic limits of soils are used to correlate or estimate the engineering behavior of soils in their natural moist state, samples should not be permitted to dry before testing unless data on dried samples are specifically desired.

1.7 The composition and concentration of soluble salts in a soil affect the values of the liquid and plastic limits as well as the water content values of soils (see Method D 2216). Special consideration should therefore be given to soils from a marine environment or other sources where high soluble salt concentrations may be present. The degree to which the salts present in these soils are diluted or concentrated must be given consideration if meaningful results are to be obtained.

1.8 Since the tests described herein are performed only on that portion of a soil which passes the 425-µm (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate the properties of a soil.

1.9 The values stated in acceptable metric units are to be regarded as the standard. The values given in parentheses are for information only.

1.10 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Applicable Documents

2.1 *ASTM Standards:*

C 702 Methods for Reducing Field Samples of Aggregate to Testing Size[2]

D 75 Practice for Sampling Aggregates[3]

D 420 Recommended Practice for Investigating and Sampling Soil and Rock for Engineering Purposes[4]

D 653 Terms and Symbols Relating to Soil and Rock[4]

D 1241 Specification for Materials for Soil-Aggregate Subbase, Base, and Surface Courses[4]

D 2216 Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures[4]

D 2240 Test Method for Rubber Property—Durometer Hardness[5]

D 2487 Test Method for Classification of Soils for Engineering Purposes[4]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[4]

D 3282 Practice for Classification of Soils and Soil-Aggregate Mixtures for Highway Construction Purposes[4]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

E 319 Methods of Testing Single-Arm Balances[6]

E 898 Method of Testing Top-Loading, Direct-Reading Laboratory Scales and Balances[6]

## 3. Definitions

3.1 *Atterberg limits*—originally, seven "limits of consistency" of fine-grained soils were defined by Albert Atterberg. In current engineering usage, the term usually refers only to the liquid limit, plastic limit, and in some references, the shrinkage limit.

3.2 *consistency*—the relative ease with which a soil can be deformed.

3.3 *liquid limit (LL)*—the water content, in percent, of a soil at the arbitrarily defined boundary between the liquid and plastic states. This water content is defined as the water content at which a pat of soil placed in a standard cup and cut by a groove of standard dimensions will flow together at the base of the groove for a distance of 13 mm (½ in.) when subjected to 25 shocks from the cup being dropped 10 mm in a standard liquid limit apparatus operated at a rate of 2 shocks per second.

[2] *Annual Book of ASTM Standards*, Vol 04.02.
[3] *Annual Book of ASTM Standards*, Vols 04.02, 04.03, and 04.08.
[4] *Annual Book of ASTM Standards*, Vol 04.08.
[5] *Annual Book of ASTM Standards*, Vol 09.01.
[6] *Annual Book of ASTM Standards*, Vol 14.02.

NOTE 2—The undrained shear str
liquid limit is considered to be 2 ±0.2

3.4 *plastic limit (PL)*—the wa
percent, of a soil at the boundar
plastic and brittle states. The w
this boundary is the water content
can no longer be deformed by r
mm (⅛ in.) in diameter threads
bling.

3.5 *plastic soil*—a soil which l
water content over which it exh
and which will retain its shape on

3.6 *plasticity index (PI)*—the r
content over which a soil behav
Numerically, it is the difference b
uid limit and the plastic limit.

3.7 *liquidity index*—the ratio, i
percentage, of (1) the natural wate
soil minus its plastic limit, to (2
index.

3.8 *activity number (A)*—the r
plasticity index of a soil to (2) tl
weight of particles having an equiv
smaller than 0.002 mm.

## 4. Summary of Method

4.1 The sample is processed to
material retained on a 425-µm (N
The liquid limit is determined b
trials in which a portion of the san
in a brass cup, divided in two by a g
and then allowed to flow togeth
shocks caused by repeatedly droppi
a standard mechanical device. Th
liquid limit, Procedures A and B, r
or more trials over a range of wate
be performed and the data from the
or calculated to make a relationship
the liquid limit is determined. Th
liquid limit, Procedures C and D, i
from two trials at one water conte
by a correction factor to determir
limit.

4.2 The plastic limit is determir
nately pressing together and rollin
mm (⅛ in.) diameter thread a sma
plastic soil until its water content is
point at which the thread crumble
longer able to be pressed together
The water content of the soil at
reported as the plastic limit.

NOTE 2—The undrained shear strength of soil at the liquid limit is considered to be 2 ±0.2 kPa (0.28 psi).

3.4 *plastic limit (PL)*—the water content, in percent, of a soil at the boundary between the plastic and brittle states. The water content at this boundary is the water content at which a soil can no longer be deformed by rolling into 3.2 mm (⅛ in.) in diameter threads without crumbling.

3.5 *plastic soil*—a soil which has a range of water content over which it exhibits plasticity and which will retain its shape on drying.

3.6 *plasticity index (PI)*—the range of water content over which a soil behaves plastically. Numerically, it is the difference between the liquid limit and the plastic limit.

3.7 *liquidity index*—the ratio, expressed as a percentage, of (*1*) the natural water content of a soil minus its plastic limit, to (*2*) its plasticity index.

3.8 *activity number (A)*—the ratio of (*1*) the plasticity index of a soil to (*2*) the percent by weight of particles having an equivalent diameter smaller than 0.002 mm.

## 4. Summary of Method

4.1 The sample is processed to remove any material retained on a 425-µm (No. 40) sieve. The liquid limit is determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the shocks caused by repeatedly dropping the cup in a standard mechanical device. The multipoint liquid limit, Procedures A and B, requires three or more trials over a range of water contents to be performed and the data from the trials plotted or calculated to make a relationship from which the liquid limit is determined. The one-point liquid limit, Procedures C and D, uses the data from two trials at one water content multiplied by a correction factor to determine the liquid limit.

4.2 The plastic limit is determined by alternately pressing together and rolling into a 3.2 mm (⅛ in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and is no longer able to be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

4.3 The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

## 5. Significance and Use

5.1 This test method is used as an integral part of several engineering classification systems to characterize the fine-grained fractions of soils (see Test Method D 2487 and Practice D 3282) and to specify the fine-grained fraction of construction materials (see Specification D 1241). The liquid limit, plastic limit, and plasticity index of soils are also used extensively, either individually or together with other soil properties to correlate with engineering behavior such as compressibility, permeability, compactibility, shrink-swell, and shear strength.

5.2 The liquid and plastic limits of a soil can be used with the natural water content of the soil to express its relative consistency or liquidity index and can be used with the percentage finer than 2-µm size to determine its activity number.

5.3 The one-point liquid limit procedure is frequently used for routine classification purposes. When greater precision is required, as when used for the acceptance of a material or for correlation with other test data, the multipoint procedure should be used.

