SPLIT SAMPLING PLAN

Red Hill Fueling Facility

Honolulu, Hawai'i

GROUNDWATER MONITORING
2016-2017

Prepared by:

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This split sampling plan has been created based on Guidance for Quality Assurance Project Plans (EPA QA/G-5, December 2002); Guidance for the Data Quality Objectives Process for Hazardous Waste Site Investigations (EPA QA/G-4HW, January 2000); and Sampling And Analysis Plan Guidance, (R9QA/009.1, May 2014).

1 Introduction

The United States Environmental Protection Agency (EPA) Region 9 Land Division prepared this Split Sampling Plan (SSP). The purpose of the SSP is to specify the anticipated split sample locations and present the data comparison criteria. This SSP is applicable to groundwater sampling activities supporting the Red Hill Storage Facility (RHSF) groundwater-monitoring program.

As a part of EPA's and Hawaii Department of Health's ("Regulatory Agencies") oversight role, the Regulatory Agencies conducting a split sampling assessment as a spot check on the accuracy of data reported by the Navy's contracted laboratory by conducting simultaneous analysis of groundwater samples. Hawaii Department of Health (DOH), in cooperation with the EPA Region 9 Land Division, will observe the Navy field sampling team during all split sampling events, including the collection of samples and the packaging of samples in preparation for shipment to the respective laboratories. The Navy will ship the primary samples for analysis their contracted labratory. HDOH is responsible for taking custody of one of each packaged split sample and shipping it overnight to the EPA Region 9 Laboratory. EPA Region 9's Laboratory will receive the split samples from all of the groundwater-monitoring wells. The samples will be analyzed for volatile organic compounds (VOC) analysis, Total Petroleum Hydrocarbons for Diesel, Oil and Gasoline (TPH-d, TPH-o and TPH-g), Volatile Organic Compounds (VOC's) and Polycyclic Aromatic Hydrocarbons (PAH's).

The purpose of the split sampling is an initial check on the Navy's laboratory; the results of this comparison may lead to other types of QA checks. Additional QA checks may include single or double blind performance evaluation (PE) samples, review of laboratory SOP's relevant to the types of testing for this project, and reviews of lab data validation reports.

1.1 Project Organization

The following is a list of project personnel and their responsibilities:

Navy Sampling Coordinator : Navy sampling coordinator is the primary contact for the days of the sampling events.

John (Jack) Kronen, PhD Senior Geologist, Environment, Pacific D 1-808-954-4507 | C 1-808-927-3240 john.kronen@aecom.com

Table 1: Organizational Chart

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Title/Responsibility	Name	Phone Number
EPA Project Manager	Robert Pallarino	(415) 947-4128
EPA UST Project Officer	Lyndsey Tu	(415) 972-3269
EPA Quality Assurance Manager	Eugenia McNaughton	(415) 972-3411
EPA QA Reviewer	Marlon Mezquita	(415) 972-3808
EPA Region 9 Sample Control Coordinator	Susan Sturges	(510) 412-2383

1.2 Distribution List

Copies of the final SAP will be distributed to the following persons and organizations:

Roxanne Kwan Hawaii Department of Health roxanne.kwan@doh.hawaii.gov	Cory Waki NAVFAC Hawai'i cory.waki@navy.mil	Mark Manfredi Navy Project Coordinatior TBD

2 Site Location and Background

The Facility is located in the south-central portion of the island of O'ahu, Hawai'i. It is owned and operated by the United States Navy ("Navy"). Currently, the Facility contains 18 active and 2 inactive fuel tanks operated by the Naval Supply Systems Command Fleet Logistics Center, Pearl Harbor, Hawai'i. Each tank has a capacity of approximately 12.5 million gallons. The bottoms of the tanks are located approximately 100 feet (ft) above a groundwater aquifer, which is used as a drinking water source for the Navy and the City and County of Honolulu.

Groundwater split sampling will be performed on wells by the Navy at the Red Hill Storage Facility in support of ongoing groundwater monitoring efforts. The sampling will be performed on the twelve (12) existing wells (Figure 2) and the samples will be analyzed for petroleum related and other chemical analyses as needed or availible. The wells sampled and number of samples taken will be determined by the Navy, and the split samples will be submitted for analysis.

3 Project Data Quality Objectives

The Red Hill facility is known to have experienced a release of fuel in 2014. While the Navy has responded to the release, the extent of impact to the environment has not yet been fully defined. Due to the magnitude of the facility, the complex local geology and high levels of public concern, EPA Region 9 is pursuing a split sampling plan to independently verify the accuracy of the environmental data as reported by the Navy.

This split sampling plan is an initial check on the quality of the data produced by the Navy's contracted laboratory. Results of this comparison may lead to other types of QA checks. Additional QA checks may include: single or double blind performance evaluation (PE) samples, review of

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laboratory SOP's relevant to the types of testing for this project, reviews of lab data validation reports, and/or laboratory audits. The objective is to verify that the Navy produces defensible results and follows the approved procedures specified in the QAPP, FSP and published EPA guidelines.

The scope of the split sampling includes analysis of groundwater samples for Metals, VOCs, PAH's, TPH-g, TPH-d, and TPH-o. Attachment 2 on lab reporting limits and comparison to health based action levels will be used to document that the data we seek to obtain is of adequate quality.

Groundwater split sampling will be performed on wells sampled by the Navy at the Red Hill Storage Facility in support of ongoing groundwater monitoring efforts. The sampling will be performed on the twelve (12) existing wells as scheduled by the Navy (Figure 2). The order of well sampling and number wells sampled per day will be determined by the Navy.The Navy will submit information regarding quantity and types of bottles, order of sampling and schedules for sampling events with as much advance notice as possible to EPA.

The objective of the split sampling is to determine if the values obtained by the Navy are comparable to those values reported by the EPA Region 9 Laboratory. The scope of the comparison of the results pertains to sample analysis, preservation, packing, shipment, and documentation procedures. DQO Step 5 "Decision Rules" are described in further detail below in Section 7 -Data Review and Evaluation of Usability.

4 Rationale for Sample Locations

4.1 Tolerable Limits On Decision Errors

Decision errors occur when limitations in the available data lead the site manager to decide that the baseline condition is false when it is true, or to decide that the baseline condition is true when it is actually false. These two types of decision errors are classified as Type 1 errors and Type 2 errors, respectively.

The two main contributors to decision errors are: 1) limitations from the sampling design, and 2) measurement error, i.e., factors attributable to data quantity and data quality.