5.4 These methods are sometimes used to evaluate the weathering characteristics of clay-shale materials. When subjected to repeated wetting and drying cycles, the liquid limits of these materials tend to increase. The amount of increase is considered to be a measure of a shale's susceptibility to weathering.

5.5 The liquid limit of a soil containing substantial amounts of organic matter decreases dramatically when the soil is oven-dried before testing. Comparison of the liquid limit of a sample before and after oven-drying can therefore be used as a qualitative measure of organic matter content of a soil.

## 6. Apparatus

6.1 *Liquid Limit Device*—A mechanical device consisting of a brass cup suspended from a carriage designed to control its drop onto a hard rubber base. A drawing showing the essential features of the device and the critical dimensions is given in Fig. 1. The design of the device may vary provided that the essential functions are

preserved. The device may be operated either by a hand crank or by an electric motor.

6.1.1 *Base*—The base shall be hard rubber having a D Durometer hardness of 80 to 90, and a resilience such that an 8-mm (5/16-in.) diameter polished steel ball, when dropped from a height of 25 cm (9.84 in.) will have an average rebound of at least 80 % but no more than 90 %. The tests shall be conducted on the finished base with feet attached.

6.1.2 *Feet*—The base shall be supported by rubber feet designed to provide isolation of the base from the work surface and having an A Durometer hardness no greater than 60 as measured on the finished feet attached to the base.

6.1.3 *Cup*—The cup shall be brass and have a weight, including cup hanger, of 185 to 215 g.

6.1.4 *Cam*—The cam shall raise the cup smoothly and continuously to its maximum height, over a distance of at least 180° of cam rotation. The preferred cam motion is a uniformly accelerated lift curve. The design of the cam and follower combination shall be such that there is no upward or downward velocity of the cup when the cam follower leaves the cam.

NOTE 3—The cam and follower design in Fig. 1 is for uniformly accelerated (parabolic) motion after contact and assures that the cup has no velocity at drop off. Other cam designs also provide this feature and may be used. However, if the cam-follower lift pattern is not known, zero velocity at drop off can be assured by carefully filing or machining the cam and follower so that the cup height remains constant over the last 20 to 45° of cam rotation.

6.1.5 *Carriage*—The cup carriage shall be constructed in a way that allows convenient but secure adjustment of the height of drop of the cup to 10 mm (0.394 in.). The cup hanger shall be attached to the carriage by means of a pin which allows removal of the cup and cup hanger for cleaning and inspection.

6.1.6 *Optional Motor Drive*—As an alternative to the hand crank shown in Fig. 1, the device may be equipped with a motor to turn the cam. Such a motor must turn the cam at 2 ±0.1 revolutions per second, and must be isolated from the rest of the device by rubber mounts or in some other way that prevents vibration from the motor being transmitted to the rest of the apparatus. It must be equipped with an ON-OFF switch and a means of conveniently positioning the cam for height of drop adjustments. The results obtained using a motor-driven device must not differ from those obtained using a manually operated device.

6.2 *Flat Grooving Tool*—A grooving tool having dimensions shown in Fig. 2. The tool shall be made of plastic or noncorroding metal. The design of the tool may vary as long as the essential dimensions are maintained. The tool may, but need not, incorporate the gage for adjusting the height of drop of the liquid limit device.

6.3 *Gage*—A metal gage block for adjusting the height of drop of the cup, having the dimensions shown in Fig. 3. The design of the tool may vary provided the gage will rest securely on the base without being susceptible to rocking, and the edge which contacts the cup during adjustment is straight, at least 10 mm (⅜ in.) wide, and without bevel or radius.

6.4 *Containers*—Small corrosion-resistant containers with snug-fitting lids for water content specimens. Aluminum or stainless steel cans 2.5 cm (1 in.) high by 5 cm (2 in.) in diameter are appropriate.

6.5 *Balance*—A balance readable to at least 0.01 g and having an accuracy of 0.03 g within three standard deviations within the range of use. Within any 15-g range, a difference between readings shall be accurate within 0.01 g (Notes 4 and 5).

NOTE 4—See Methods E 898 and E 319 for an explanation of terms relating to balance performance.

NOTE 5—For frequent use, a top-loading type balance with automatic load indication, readable to 0.01 g, and having an index of precision (standard deviation) of 0.003 or better is most suitable for this method. However, nonautomatic indicating equal-arm analytical balances and some small equal arm top pan balances having readabilities and sensitivities of 0.002 g or better provide the required accuracy when used with a weight set of ASTM Class 4 (National Bureau of Standards Class P) or better. Ordinary commercial and classroom type balances such as beam balances are not suitable for this method.

6.6 *Storage Container*—A container in which to store the prepared soil specimen that will not contaminate the specimen in any way, and which prevents moisture loss. A porcelain, glass, or plastic dish about 11.4 cm (4½ in.) in diameter and a plastic bag large enough to enclose the dish and be folded over is adequate.

6.7 *Ground Glass Plate*—A ground glass plate at least 30 cm (12 in.) square by 1 cm (⅜ in.) thick for mixing soil and rolling plastic limit threads.

6.8 *Spatula*—A spatula or pill knife having a blade about 2 cm (¾ in.) wide by abo (4 in.) long. In addition, a spatula hav about 2.5 cm (1 in.) wide and 15 cm ( has been found useful for initial mixi ples.

6.9 *Sieve*—A 20.3 cm (8 in.) diam µm (No. 40) sieve conforming to th ments of Specification E 11 and havin least 5 cm (2 in.) above the mesh. A 2- 10) sieve meeting the same requirem also be needed.

6.10 *Wash Bottle*, or similar cont adding controlled amounts of water to washing fines from coarse particles.

6.11 *Drying Oven*—A thermostatic trolled oven, preferably of the forced-d capable of continuously maintaining a ture of 110 ±5°C throughout the drying The oven shall be equipped with a ther of suitable range and accuracy for m oven temperature.

6.12 *Washing Pan*—A round, flat-b pan at least 7.6 cm (3 in.) deep, slightly the bottom than a 20.3-cm (8-in.) diame

6.13 *Rod* (optional)—A metal or pl or tube 3.2 mm (⅛ in.) in diameter and cm (4 in.) long for judging the size of pla threads.

## 7. Materials

7.1 A supply of distilled or demineral ter.

## 8. Sampling

8.1 Samples may be taken from any that satisfies testing needs. However, C 702, and Practice D 75, and Recom Practice D 420 should be used as guide lecting and preserving samples from types of sampling operations. Samples wl be prepared using the wet preparation pr 10.1, must be kept at their natural water prior to preparation.

8.2 Where sampling operations ha served the natural stratification of a sam various strata must be kept separated a performed on the particular stratum of with as little contamination as possib other strata. Where a mixture of mater be used in construction, combine the components in such proportions that th ant sample represents the actual const case.

blade about 2 cm (¾ in.) wide by about 10 cm (4 in.) long. In addition, a spatula having a blade about 2.5 cm (1 in.) wide and 15 cm (6 in.) long has been found useful for initial mixing of samples.

6.9 *Sieve*—A 20.3 cm (8 in.) diameter, 425-µm (No. 40) sieve conforming to the requirements of Specification E 11 and having a rim at least 5 cm (2 in.) above the mesh. A 2-mm (No. 10) sieve meeting the same requirements may also be needed.

6.10 *Wash Bottle*, or similar container for adding controlled amounts of water to soil and washing fines from coarse particles.

6.11 *Drying Oven*—A thermostatically controlled oven, preferably of the forced-draft type, capable of continuously maintaining a temperature of 110 ±5°C throughout the drying chamber. The oven shall be equipped with a thermometer of suitable range and accuracy for monitoring oven temperature.

6.12 *Washing Pan*—A round, flat-bottomed pan at least 7.6 cm (3 in.) deep, slightly larger at the bottom than a 20.3-cm (8-in.) diameter sieve.

6.13 *Rod* (optional)—A metal or plastic rod or tube 3.2 mm (⅛ in.) in diameter and about 10 cm (4 in.) long for judging the size of plastic limit threads.

## 7. Materials

7.1 A supply of distilled or demineralized water.

## 8. Sampling

8.1 Samples may be taken from any location that satisfies testing needs. However, Methods C 702, and Practice D 75, and Recommended Practice D 420 should be used as guides for selecting and preserving samples from various types of sampling operations. Samples which will be prepared using the wet preparation procedure, 10.1, must be kept at their natural water content prior to preparation.

8.2 Where sampling operations have preserved the natural stratification of a sample, the various strata must be kept separated and tests performed on the particular stratum of interest with as little contamination as possible from other strata. Where a mixture of materials will be used in construction, combine the various components in such proportions that the resultant sample represents the actual construction case.

8.3 Where data from this test method are to be used for correlation with other laboratory or field test data, use the same material as used for these tests where possible.

8.4 Obtain a representative portion from the total sample sufficient to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve. Free flowing samples may be reduced by the methods of quartering or splitting. Cohesive samples shall be mixed thoroughly in a pan with a spatula, or scoop and a representative portion scooped from the total mass by making one or more sweeps with a scoop through the mixed mass.

## 9. Calibration of Apparatus

9.1 *Inspection of Wear:*

9.1.1 *Liquid Limit Device*—Determine that the liquid limit device is clean and in good working order. The following specific points should be checked:

9.1.1.1 *Wear of Base*—The spot on the base where the cup makes contact should be worn no greater than 10 mm (⅜ in.) in diameter. If the wear spot is greater than this, the base can be machined to remove the worn spot provided the resurfacing does not make the base thinner than specified in 6.1 and the other dimensional relationships are maintained.

9.1.1.2 *Wear of Cup*—The cup must be replaced when the grooving tool has worn a depression in the cup 0.1 mm (0.004 in.) deep or when the edge of the cup has been reduced to half its original thickness. Verify that the cup is firmly attached to the cup hanger.

9.1.1.3 *Wear of Cup Hanger*—Verify that the cup hanger pivot does not bind and is not worn to an extent that allows more than 3-mm (⅛-in.) side-to-side movement of the lowest point on the rim.

9.1.1.4 *Wear of Cam*—The cam shall not be worn to an extent that the cup drops before the cup hanger (cam follower) loses contact with the cam.

9.1.2 *Grooving Tools*—Inspect grooving tools for wear on a frequent and regular basis. The rapidity of wear depends on the material from which the tool is made and the types of soils being tested. Sandy soils cause rapid wear of grooving tools; therefore, when testing these materials, tools should be inspected more frequently than for other soils. Any tool with a tip width greater than 2.1 mm must not be used. The depth

of the tip of the grooving tool must be 7.9 to 8.1 mm.

NOTE 6—The width of the tip of grooving tools is conveniently checked using a pocket-sized measuring magnifier equipped with a millimetre scale. Magnifiers of this type are available from most laboratory supply companies. The depth of the tip of grooving tools can be checked using the depth measuring feature of vernier calipers.

9.2 *Adjustment of Height of Drop*—Adjust the height of drop of the cup so that the point on the cup that comes in contact with the base rises to a height of 10 ±0.2 mm. See Fig. 4 for proper location of the gage relative to the cup during adjustment.

NOTE 7—A convenient procedure for adjusting the height of drop is as follows: place a piece of masking tape across the outside bottom of the cup parallel with the axis of the cup hanger pivot. The edge of the tape away from the cup hanger should bisect the spot on the cup that contacts the base. For new cups, placing a piece of carbon paper on the base and allowing the cup to drop several times will mark the contact spot. Attach the cup to the device and turn the crank until the cup is raised to its maximum height. Slide the height gage under the cup from the front, and observe whether the gage contacts the cup or the tape. See Fig. 4. If the tape and cup are both contacted, the height of drop is approximately correct. If not, adjust the cup until simultaneous contact is made. Check adjustment by turning the crank at 2 revolutions per second while holding the gage in position against the tape and cup. If a ringing or clicking sound is heard without the cup rising from the gage, the adjustment is correct. If no ringing is heard or if the cup rises from the gage, readjust the height of drop. If the cup rocks on the gage during this checking operation, the cam follower pivot is excessively worn and the worn parts should be replaced. Always remove tape after completion of adjustment operation.

## MULTIPOINT LIQUID LIMIT—PROCEDURES A AND B

### 10. Preparation of Test Specimens

10.1 *Wet Preparation*—Except where the dry method of specimen preparation is specified (10.2), prepare specimens for test as described in the following sections.

10.1.1 *Samples Passing the 425-µm (No. 40) Sieve*—When by visual and manual procedures it is determined that the sample has little or no material retained on a 425-µm (No. 40) sieve, prepare a specimen of 150 to 200 g by mixing thoroughly with distilled or demineralized water on the glass plate using the spatula. If desired, soak soil in a storage dish with small amount of water to soften the soil before the start of mixing. Adjust the water content of the soil to bring it to a consistency that would require 25 to 35 blows of the liquid limit device to close the groove (Note 8). If, during mixing, a small percentage of material is encountered that would be retained on a 425-µm (No. 40) sieve, remove these particles by hand, if possible. If it is impractical to remove the coarser material by hand, remove small percentages (less than about 15 %) of coarser material by working the specimen through a 425-µm (No. 40) sieve using a piece of rubber sheeting, rubber stopper, or other convenient device provided the operation does not distort the sieve or degrade material that would be retained if the washing method described in 10.1.2 were used. If larger percentages of coarse material are encountered during mixing, or it is considered impractical to remove the coarser material by the methods just described, wash the sample as described in 10.1.2. When the coarse particles found during mixing are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-µm (No. 40) sieve, but remove by hand or by washing. Place the mixed soil in the storage dish, cover to prevent loss of moisture, and allow to stand for at least 16 h (overnight). After the standing period and immediately before starting the test, thoroughly remix the soil.