Data Quantity: DQO Step 6 is intended to help projects describe acceptable Type 1 and Type 2 decision error rates, when scoping out the probabilistic sampling design. This is done in order to define a reasonable "sample size = n" that yields a sufficient quantity of data to provide a representative snap shot of the actual site conditions. Typical split sampling efforts aim for somewhere between 10% to 20% of the parent population of samples. However, for this split sampling project, we have the opportunity to sample 100% of the available groundwater monitoring wells (12 available wells). Therefore, the project will clearly obtain a sufficiently representative picture of the Navy's sampling design.

Data Quality: This error (variability) is influenced by imperfections in the measurement and analysis system. To control this error, the planning team has ensured that analytical measurements are undertaken under the US EPA Region 9 analytical system. All samples will be collected and analyzed by adhering to the methods governed by strict quality assurance/quality

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control (QA/QC) requirements as documented in the attached standard operating procedures. All samples will be collected, packed, and shipped by the Navy's contractor, following their documented protocols, to ensure that the exact sample handling procedures are used for both the parent sampling and the split sampling data sets.

4.2 Optimize the Design For Obtaining Data

Phase one of the split sampling event in December will function as a 'dry run', where the DOH staff will observe the Navy's sampling process, including sample collection, packaging and preparation for shipment to the analysis laboratory. Split samples for analysis by the EPA laboratory will not be taken during this sampling event. This will be to ensure that the parties involved are ready for a full sampling event the following month and so that corrections can be made if necessary. HDOH will inform EPA Region 9 and the Navy if any issues are perceived during this trial.

Phase two will begin in January 2017. Split samples will be collected from all twelve (12) current Red Hill groundwater monitoring wells. As a part of the agreement between US EPA, HDOH, the US Navy and Hawai'i Board of Water Supply, split sampling will occur monthly through March or until Quarterly sampling resumes. Split sampling will continue through March, at which time the need for additional sampling will be assessed.

Attachment 1 - Split Sampling Summary specifies the split sample locations and order for collection and field observation. Attachment 2 – EPA Target Analyte List presents the list of analytes for each analytical procedure specified above. Attachment 3- Navy Laboratory Reporting Limits for Analyte list.

5 Field Methods and Procedures

5.1 Sample Collection

See Attachment 3 – which includes Navy Sampling SOP and Decontamination SOP

5.2 Quality Control Samples

Quality control (QC) samples for this project will include a trip blank and a temperature blank for each shipment, and a matrix spike/matrix spike duplicate. Attachment 1 lists the QC samples to be collected for this split sampling event. All QC samples will be produced in duplicate for the split sampling events so that each lab will have QC samples as a part of their analysis.

5.3 Methods of Analysis

The Navy will submit the samples to their laboratory and the EPA Region 9 Laboratory respectively. EPA Region 9 laboratory will preform the analyses summarized below.

Analysis	Method	EPA Region 9 Lab SOP
Lead, Manganese	200.8	507
VOCs	524.2	354

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VOCs, Low Level	524.2 (SIM)	353
SVOCs	8270D	315
PAHs, Low Level	8270D (SIM)	375
TPH-GRO	8015C	380
TPH-DRO, ORO	8015C	385
Iron	200.7	505
Anions (nitrate, sulfate)	300.0	530

Attachment 1 presents anticipated split sample locations, container type, sample volume, chemical preservation, and holding time requirements as provided by the Navy. Attachment 2- provides a list of analytes and quantitation limits as provided by the EPA Region 9 Lab.

The EPA Region 9 Laboratory will test for the majority of the analytes reported by Navy, but will report other analytes, that are a part of those test methods, which the Navy is not required to report. This is in an effort to provide as much information as possible to the public, without negating the agreements the Navy has reached regarding testing and reporting parameters.

New test methods will not be added unless the results of EPA's laboratory analysis indicate that the additional analytes are likely present. HBWS has provided a list of analytes, which is more extensive than that of the test methods the EPA is planning to use. While some of the HBWS analytes will be reported on as a part of the test methods– further analytes and new test methods will only be added if the wholesale comparison of EPA Region 9 data to Navy data indicates a need for additional analytes for comparison and analysis.

Region 9 EPA is committed to the expedient processing of samples as an effort to compare the results of two different laboratories, therefore the first sampling events will prioritize generating data for comparison with the Navy's analysis. More analysis types or QA samples may be added by EPA Region 9 for future sampling events.

6 Sample Containers, Preservation and Packing

6.1 Chain of Custody

The Navy will relinquish custody of the samples immediately after packing in coolers containing sufficient ice to keep the samples at 4±2°C, to Hawai'i DOH. Hawai'i DOH will ship coolers as packed by the Navy. The ice in the cooler will be double-bagged to prevent leakage if Blue Ice is not used. The cooler will have a custody seal affixed across the cooler lid. The samples will remain in the custody of DOH until relinquished for shipment to the laboratory. Attachment 4 contains SOP for sample packing and shipping provided by the Navy.

6.2 Shipping

DOH will ship all samples using an overnight carrier. A COC form will accompany the samples from the point of origin to the designated laboratory in a plastic bag taped to the inside of the cooler lid. If samples are shipped on a Friday, the Regional Sample Coordination Center (RSCC) will be contacted

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510.412.2383 with information (number of samples, tracking number) regarding Saturday delivery. All sample coolers must be submitted to FedEx no later than **1530** for same-day shipping.

6.3 Labeling

Bottle labels will be provided by the Navy's laboratory, and filled out by the Navy's sample collection team. The EPA Region 9 Laboratory will make it known after the first samples are received if any issue is encountered regarding the proper labeling of samples.

6.4 Field Notes

Due to the security considerations surrounding the sampling location, and in cooperation the Navy, any notes and or photographs collected during the sampling events will be approved by the Navy before being released by EPA or DOH.

7 Data Review and Evaluation of Usability

Region 9 EPA will compare results reported by the Navy's contracted laboratory to the results reported by the Region 9 Laboratory, and determine if the results are comparable using the criteria below.

Upon receipt of EPA and the Navy's data sets, a split-sampling report will be generated containing all the split and primary sample results, calculated relative percent difference (RPD), an evaluation of any outliers, and an overall assessment of the sample data.

The EPA and PRP data sets will be compared using a matched-pairs statistical design. The main objective of the matched-pairs analysis will be to assess the overall agreement between independent sets of analytical results provided by the EPA and PRP laboratories. Agreement signifies that the two sets of results are effectively comparable and/or interchangeable within statistical and practical limits.

A hierarchical approach employing both formal statistical methods and qualitative assessment will used to determine agreement between the EPA and PRP results. All tests will focus on the paired differences, calculated as the EPA result – PRP result. **An overall weight-of-evidence (WOE) process will be followed to draw final conclusions concerning comparability or agreement of the results.** Formal statistical tests will be used as the primary line-of-evidence (LOE), and various graphical methods will be used to complement the statistical results, as well as refine the interpretation in cases where more complex patterns are found in the data that would not be revealed using standard hypothesis testing approaches.