NOTE 8—The time taken to adequately mix a soil will vary greatly, depending on the plasticity and initial water content. Initial mixing times of more than 30 min may be needed for stiff, fat clays.

10.1.2 *Samples Containing Material Retained on a 425-µm (No. 40) Sieve:*

10.1.2.1 Select a sufficient quantity of soil at natural water content to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve. Place in a pan or dish and add sufficient water to cover the soil. Allow to soak until all lumps have softened and the fines no longer adhere to the surfaces of the corase particles (Note 9).

NOTE 9—In some cases, the cations of salts present in tap water will exchange with the natural cations in the soil and significantly alter the test results should tap water be used in the soaking and washing operations. Unless it is known that such cations are not present in the tap water, distilled or demineralized water should be used. As a general rule, water containing more than 100 mg/L of dissolved solids should not be used for washing operations.

10.1.2.2 When the sample contains a large percentage of material retained on the 425-µm (No. 40) sieve, perform the following operation in increments, washing no m 0.5 kg (1 lb) of material at one time. P 425-µm (No. 40) sieve in the bottom of t pan. Pour the soil water mixture onto th If gravel or coarse sand particles are prese as many of these as possible with small qu of water from a wash bottle and discard natively, pour the soil water mixture ov mm (No. 10) sieve nested atop the 425-µ 40) sieve, rinse the fine material throu remove the 2-mm (No. 10) sieve. After and removing as much of the coarser mat possible, add sufficient water to the pan t the level to about 13 mm (½ in.) above the of the 425-µm (No. 40) sieve. Agitate the by stirring with the fingers while raisi lowering the sieve in the pan and swirl suspension so that fine material is washe the coarser particles. Disaggregate fine soil that have not slaked by gently rubbing the the sieve with the fingertips. Complete the ing operation by raising the sieve above the surface and rinsing the material retained small amount of clean water. Discard m retained on the 425-µm (No. 40) sieve.

10.1.2.3 Reduce the water content of th terial passing the 425-µm (No. 40) sieve approaches the liquid limit. Reduction of content may be accomplished by one or bination of the following methods: (*a*) ex the air currents at ordinary room tempe (*b*) exposing to warm air currents from a such as an electric hair dryer, (*c*) filterin Buckner funnel or using filter candles, ( canting clear water from surface of suspe or (*e*) draining in a colander or plaster of dish lined with high retentivity, high wet-str filter paper.[7] If a plaster of paris dish is use care that the dish never becomes suffic saturated that it fails to actively absorb wate its surface. Thoroughly dry dishes betwee During evaporation and cooling, stir the s often enough to prevent overdrying of the and soil pinnacles on the surface of the m For soil samples containing soluble salts method of water reduction such as *a* or will not eliminate the soluble salts from th specimen.

10.1.2.4 Thoroughly mix the material p the 425-µm (No. 40) sieve on the glass plate the spatula. Adjust the water content of the ture, if necessary, by adding small increme

(No. 40) sieve, perform the following washing operation in increments, washing no more than 0.5 kg (1 lb) of material at one time. Place the 425-µm (No. 40) sieve in the bottom of the clean pan. Pour the soil water mixture onto the sieve. If gravel or coarse sand particles are present, rinse as many of these as possible with small quantities of water from a wash bottle, and discard. Alternatively, pour the soil water mixture over a 2-mm (No. 10) sieve nested atop the 425-µm (No. 40) sieve, rinse the fine material through and remove the 2-mm (No. 10) sieve. After washing and removing as much of the coarser material as possible, add sufficient water to the pan to bring the level to about 13 mm (½ in.) above the surface of the 425-µm (No. 40) sieve. Agitate the slurry by stirring with the fingers while raising and lowering the sieve in the pan and swirling the suspension so that fine material is washed from the coarser particles. Disaggregate fine soil lumps that have not slaked by gently rubbing them over the sieve with the fingertips. Complete the washing operation by raising the sieve above the water surface and rinsing the material retained with a small amount of clean water. Discard material retained on the 425-µm (No. 40) sieve.

10.1.2.3 Reduce the water content of the material passing the 425-µm (No. 40) sieve until it approaches the liquid limit. Reduction of water content may be accomplished by one or a combination of the following methods: (*a*) exposing the air currents at ordinary room temperature, (*b*) exposing to warm air currents from a source such as an electric hair dryer, (*c*) filtering in a Buckner funnel or using filter candles, (*d*) decanting clear water from surface of suspension, or (*e*) draining in a colander or plaster of paris dish lined with high retentivity, high wet-strength filter paper.[7] If a plaster of paris dish is used, take care that the dish never becomes sufficiently saturated that it fails to actively absorb water into its surface. Thoroughly dry dishes between uses. During evaporation and cooling, stir the sample often enough to prevent overdrying of the fringes and soil pinnacles on the surface of the mixture. For soil samples containing soluble salts, use a method of water reduction such as *a* or *b* that will not eliminate the soluble salts from the test specimen.

10.1.2.4 Thoroughly mix the material passing the 425-µm (No. 40) sieve on the glass plate using the spatula. Adjust the water content of the mixture, if necessary, by adding small increments of distilled or demineralized water or by allowing the mixture to dry at room temperature while mixing on the glass plate. The soil should be at a water content that will result in closure of the groove in 25 to 35 blows. Return the mixed soil to the mixing dish, cover to prevent loss of moisture, and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, remix the soil thoroughly.

10.2 *Dry Preparation:*

10.2.1 Select sufficient soil to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve after processing. Dry the sample at room temperature or in an oven at a temperature not exceeding 60°C until the soil clods will pulverize readily. Disaggregation is expedited if the sample is not allowed to completely dry. However, the soil should have a dry appearance when pulverized. Pulverize the sample in a mortar with a rubber tipped pestal or in some other way that does not cause breakdown of individual grains. When the coarse particles found during pulverization are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-µm (No. 40) sieve, but remove by hand or other suitable means, such as washing.

10.2.2 Separate the sample on a 425-µm (No. 40) sieve, shaking the sieve by hand to assure thorough separation of the finer fraction. Return the material retained on the 425-µm (No. 40) sieve to the pulverizing apparatus and repeat the pulverizing and sieving operations as many times as necessary to assure that all finer material has been disaggregated and material retained on the 425-µm (No. 40) sieve consists only of individual sand or gravel grains.

10.2.3 Place material remaining on the 425-µm (No. 40) sieve after the final pulverizing operations in a dish and soak in a small amount of water. Stir the soil water mixture and pour over the 425-µm (No. 40) sieve, catching the water and any suspended fines in the washing pan. Pour this suspension into a dish containing the dry soil previously sieved through the 425-µm (No. 40) sieve. Discard material retained on the 425-µm (No. 40) sieve.

10.2.4 Adjust the water content as necessary by drying as described in 10.1.2.3 or by mixing on the glass plate, using the spatula while adding increments of distilled or demineralized water,

[7] S and S 595 filter paper, available in 32-cm circles, has proven satisfactory.

until the soil is at a water content that will result in closure of the groove in 25 to 35 blows.

10.2.5 Put soil in the storage dish, cover to prevent loss of moisture and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, thoroughly remix the soil (Note 8).

## 11. Procedure

11.1 Place a portion of the prepared soil in the cup of the liquid limit device at the point where the cup rests on the base, squeeze it down, and spread it into the cup to a depth of about 10 mm at its deepest point, tapering to form an approximately horizontal surface. Take care to eliminate air bubbles from the soil pat but form the pat with as few strokes as possible. Heap the unused soil on the glass plate and cover with the inverted storage dish or a wet towel.

11.2 Form a groove in the soil pat by drawing the tool, beveled edge forward, through the soil on a line joining the highest point to the lowest point on the rim of the cup. When cutting the groove, hold the grooving tool against the surface of the cup and draw in an arc, maintaining the tool perpendicular to the surface of the cup throughout its movement. See Fig. 5. In soils where a groove cannot be made in one stroke without tearing the soil, cut the groove with several strokes of the grooving tool. Alternatively, cut the groove to slightly less than required dimensions with a spatula and use the grooving tool to bring the groove to final dimensions. Exercise extreme care to prevent sliding the soil pat relative to the surface of the cup.

11.3 Verify that no crumbs of soil are present on the base or the underside of the cup. Lift and drop the cup by turning the crank at a rate of 1.9 to 2.1 drops per second until the two halves of the soil pat come in contact at the bottom of the groove along a distance of 13 mm (½ in.). See Fig. 6.

NOTE 10—Use the end of the grooving tool, Fig. 2, or a scale to verify that the groove has closed 13 mm (½ in.).

11.4 Verify that an air bubble has not caused premature closing of the groove by observing that both sides of the groove have flowed together with approximately the same shape. If a bubble has caused premature closing of the groove, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving operation and repeat 11.1 to 11.3. If the soil slides on the surface of the cup, repeat 11.1 through 11.3 at a higher water content. If, after several trials at successively higher water contents, the soil pat continues to slide in the cup or if the number of blows required to close the groove is always less than 25, record that the liquid limit could not be determined, and report the soil as nonplastic without performing the plastic limit test.

11.5 Record the number of drops, $N$, required to close the groove. Remove a slice of soil approximately the width of the spatula, extending from edge to edge of the soil cake at right angles to the groove and including that portion of the groove in which the soil flowed together, place in a weighed container, and cover.

11.6 Return the soil remaining in the cup to the glass plate. Wash and dry the cup and grooving tool and reattach the cup to the carriage in preparation for the next trial.

11.7 Remix the entire soil specimen on the glass plate adding distilled water to increase the water content of the soil and decrease the number of blows required to close the groove. Repeat 11.1 through 11.6 for at least two additional trials producing successively lower numbers of blows to close the groove. One of the trials shall be for a closure requiring 25 to 35 blows, one for closure between 20 and 30 blows, and one trial for a closure requiring 15 to 25 blows.

11.8 Determine the water content, $W_N$, of the soil specimen from each trial in accordance with Method D 2216. Make all weighings on the same balance. Initial weighings should be performed immediately after completion of the test. If the test is to be interrupted for more than about 15 min, the specimens already obtained should be weighed at the time of the interruption.

## 12. Calculations

12.1 Plot the relationship between the water content, $W_N$, and the corresponding number of drops, $N$, of the cup on a semilogarithmic graph with the water content as ordinates on the arithmetical scale, and the number of drops as abscissas on the logarithmic scale. Draw the best straight line through the three or more plotted points.

12.2 Take the water content corresponding to the intersection of the line with the 25-drop abscissa as the liquid limit of the soil. Computational methods may be substituted for th ical method for fitting a straight line to and determining the liquid limit

## ONE-POINT LIQUID LIMIT—PROCE C AND D

## 13. Preparation of Test Specimens

13.1 Prepare the specimen in the sam ner as described in Section 10, except mixing, adjust the water content to a con requiring 20 to 30 drops of the liquid lir to close the groove.

## 14. Procedure

14.1 Proceed as described in 11.1 tl 11.5 except that the number of blows requ close the groove shall be 20 to 30. If less tl or more than 30 blows are required, adj water content of the soil and repeat the dure.

14.2 Immediately after removing a content specimen as described in 11.5 r the soil in the cup, adding a small amou soil to make up for that lost in the groovin water content sampling operations. Repea through 11.5, and, if the second closing groove requires the same number of drops more than two drops difference, secure an water content specimen. Otherwise, remi entire specimen and repeat.

NOTE 11—Excessive drying or inadequate n will cause the number of blows to vary.

14.3 Determine water contents of speci as described in 11.8.

## 15. Calculations

15.1 Determine the liquid limit for each w content specimen using one of the follo equations:

$$LL = W_N\left(\frac{N}{25}\right)^{0.121} \quad \text{or}$$

$$LL = K(W_N)$$

where:

$N$ = the number of blows causing closure of groove at water content,

$W_N$ = water content, and

$K$ = a factor given in Table 1.

The liquid limit is the average of the two liquid limit values.

15.2 If the difference between the two

tional methods may be substituted for the graphical method for fitting a straight line to the data and determining the liquid limit.

## ONE-POINT LIQUID LIMIT—PROCEDURES C AND D

### 13. Preparation of Test Specimens

13.1 Prepare the specimen in the same manner as described in Section 10, except that at mixing, adjust the water content to a consistency requiring 20 to 30 drops of the liquid limit cup to close the groove.

### 14. Procedure

14.1 Proceed as described in 11.1 through 11.5 except that the number of blows required to close the groove shall be 20 to 30. If less than 20 or more than 30 blows are required, adjust the water content of the soil and repeat the procedure.

14.2 Immediately after removing a water content specimen as described in 11.5, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving and water content sampling operations. Repeat 11.2 through 11.5, and, if the second closing of the groove requires the same number of drops or no more than two drops difference, secure another water content specimen. Otherwise, remix the entire specimen and repeat.

NOTE 11—Excessive drying or inadequate mixing will cause the number of blows to vary.

14.3 Determine water contents of specimens as described in 11.8.

### 15. Calculations

15.1 Determine the liquid limit for each water content specimen using one of the following equations:

$$LL = W_N\left(\frac{N}{25}\right)^{0.121} \quad \text{or}$$

$$LL = K(W_N)$$

where:

$N$ = the number of blows causing closure of the groove at water content,

$W_N$ = water content, and

$K$ = a factor given in Table 1.