Professional judgment, aided by examination of graphical presentations of the data, will be used to draw conclusions concerning agreement in cases where assumptions are not met for the formal statistical tests, or where statistical tests could not be performed, or findings from the statistical tests are equivocal.

Both parametric (t-test) and nonparametric (Wilcoxon signed-rank test and Fong's modified sign test) paired-difference tests will be used to determine whether the reported results for individual

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analytes are statistically significantly different between the two groups of data. All tests will be conducted using the "R-Studio" statistical software package and will follow methods described in EPA (1996), Helsel (2005), and Fong and others (2003).

All tests will evaluate the following two-sided null (H0) and alternative (HA) hypotheses:
H0: EPA = PRP
HA: EPA ≠ PRP

A 5 percent ($p < 0.05$) level of significance (sometimes referred to as the critical p value or "pcrit"), will be used to interpret the test results. The significance level or p-crit is equivalent to a 95 percent confidence level in the interpretation of test conclusions. The p-crit sets an upper threshold for the largest average deviation that can be willingly accepted if the test conclusion arose from "pure chance." Low p values (that is, less than or equal to 0.05) provide statistical evidence that the observed average difference is unlikely to be the result of random chance and, therefore, represents a "true effect." As the observed p value increases beyond p-crit, there is more confidence that the two data sets are not statistically different and, therefore, can conclude that the observed differences are not greater than what might be expected from random chance alone.

Findings of statistical significance require further investigation to uncover the possible underlying cause for the observed differences. Moreover, additional scrutiny of the results is needed to determine whether statistically significant differences are also of practical/environmental significance (for example, would differences affect comparisons to action levels or other effects benchmarks).

Test selection depends on the detection status of the paired results. Both the paired-difference t-test and Wilcoxon signed-rank test will be conducted for analytes where all pairs of results are detected. These paired-difference tests test whether the overall mean (or median in the case of the nonparametric test) difference for all matched pairs of samples is zero. That is, some differences (EPA – PRP) may be positive (indicating the higher result is from the EPA sample) and some may be negative (indicating the higher result is from the PRP sample), but if there is no net difference between pairs, the mean difference will be zero (or not distinguishable from zero within the context of the statistical tests).

A key assumption of the paired-difference tests is that the differences are normally distributed (parametric test) or that the distribution is symmetrical about the median (nonparametric test). The Shapiro-Wilk W test is a powerful and highly recommended goodness-of-fit (GOF) test that can be used to determine whether data follow a normal distribution (EPA 2006). A significance level of $p < 0.05$ (5 percent) will be used to test the H0 for the Shapiro-Wilk W test that the data follow a normal distribution. It should be noted, however, that both the t-test and Wilcoxon signed-rank test are robust to moderate departures from normality.

A WOE process will be used to determine which of the statistical test results (that is, the primary LOE) is most appropriate, or whether supplemental LOEs (that is, graphical presentations of the data) should be used to draw final conclusions. When all of the results are detected, the primary

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LOE will be application of the t-test and Wilcoxon signed-rank test. If the assumptions for both tests are met, then conclusions will be drawn based on the most sensitive test result (that is, lowest p value- in general, the parametric t-test will be slightly more powerful than the Wilcoxon signed-rank test in these cases). If the assumptions for only one test are met, then the results for that test will be used. If the assumptions for neither test are met, then results of the sign test will be used. The modified sign test will be the only test conducted for analytes with censored data. In all cases, graphical presentations of the results (that is, supplemental LOEs) will be examined to determine whether there are patterns in the data that would not be accounted for or revealed by the standard statistical tests (for example, differences that vary as a function of concentration, and the relationship between the EPA and PRP results is reversed as a function of concentration or location; or comparison of mostly censored results in cases where different method detection limits are used by the EPA and PRP laboratories).

All data generated by the Navy's contracted labratory is subject to computer-aided data review. The EPA Region 9 EPA Region 9 Laboratory manually reviews data in accordance with SOPs 846 Internal Laboratory EPA Review of ESAT and EPA Generated Data, and 845 Final Chemistry Review and Report Generation. If the results of the split sampling indicate disagreement between the laboratories, additional manual data review and/or external data validation may be required.

8 Health and Safety

For these activities, any non-Navy parties present at the sampling event will follow the Navy's Health and Safety Plan included as a component of Attachment 3.

9 Schedule

Split sampling activities will begin during the week of December 12, 2016 and each individual event will be complete within four days' time. Standard laboratory turn-around time is typically 30 days from verified receipt of the last sample in a sample delivery group. EPA Region 9 will create a Split Sample Summery within 21 business days of receipt of the laboratory data. The anticipated schedule is as follows:

December 2016

- EPA Region 9 to prepare a Sampling Plan for laboratory comparison as an oversight action.
- Hawaii Department of Health to become familiarized with the Navy's sampling process to prepare for week of January 16th.

January 2017

- Split Sampling to occur at all wells sampled by the Navy, with HDOH shipping the samples to the EPA R9 Lab after they are collected by the Navy.

February 2017

- First round of sapling data to be analyzed, compared and reported on by EPA Region 9 Lab.
- Second round of sampling to occur with HDOH shipping samples collected by the Navy.

March 2017

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- Second round of data to be analyzed, compared and reported on by EPA Region 9 Lab.
- EPA Region 9 to report on findings from first sampling event to stakeholders.
- Third round of sampling to occur with HDOH shipping samples collected by the Navy (subsequent sampling to occur quarterly).

April 2017

- Second summery of findings from split sampling analysis to stakeholders

May 2017

- Final summery of findings from monthly split sampling analysis with recommendations from EPA Region 9 to Navy.
- Subsequent summaries of sampling events will follow within 60 days of the sampling event if the Regulatory Agencies determine that additional split sampling events are necessary.

The timeframes are estimates based on presumed sampling dates, EPA will make every effort to provide up to date schedules as the sampling events continue.

10 References

[U.S. Environmental Protection Agency (EPA). 1996. "Test Methods for Evaluating Solid Waste, Volume IA through IC, SW-846, Third Edition." Updated I, II, IIA, IIB, and III. OSWER. Washington, D.C. December.]

[Helsel, D.R. 2005. Nondetects and Data Analysis. Statistics for Censored Environmental Data. John Wiley and Sons, Inc. Hoboken, New Jersey. 250 p.]

[Fong, D.Y.T., Kwan, C.W., Lam, K.F., K.S.L. Lam. 2003. Use of the Sign Test for the Median in the Presence of Ties. American Statistician, 57: 237-240.]