The liquid limit is the average of the two trial liquid limit values.

15.2 If the difference between the two trial liquid limit values is greater than one percentage point, repeat the test.

## PLASTIC LIMIT

### 16. Preparation of Test Specimen

16.1 Select a 20-g portion of soil from the material prepared for the liquid limit test, either after the second mixing before the test, or from the soil remaining after completion of the test. Reduce the water content of the soil to a consistency at which it can be rolled without sticking to the hands by spreading and mixing continuously on the glass plate. The drying process may be accelerated by exposing the soil to the air current from an electric fan, or by blotting with paper that does not add any fiber to the soil, such as hard surface paper toweling or high wet strength filter paper.

### 17. Procedure

17.1 From the 20-g mass, select a portion of 1.5 to 2.0 g. Form the test specimen into an ellipsoidal mass. Roll this mass between the palm or fingers and the ground-glass plate with just sufficient pressure to roll the mass into a thread of uniform diameter throughout its length (Note 12). The thread shall be further deformed on each stroke so that its diameter is continuously reduced and its length extended until the diameter reaches 3.2 ±0.5 mm (0.125 ±.020 in.), taking no more than 2 min (Note 13). The amount of hand or finger pressure required will vary greatly, according to the soil. Fragile soils of low plasticity are best rolled under the outer edge of the palm or at the base of the thumb.

NOTE 12—A normal rate of rolling for most soils should be 80 to 90 strokes per minute, counting a stroke as one complete motion of the hand forward and back to the starting position. This rate of rolling may have to be decreased for very fragile soils.

NOTE 13—A 3.2-mm (⅛-in.) diameter rod or tube is useful for frequent comparison with the soil thread to ascertain when the thread has reached the proper diameter, especially for inexperienced operators.

17.1.1 When the diameter of the thread becomes 3.2 mm, break the thread into several pieces. Squeeze the pieces together, knead between the thumb and first finger of each hand, reform into an ellipsoidal mass, and reroll. Continue this alternate rolling to a thread 3.2 mm in diameter, gathering together, kneading and rerolling, until the thread crumbles under the pres-

sure required for rolling and the soil can no longer be rolled into a 3.2-mm diameter thread (See Fig. 7). It has no significance if the thread breaks into threads of shorter length. Roll each of these shorter threads to 3.2 mm in diameter. The only requirement for continuing the test is that they are able to be reformed into an ellipsoidal mass and rolled out again. The operator shall at no time attempt to produce failure at exactly 3.2 mm diameter by allowing the thread to reach 3.2 mm, then reducing the rate of rolling or the hand pressure, or both, while continuing the rolling without further deformation until the thread falls apart. It is permissible, however, to reduce the total amount of deformation for feebly plastic soils by making the initial diameter of the ellipsoidal mass nearer to the required 3.2-mm final diameter. If crumbling occurs when the thread has a diameter greater than 3.2 mm, this shall be considered a satisfactory end point, provided the soil has been previously rolled into a thread 3.2 mm in diameter. Crumbling of the thread will manifest itself differently with the various types of soil. Some soils fall apart in numerous small aggregations of particles, others may form an outside tubular layer that starts splitting at both ends. The splitting progresses toward the middle, and finally, the thread falls apart in many small platy particles. Fat clay soils require much pressure to deform the thread, particularly as they approach the plastic limit. With these soils, the thread breaks into a series of barrel-shaped segments about 3.2 to 9.5 mm (⅛ to ⅜ in.) in length.

17.2 Gather the portions of the crumbled thread together and place in a weighed container. Immediately cover the container

17.3 Select another 1.5 to 2.0 g portion of soil from the original 20-g specimen and repeat the operations described in 17.1 and 17.2 until the container has at least 6 g of soil.

17.4 Repeat 17.1 through 17.3 to make another container holding at least 6 g of soil. Determine the water content, in percent, of the soil contained in the containers in accordance with Method D 2216. Make all weighings on the same balance.

NOTE 14—The intent of performing two plastic limit trials is to verify the consistency of the test results. It is acceptable practice to perform only one plastic limit trial when the consistency in the test results can be confirmed by other means.

## 18. Calculations

18.1 Compute the average of the two water contents. If the difference between the two water contents is greater than two percentage points, repeat the test. The plastic limit is the average of the two water contents.

## PLASTICITY INDEX

## 19. Calculations

19.1 Calculate the plasticity index as follows:

$$PI = LL - PL$$

where:

$LL$ = the liquid limit,

$PL$ = the plastic limit.

Both $LL$ and $PL$ are whole numbers. If either the liquid limit or plastic limit could not be determined, or if the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP.

## 20. Report

20.1 Report the following information:

20.1.1 Sample identifying information,

20.1.2 Any special specimen selection process used, such as removal of sand lenses from undisturbed sample,

20.1.3 Report sample as airdried if the sample was airdried before or during preparation,

20.1.4 Liquid limit, plastic limit, and plasticity index to the nearest whole number and omitting the percent designation. If the liquid limit or plastic limit tests could not be performed, or if the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP,

20.1.5 An estimate of the percentage of sample retained on the 425-µm (No. 40) sieve, and

20.1.6 Procedure by which liquid limit was performed, if it differs from the multipoint method.

## 21. Precision and Bias

21.1 No interlaboratory testing program has as yet been conducted using this test method to determine multilaboratory precision.

21.2 The within laboratory precision of the results of tests performed by different operators at one laboratory on two soils using Procedure A for the liquid limit is shown in Table 2.

TABLE 1 Factors for Obtaining Liquid Limit Content and Number of Drops Causing Closure

| N (Number of Drops) | K (Factor for Liquid Limit) |
|---|---|
| 20 | 0.974 |
| 21 | 0.979 |
| 22 | 0.985 |
| 23 | 0.990 |
| 24 | 0.995 |
| 25 | 1.000 |
| 26 | 1.005 |
| 27 | 1.009 |
| 28 | 1.014 |
| 29 | 1.018 |
| 30 | 1.022 |

TABLE 1 Factors for Obtaining Liquid Limit from Water Content and Number of Drops Causing Closure of Groove

| N (Number of Drops) | K (Factor for Liquid Limit) |
|---|---|
| 20 | 0.974 |
| 21 | 0.979 |
| 22 | 0.985 |
| 23 | 0.990 |
| 24 | 0.995 |
| 25 | 1.000 |
| 26 | 1.005 |
| 27 | 1.009 |
| 28 | 1.014 |
| 29 | 1.018 |
| 30 | 1.022 |

TABLE 2 Within Laboratory Precision for Liquid Limit

| | Average Value, $\bar{x}$ | Standard Deviation, s |
|---|---|---|
| *Soil A* | | |
| *PL* | 21.9 | 1.07 |
| *LL* | 27.9 | 1.07 |
| *Soil B* | | |
| *PL* | 20.1 | 1.21 |
| *LL* | 32.6 | 0.98 |

DIMENSIONS

| LETTER | A△ | B△ | C△ | E△ | F | G | H | J△ | K△ | L△ | M△ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MM | 54 ± 0.5 | 2 ± 0.1 | 27 ± 0.5 | 56 ± 2.0 | 32 | 10 | 16 | 60 ± 1.0 | 50 ± 2.0 | 150 ± 2.0 | 125 ± 2.0 |

| LETTER | N | P | R | T | U△ | V | W | Z |
|---|---|---|---|---|---|---|---|---|
| MM | 24 | 28 | 24 | 45 | 47 ± 1.0 | 3.8 | 13 | 6.5 |

△ ESSENTIAL DIMENSIONS

| CAM ANGLE DEGREES | CAM RADIUS |
|---|---|
| 0 | 0.742 R |
| 30 | 0.753 R |
| 60 | 0.764 R |
| 90 | 0.773 R |
| 120 | 0.784 R |
| 150 | 0.796 R |
| 180 | 0.818 R |
| 210 | 0.854 R |
| 240 | 0.901 R |
| 270 | 0.945 R |
| 300 | 0.974 R |
| 330 | 0.995 R |
| 360 | 1.000 R |

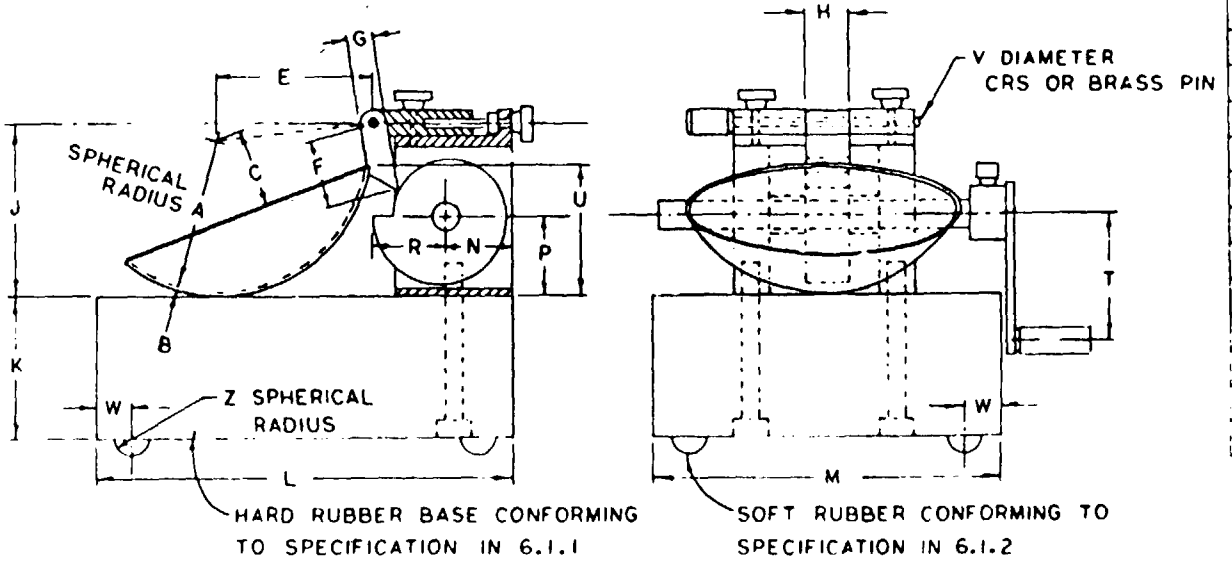



FIG. 1 Hand-Operated Liquid Limit Device

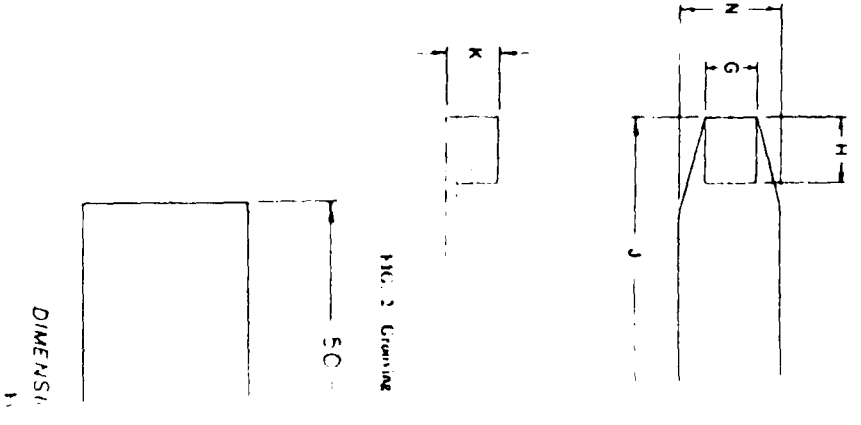



FIG. 2 Grooving

DIMENSIONS

| LETTER | A△ | B△ |
|---|---|---|
| MM | 2 ± 0.1 | 11 ± 0.2 |
| LETTER | G | H |
| MM | 10 MINIMUM | 13 |

△ ESSENTIAL DIMENSION

□ BACK AT LEAST 15 MM F

NOTE: DIMENSION A SHOULD BE 8.0–8.1 ADEQUATE SERVICE

DIMENSIONS

| LETTER | A△ | B△ | C△ | D△ | E△ | F△ |
|---|---|---|---|---|---|---|
| MM | 2 ± 0.1 | 11 ± 0.2 | 40 ± 0.5 | 8 ± 0.1 | 50 ± 0.5 | 2 ± 0.1 |
| LETTER | G | H | J | K△ | L△ | N |
| MM | 10 MINIMUM | 13 | 60 | 10 ±0.05 | 60 DEG ± 1 DEG | 20 |