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Figure 1 – Site Location

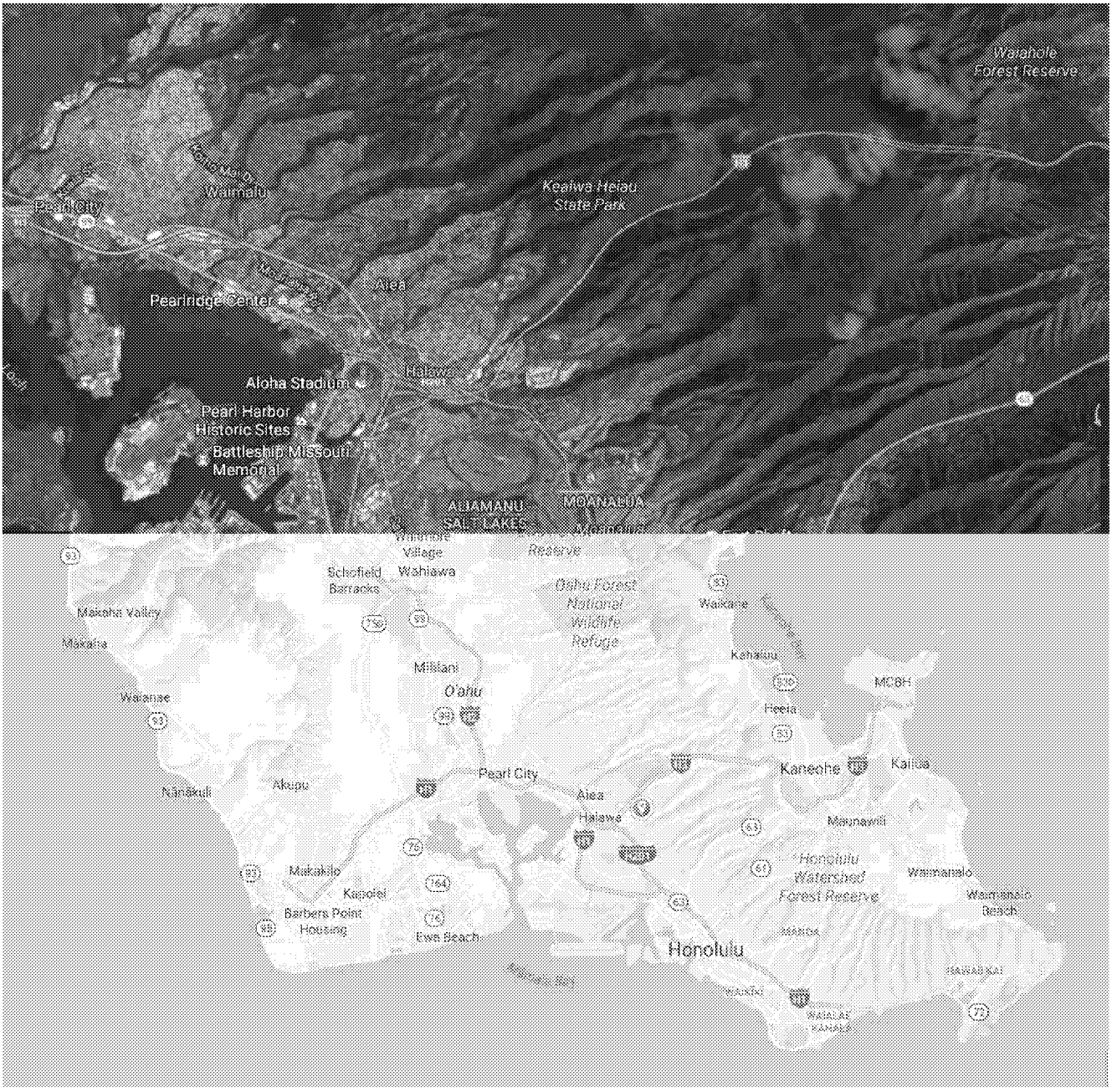
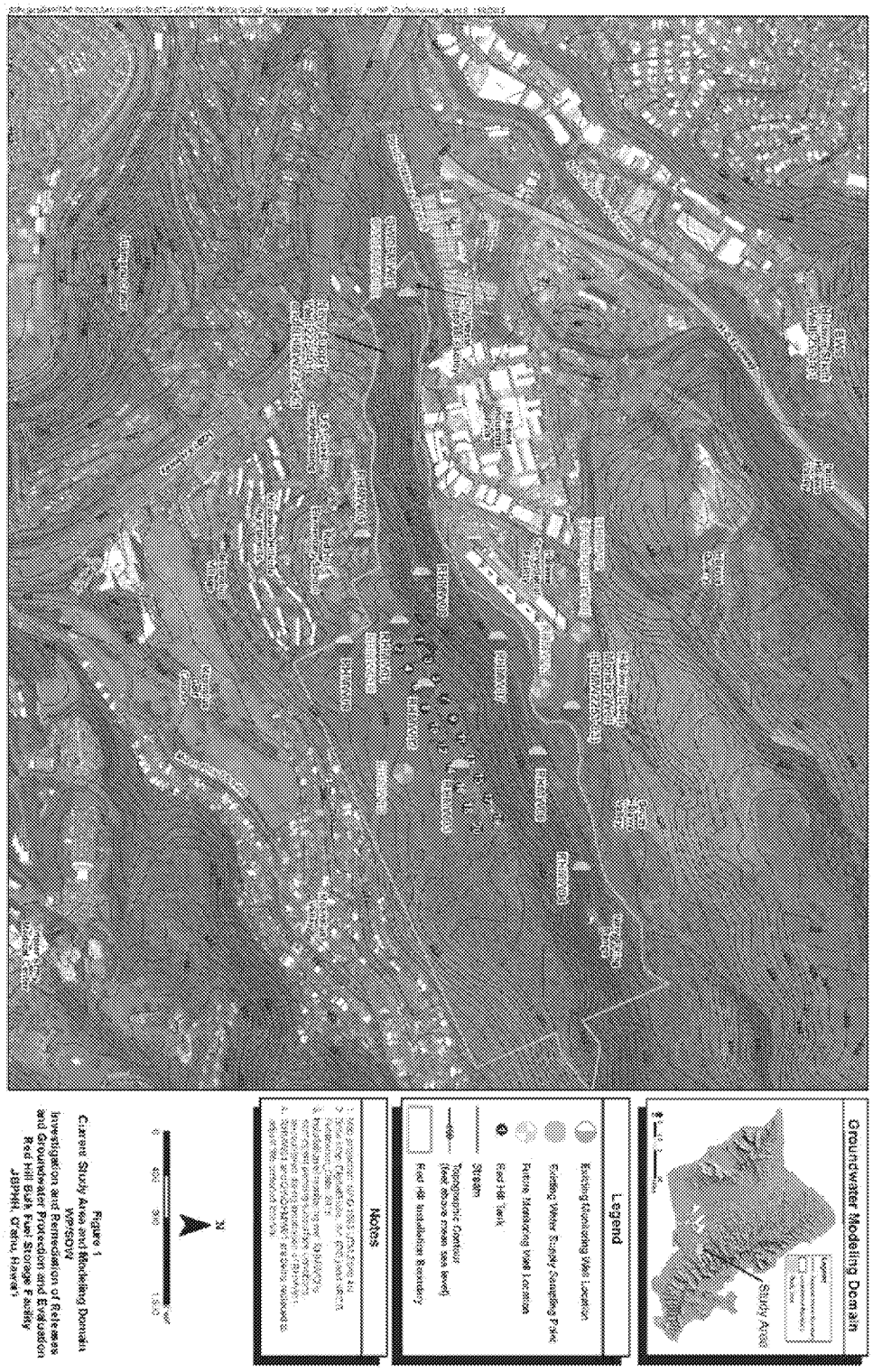


Figure 1 Map data: Google, DigitalGlobe.