△ ESSENTIAL DIMENSIONS

□ BACK AT LEAST 15 MM FROM TIP

NOTE : DIMENSION A SHOULD BE 1.9–2.0 AND DIMENSION D SHOULD BE 8.0–8.1 WHEN NEW TO ALLOW FOR ADEQUATE SERVICE LIFE

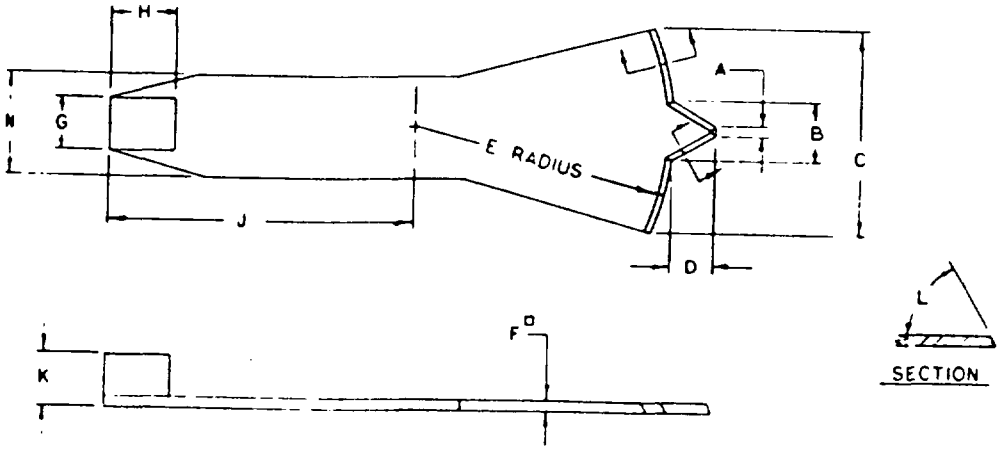
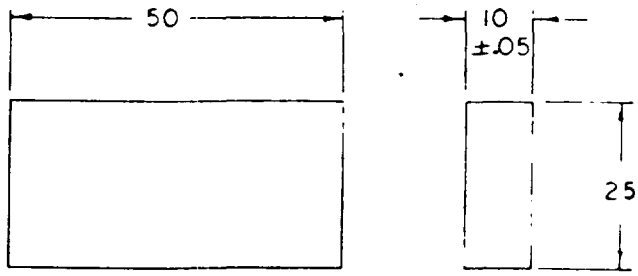



FIG. 2 Grooving Tool (Optional Height-of-Drop Gage Attached)




DIMENSIONS IN MILLIMETRES

FIG. 3 Height of Drop Gage

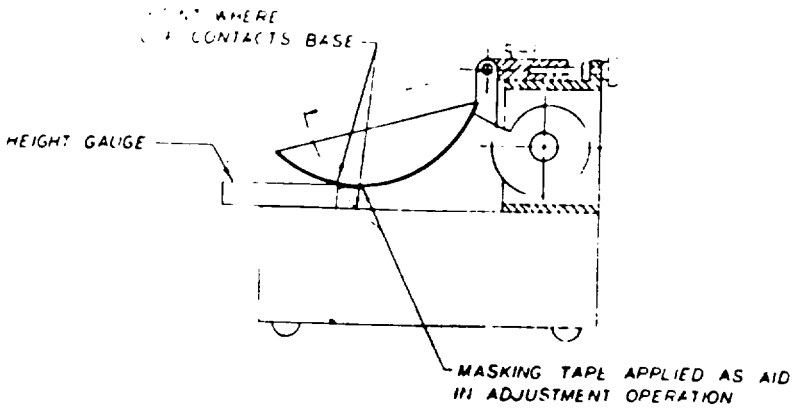



FIG. 4 Calibration for Height of Drop

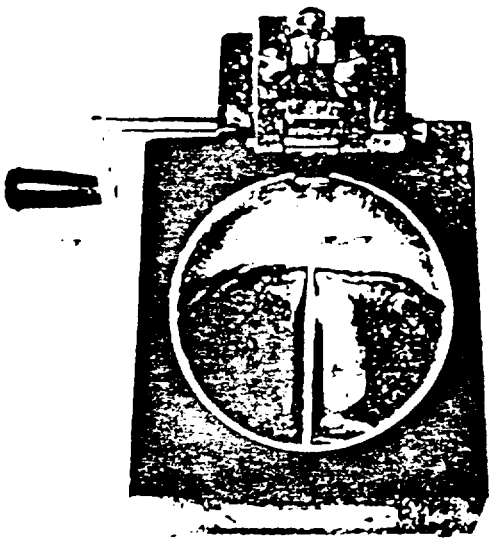


FIG. 5 Grooved Soil Pat in Liquid Limit Device

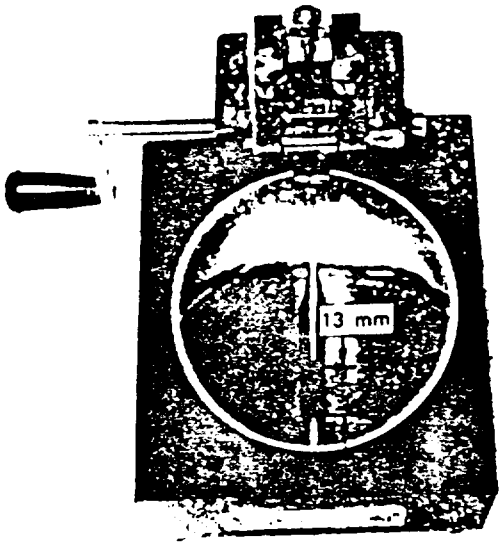



FIG. 6 Soil Pat After Groove Has Closed

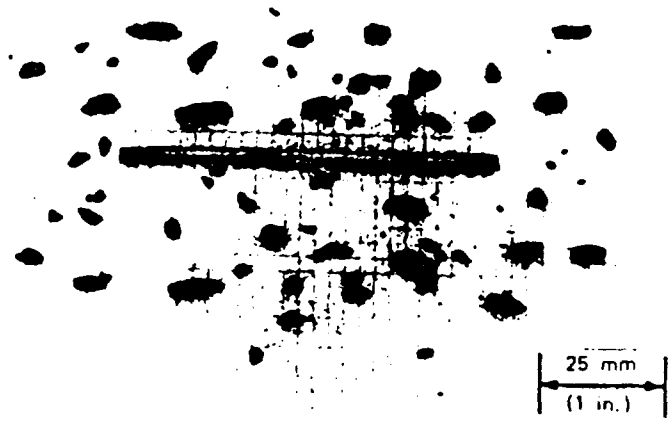



FIG. 7 Lean Clay Soil at the Plastic Limit

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Designation: D 4319 - 83

# Standard Test Method f DISTRIBUTION RATIC METHOD[1]

This standard is issued under the fixed designation D original adoption or, in the case of revision, the year A superscript epsilon (ε) indicates an editorial change

As an aqueous fluid migrates dependent upon the chemistry of other fluids and solid phas interactions determine the relat (such as ions) travel with respec importance in retarding the flow species at velocities less than the complex formation, precipitati precipitating as the sulfate), oxi test method applies to situation exchange) are operable for the s porous media.

It is difficult to derive generali in the geological environment. I ($K_d$) has been used to quantify modeling (usually, but not solely used to assess the degree to which fluid migrates through the geolog indication of how rapidly an ion under the geochemical conditior

This test method is for the labo may be used by qualified experts i given underground geochemical important site-specific factors. It is qualifications required, or to just predictive purposes. Rather, this technique for determining the dis and solid, under a certain set of la

Justification for the distributio based on expediency in modeling to partitioning in soils, equilibrium

[1] This method is under the jurisdiction of ASTM C Subcommittee D18.14 on Geotechnics of Waste Manage Current edition approved Nov. 28, 1983. Published Ja