Figure 2 – Well Locations



Attachment 1 - Split Sample Schedule Summary (December Example)

Long-term Groundwater Monitoring Program, December 2016 Event for Monthly Sampling Red Hill Bulk Fuel Storage Facility, JBPHH, HI

Monday, December 12, 2016, to Thursday, December 15, 2016 [a]

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IMPORTANT EVENT NOTES

1) Sampling events are performed by three teams: 1 inside-tunnel team, 1 outside-tunnel team, and 1 sample packing/shipping team.

2) The Navy collects, prepares, and handles groundwater samples in accordance with the standard operating procedures (SOPs) presented in the *Project Procedures Manual* (DON 2015).

3) Groundwater samples collected before 1100 are prepped, packed, and shipped **same-day via FedEx due to short holding times for nitrate analysis (48-hour hold time)**.

4) **All sample coolers must be submitted to FedEx no later than 1530 for same-day shipping**.

5) Groundwater samples collected after 1100 are stored overnight at the AECOM warehouse then prepped, packed, and shipped via FedEx the next day.

SAMPLING & ANALYSIS NOTES

1) Groundwater samples are analyzed by a Department of Defense (DoD) Environmental Laboratory Accreditation Program (ELAP)-certified analytical chemistry laboratory.

   - Laboratory QC samples will include method blanks, laboratory control samples, matrix spikes/matrix spike duplicates (MS/MSDs), and duplicates as described in the DoD Quality Systems Manual (QSM) Version 5.0 (DoD 2013).

2) Analytical laboratory results are validated by a third-party data validation firm.

   - Third-party data validation consists of standard validation (90 percent) and full validation (10 percent), ensuring the laboratory has complied with the requirements outlined in both the analytical methods and the DoD QSM (DoD 2013).

   - Additionally, analytical data are validated by a third-party data validation firm in accordance with NAVFAC Pacific Environmental Restoration Program Data Validation Procedures (DON 2015).

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Table 1: Current COPC List for and Screening Criteria for AOC Statement of Work Sections 6 and 7 Investigation, Red Hill Bulk Fuel Storage Facility, JBPHH, HI

Parameter	Analytical Method	Analyte(s)	Screening Criterion (µg/L)
TPH	EPA SW-846 8015	TPH-g	100
		TPH-d	100
		TPH-o	100
TPH with Silica Gel Cleanup	EPA SW-846 3630/ 8015	TPH-d	100
		TPH-o	100
VOCs	EPA SW-846 8260	Benzene	5.0
		Ethylbenzene	30
		Toluene	40
		Total Xylenes	20
PAHs	EPA SW-846 8270 SIM	1-Methylnaphthalene	4.7
		2-Methylnaphthalene	10
		Naphthalene	17
NAPs	Field parameter	Dissolved Oxygen	—
	SM 3500-Fe	Ferrous Iron	—
	RSK 175M	Methane	—
	EPA 300.0	Nitrate, Sulfate, Chloride	—
	SM2320	Alkalinity (bicarbonate, carbonate, and total alkalinity)	—
Lead Scavengers	SW-846 8260	1,2-Dibromoethane	0.04
		1,2-Dichloroethane	5.0
Fuel Additives	SW-846 8270	Phenol	5.0 [a]
	Lab Procedure	2-(2-methoxyethoxy)-ethanol	800 [b]
Groundwater Chemistry (Major Ions and Silica)	EPA 300.0	Bromide, chloride, fluoride, and sulfate	—
	EPA SW-846 6010	Total calcium, total magnesium, total manganese, total potassium, and total sodium	—
	SM4500-SID	Total and dissolved silica	—

Note: COPC screening criteria were provided in the February 4, 2016 scoping completion letter.

— no criterion
µg/L microgram per liter
PAH polynuclear aromatic hydrocarbon
TPH total petroleum hydrocarbons
TPH-d total petroleum hydrocarbons – diesel range organics TPH-g
total petroleum hydrocarbons – gasoline range organics
TPH-o total petroleum hydrocarbons – residual range organics (i.e., TPH-oil)

[a] Screening criterion from DOH Tier 1 EALs, Table D-1b, Groundwater Action Levels (groundwater is a current or potential drinking water resource, and surface water body is not located within 150m of release site) (DOH 2016a).

[b] Screening criterion from EPA Tap Water Regional Screening Levels, THQ=1.0, May 2016 (EPA 2016).

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DECEMBER 2016 - APRIL 2017 GWM EVENT

RHMW01, RHMW02, RHMW03, RHMW05, and RHMW04, RHMW06, RHMW07, OWDFMW01, HDMW2253-03, RHMW2254-01

Parameter	Containers (per sample)	Total per Container Type (per sample)
VOCs by 8260	40-mL VOAs w/ HCl, Teflon-lined septum caps	4
TPH-g by 8260		
TPH-d, TPH-o by 8015	1 L amber unpreserved	6
PAHs (Naph, 1-&2-MN) by 8270 SIM		
SVOCs (phenol and 2-(2-methoxyethoxy)-ethanol) by 8270		
Methane by RSK175	40-mL VOAs w/ HCl, Teflon-lined septum caps	2
Ferrous Iron by SM 3500-Fe	250-mL brown plastic w/ HCl (field filtered)	1
Nitrate, Sulfate and Chloride by EPA 300.0	250-mL plastic unpreserved	1

RHMW08 and RHMW09 (any newly installed wells)

Parameter	Containers (per sample)	Total per Container Type (per sample)
VOCs by 8260	40-mL VOAs w/ HCl, Teflon-lined septum caps	5
TPH-g by 8260		
DCA by 8260		
EDB by 8011	40-mL VOAs unpreserved, Teflon-lined septum caps	3
TPH-d, TPH-o by 8015	1 L amber unpreserved	6
PAHs (Naph, 1-&2-MN) by 8270 SIM		
SVOCs (phenol and 2-(2-methoxyethoxy)-ethanol) by 8270		
Methane by RSK175	40-mL VOAs w/ HCl, Teflon-lined septum caps	2
Ferrous Iron by SM 3500-Fe	250-mL brown plastic w/ HCl (field filtered)	1
Nitrate, Sulfate and Chloride by EPA 300.0	250-mL plastic unpreserved	1

Equipment Blanks / Field Blanks

Parameter	Containers (per sample)	Total per Container Type (per sample)
VOCs by 8260	40-mL VOAs w/ HCl, Teflon-lined septum caps	5
TPH-g by 8260		
TPH-d, TPH-o by 8015	1 L amber unpreserved	6
PAHs (Naph, 1-&2-MN) by 8270 SIM		
SVOCs (phenol and 2-(2-methoxyethoxy)-ethanol) by 8270		

Trip Blanks

Parameter	Containers (per sample)	Total per Container Type (per sample)
VOCs by 8260	40-mL VOAs w/ HCl, Teflon-lined septum caps	4
TPH-g by 8260		
DCA by 8260		
EDB by 8011	40-mL VOAs unpreserved, Teflon-lined septum caps	3
Methane by RSK 175	40-mL VOAs w/ HCl, Teflon-lined septum caps	1

Mark Chain-of-Custody for EDB and DCA only if Trip Blank is associated with newly installed well

Parameters not analyzed during these events:

TPH-d, TPH-o w/ Silica Gel Cleanup by 3630 & 8015	1 wet season (Oct 2016), and 1 dry season (tentative Jul 2017)
Bromide and Fluoride by EPA 300.0	Groundwater chemistry to profile aquifer (sampled Nov 2016 event)
Total silica by SM4500-SID	
Total, bicarbonate, and carbonate alkalinity by SM2320B	
Dissolved silica by SM4500-SID	
Total calcium, total magnesium, total manganese, total potassium, and total sodium by 6010	

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Attachment 2 – EPA Region 9 Lab Analyte List

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SpecificMethod	Analysis	Matrix	Analyte	MDL	MRL	Units
200.8	Metals, ICP/MS, Total	Water	Lead	0.50	1.0	ug/L
200.8	Metals, ICP/MS, Total	Water	Manganese	1.0	2.0	ug/L
200.7	Metals by 200.7, Total	Water	Iron	50	100	ug/L
300.0	Anions	Water	Nitrate as N	0.05	0.1	mg/L
300.0	Anions	Water	Sulfate	0.25	0.5	mg/L
8270D (SIM)	PAH-Low	Water	Naphthalene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	2-Methylnaphthalene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	1-Methylnaphthalene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Acenaphthylene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Acenaphthene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Fluorene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Phenanthrene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Anthracene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Fluoranthene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Pyrene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Benzo(a)anthracene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Chrysene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Benzo(b)fluoranthene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Benzo(k)fluoranthene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Benzo(a)pyrene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Indeno(1,2,3-cd)pyrene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Dibenz(a,h)anthracene	25	50	ng/L
8270D (SIM)	PAH-Low	Water	Benzo(g,h,i)perylene	25	50	ng/L
8270D	SVOCs	Water	1,4-Dioxane	0.5	1.0	ug/L
8270D	SVOCs	Water	Phenol	2.5	5.0	ug/L
8270D	SVOCs	Water	Bis(2-chloroethyl)ether	0.5	1.0	ug/L
8270D	SVOCs	Water	2-Chlorophenol	2.5	5.0	ug/L
8270D	SVOCs	Water	1,3-Dichlorobenzene	0.5	1.0	ug/L
8270D	SVOCs	Water	1,4-Dichlorobenzene	0.5	1.0	ug/L
8270D	SVOCs	Water	Benzyl alcohol	2.5	5.0	ug/L
8270D	SVOCs	Water	1,2-Dichlorobenzene	0.5	1.0	ug/L
8270D	SVOCs	Water	2-Methylphenol	2.5	5.0	ug/L
8270D	SVOCs	Water	Bis(2-chloro-1-methylethyl) ether	0.5	1.0	ug/L
8270D	SVOCs	Water	3&4-Methylphenol	2.5	5.0	ug/L
8270D	SVOCs	Water	N-Nitrosodipropylamine	0.5	1.0	ug/L
8270D	SVOCs	Water	Hexachloroethane	0.5	1.0	ug/L
8270D	SVOCs	Water	Nitrobenzene	0.5	1.0	ug/L
8270D	SVOCs	Water	Isophorone	0.5	1.0	ug/L
8270D	SVOCs	Water	2-Nitrophenol	2.5	5.0	ug/L
8270D	SVOCs	Water	2,4-Dimethylphenol	2.5	5.0	ug/L
8270D	SVOCs	Water	Bis(2-chloroethoxy)methane	0.5	1.0	ug/L
8270D	SVOCs	Water	2,4-Dichlorophenol	2.5	5.0	ug/L
8270D	SVOCs	Water	1,2,4-Trichlorobenzene	0.5	1.0	ug/L
8270D	SVOCs	Water	Naphthalene	0.5	1.0	ug/L
8270D	SVOCs	Water	4-Chloroaniline	2.5	5.0	ug/L

8270D	SVOCs	Water	Hexachlorobutadiene	0.5	1.0	ug/L
8270D	SVOCs	Water	4-Chloro-3-methylphenol	2.5	5.0	ug/L
8270D	SVOCs	Water	2-Methylnaphthalene	0.5	1.0	ug/L
8270D	SVOCs	Water	Hexachlorocyclopentadiene	2.5	5.0	ug/L
8270D	SVOCs	Water	2,4,6-Trichlorophenol	2.5	5.0	ug/L
8270D	SVOCs	Water	2,4,5-Trichlorophenol	2.5	5.0	ug/L
8270D	SVOCs	Water	2-Chloronaphthalene	0.5	1.0	ug/L
8270D	SVOCs	Water	2-Nitroaniline	2.5	5.0	ug/L
8270D	SVOCs	Water	Dimethyl phthalate	0.5	1.0	ug/L
8270D	SVOCs	Water	2,6-Dinitrotoluene	0.5	1.0	ug/L
8270D	SVOCs	Water	Acenaphthylene	0.5	1.0	ug/L
8270D	SVOCs	Water	3-Nitroaniline	2.5	5.0	ug/L
8270D	SVOCs	Water	Acenaphthene	0.5	1.0	ug/L
8270D	SVOCs	Water	2,4-Dinitrophenol	10	20	ug/L
8270D	SVOCs	Water	4-Nitrophenol	2.5	5.0	ug/L
8270D	SVOCs	Water	Dibenzofuran	0.5	1.0	ug/L
8270D	SVOCs	Water	2,4-Dinitrotoluene	0.5	1.0	ug/L
8270D	SVOCs	Water	Diethyl phthalate	0.5	1.0	ug/L
8270D	SVOCs	Water	Fluorene	0.5	1.0	ug/L
8270D	SVOCs	Water	4-Chlorophenyl phenyl ether	0.5	1.0	ug/L
8270D	SVOCs	Water	4-Nitroaniline	2.5	5.0	ug/L
8270D	SVOCs	Water	4,6-Dinitro-2-methylphenol	2.5	5.0	ug/L
8270D	SVOCs	Water	Diphenyl amine	0.5	1.0	ug/L
8270D	SVOCs	Water	4-Bromophenyl phenyl ether	0.5	1.0	ug/L
8270D	SVOCs	Water	Hexachlorobenzene	0.5	1.0	ug/L
8270D	SVOCs	Water	Pentachlorophenol	2.5	20	ug/L
8270D	SVOCs	Water	Phenanthrene	0.5	1.0	ug/L
8270D	SVOCs	Water	Anthracene	0.5	1.0	ug/L
8270D	SVOCs	Water	Carbazole	0.5	1.0	ug/L
8270D	SVOCs	Water	Di-n-butyl phthalate	0.5	1.0	ug/L
8270D	SVOCs	Water	Fluoranthene	0.5	1.0	ug/L
8270D	SVOCs	Water	Pyrene	0.5	1.0	ug/L
8270D	SVOCs	Water	Butyl benzyl phthalate	0.5	1.0	ug/L
8270D	SVOCs	Water	Benzo(a)anthracene	0.5	1.0	ug/L
8270D	SVOCs	Water	3,3'-Dichlorobenzidine	0.5	1.0	ug/L
8270D	SVOCs	Water	Chrysene	0.5	1.0	ug/L
8270D	SVOCs	Water	Bis(2-ethylhexyl) phthalate	0.5	1.0	ug/L
8270D	SVOCs	Water	Di-n-octyl phthalate	0.5	1.0	ug/L
8270D	SVOCs	Water	Benzo(b)fluoranthene	0.5	1.0	ug/L
8270D	SVOCs	Water	Benzo(k)fluoranthene	0.5	1.0	ug/L
8270D	SVOCs	Water	Benzo(a)pyrene	0.5	1.0	ug/L
8270D	SVOCs	Water	Indeno(1,2,3-cd)pyrene	0.5	1.0	ug/L
8270D	SVOCs	Water	Dibenz(a,h)anthracene	0.5	1.0	ug/L
8270D	SVOCs	Water	Benzo(g,h,i)perylene	0.5	1.0	ug/L
8270D	SVOCs	Water	Tentatively Identified Compounds	5.0	10	ug/L
8015C	TPH - Extractable	Water	TPH - Diesel Range Organics	75	150	ug/L
8015C	TPH - Extractable	Water	TPH - Oil Range Organics	300	600	ug/L
8015C	TPH - Purgeable	Water	TPH - Gasoline Range Organics	25	50	ug/L
524.2	VOCs	Water	Dichlorodifluoromethane	0.2	0.5	ug/L

524.2	VOCs	Water	Chloromethane	0.2	0.5	ug/L
524.2	VOCs	Water	Vinyl chloride	0.2	0.5	ug/L
524.2	VOCs	Water	Bromomethane	0.2	0.5	ug/L
524.2	VOCs	Water	Chloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	Trichlorofluoromethane	0.2	0.5	ug/L
524.2	VOCs	Water	1,1-Dichloroethene	0.2	0.5	ug/L
524.2	VOCs	Water	1,1,2-Trichloro-1,2,2-trifluoroethane	0.2	0.5	ug/L
524.2	VOCs	Water	Acetone	2.0	4.0	ug/L
524.2	VOCs	Water	Carbon disulfide	0.2	0.5	ug/L
524.2	VOCs	Water	Dichloromethane	0.2	0.5	ug/L
524.2	VOCs	Water	tert-Butyl alcohol	5.0	10	ug/L
524.2	VOCs	Water	trans-1,2-Dichloroethene	0.2	0.5	ug/L
524.2	VOCs	Water	tert-Butyl methyl ether (MTBE)	1.0	2.0	ug/L
524.2	VOCs	Water	1,1-Dichloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	Diisopropyl ether	1.0	2.0	ug/L
524.2	VOCs	Water	Ethyl tert-butyl ether	1.0	2.0	ug/L
524.2	VOCs	Water	2,2-Dichloropropane	0.2	0.5	ug/L
524.2	VOCs	Water	cis-1,2-Dichloroethene	0.2	0.5	ug/L
524.2	VOCs	Water	2-Butanone (MEK)	2.0	4.0	ug/L
524.2	VOCs	Water	Bromochloromethane	0.2	0.5	ug/L
524.2	VOCs	Water	Chloroform	0.2	0.5	ug/L
524.2	VOCs	Water	1,1,1-Trichloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	Carbon tetrachloride	0.2	0.5	ug/L
524.2	VOCs	Water	1,1-Dichloropropene	0.2	0.5	ug/L
524.2	VOCs	Water	Benzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,2-Dichloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	tert-Amyl methyl ether	1.0	2.0	ug/L
524.2	VOCs	Water	Trichloroethene	0.2	0.5	ug/L
524.2	VOCs	Water	1,2-Dichloropropane	0.2	0.5	ug/L
524.2	VOCs	Water	Dibromomethane	0.2	0.5	ug/L
524.2	VOCs	Water	Bromodichloromethane	0.2	0.5	ug/L
524.2	VOCs	Water	cis-1,3-Dichloropropene	0.2	0.5	ug/L
524.2	VOCs	Water	4-Methyl-2-pentanone (MIBK)	2.0	4.0	ug/L
524.2	VOCs	Water	Toluene	0.2	0.5	ug/L
524.2	VOCs	Water	trans-1,3-Dichloropropene	0.2	0.5	ug/L
524.2	VOCs	Water	tert-Butylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,2,4-Trimethylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	sec-Butylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,3-Dichlorobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	p-Isopropyltoluene	0.2	0.5	ug/L
524.2	VOCs	Water	1,4-Dichlorobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,2-Dichlorobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	Butylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,2-Dibromo-3-chloropropane	1.0	2.0	ug/L
524.2	VOCs	Water	1,2,4-Trichlorobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	Hexachlorobutadiene	0.2	0.5	ug/L
524.2	VOCs	Water	Naphthalene	0.2	0.5	ug/L
524.2	VOCs	Water	1,2,3-Trichlorobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,1,2-Trichloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	Tetrachloroethene	0.2	0.5	ug/L
524.2	VOCs	Water	1,3-Dichloropropane	0.2	0.5	ug/L
524.2	VOCs	Water	2-Hexanone	2.0	4.0	ug/L

524.2	VOCs	Water	Chlorodibromomethane	0.2	0.5	ug/L
524.2	VOCs	Water	1,2-Dibromoethane (EDB)	0.2	0.5	ug/L
524.2	VOCs	Water	Chlorobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,1,1,2-Tetrachloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	Ethylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	m&p-Xylene	0.5	1.0	ug/L
524.2	VOCs	Water	o-Xylene	0.2	0.5	ug/L
524.2	VOCs	Water	Styrene	0.2	0.5	ug/L
524.2	VOCs	Water	Bromoform	0.2	0.5	ug/L
524.2	VOCs	Water	Isopropylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	Bromobenzene	0.2	0.5	ug/L
524.2	VOCs	Water	1,1,2,2-Tetrachloroethane	0.2	0.5	ug/L
524.2	VOCs	Water	1,2,3-Trichloropropane	0.2	0.5	ug/L
524.2	VOCs	Water	Propylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	2-Chlorotoluene	0.2	0.5	ug/L
524.2	VOCs	Water	4-Chlorotoluene	0.2	0.5	ug/L
524.2	VOCs	Water	1,3,5-Trimethylbenzene	0.2	0.5	ug/L
524.2	VOCs	Water	Tentatively Identified Compounds			ug/L
524.2	VOCs, Low Level, Water	Water	1,2-Dibromoethane (EDB)	2.5	5.0	ng/L
524.2	VOCs, Low Level, Water	Water	1,2,3-Trichloropropane	2.5	5.0	ng/L
524.2	VOCs, Low Level, Water	Water	1,2-Dibromo-3-chloropropane	5.0	10	ng/L

SpecificMethod	Analysis	Matrix	Analyte	Sur	Dup	MS	MSRPD	BS
200.8	Metals, ICP/MS, Total	Water	Lead	-	20	70-130	20	85-115
200.8	Metals, ICP/MS, Total	Water	Manganese	-	20	70-130	20	85-115
200.7	Metals by 200.7, Total	Water	Iron	-	20	70-130	20	85-115
300.0	Anions	Water	Nitrate as N	-	20	80-120	20	90-110
300.0	Anions	Water	Sulfate	-	20	80-120	20	90-110
8270D (SIM)	PAH-Low	Water	Naphthalene	-		25-116	20	20-110
8270D (SIM)	PAH-Low	Water	2-Methylnaphthalene	-		40-110	20	20-110
8270D (SIM)	PAH-Low	Water	1-Methylnaphthalene	-		37-110	20	20-110
8270D (SIM)	PAH-Low	Water	Acenaphthylene	-		56-110	20	35-110
8270D (SIM)	PAH-Low	Water	Acenaphthene	-		45-111	20	25-110
8270D (SIM)	PAH-Low	Water	Fluorene	-		51-112	20	36-110
8270D (SIM)	PAH-Low	Water	Phenanthrene	-		55-110	20	49-110
8270D (SIM)	PAH-Low	Water	Anthracene	-		64-110	20	56-110
8270D (SIM)	PAH-Low	Water	Fluoranthene	-		43-123	20	65-110
8270D (SIM)	PAH-Low	Water	Pyrene	-		34-134	20	57-114
8270D (SIM)	PAH-Low	Water	Benzo(a)anthracene	-		42-136	20	70-125
8270D (SIM)	PAH-Low	Water	Chrysene	-		37-115	20	64-110
8270D (SIM)	PAH-Low	Water	Benzo(b)fluoranthene	-		28-117	20	63-111
8270D (SIM)	PAH-Low	Water	Benzo(k)fluoranthene	-		31-117	20	63-116
8270D (SIM)	PAH-Low	Water	Benzo(a)pyrene	-		32-115	20	62-110
8270D (SIM)	PAH-Low	Water	Indeno(1,2,3-cd)pyrene	-		29-116	20	60-116
8270D (SIM)	PAH-Low	Water	Dibenz(a,h)anthracene	-		32-117	20	60-121
8270D (SIM)	PAH-Low	Water	Benzo(g,h,i)perylene	-		27-110	20	59-110
8270D (SIM)	PAH-Low	Water	2-Fluorobiphenyl	32-110		-		-
8270D (SIM)	PAH-Low	Water	Terphenyl-d14	39-136		-		-
8270D	SVOCs	Water	1,4-Dioxane	-		70-130	20	66-126
8270D	SVOCs	Water	Phenol	-		70-130	20	48-110
8270D	SVOCs	Water	Bis(2-chloroethyl)ether	-		70-130	20	53-113
8270D	SVOCs	Water	2-Chlorophenol	-		50-110	20	64-110
8270D	SVOCs	Water	1,3-Dichlorobenzene	-		70-130	20	28-110
8270D	SVOCs	Water	1,4-Dichlorobenzene	-		70-130	20	29-110

8270D	SVOCs	Water	Benzyl alcohol	-		70-130	20	49-110
8270D	SVOCs	Water	1,2-Dichlorobenzene	-		70-130	20	32-110
8270D	SVOCs	Water	2-Methylphenol	-		70-130	20	47-110
8270D	SVOCs	Water	Bis(2-chloro-1-methylethyl) ether	-		70-130	20	51-111
8270D	SVOCs	Water	3&4-Methylphenol	-		52-112	20	68-110
8270D	SVOCs	Water	N-Nitrosodipropylamine	-		70-130	20	48-110
8270D	SVOCs	Water	Hexachloroethane	-		70-130	20	22-110
8270D	SVOCs	Water	Nitrobenzene	-		70-130	20	54-114
8270D	SVOCs	Water	Isophorone	-		70-130	20	53-113
8270D	SVOCs	Water	2-Nitrophenol	-		70-130	20	49-110
8270D	SVOCs	Water	2,4-Dimethylphenol	-		70-130	20	45-110
8270D	SVOCs	Water	Bis(2-chloroethoxy)methane	-		70-130	20	52-112
8270D	SVOCs	Water	2,4-Dichlorophenol	-		60-120	20	65-110
8270D	SVOCs	Water	1,2,4-Trichlorobenzene	-		70-130	20	33-110
8270D	SVOCs	Water	Naphthalene	-		70-130	20	52-110
8270D	SVOCs	Water	4-Chloroaniline	-		70-130	20	43-110
8270D	SVOCs	Water	Hexachlorobutadiene	-		70-130	20	22-110
8270D	SVOCs	Water	4-Chloro-3-methylphenol	-		70-130	20	53-113
8270D	SVOCs	Water	2-Methylnaphthalene	-		70-130	20	49-110
8270D	SVOCs	Water	Hexachlorocyclopentadiene	-		70-130	20	20-110
8270D	SVOCs	Water	2,4,6-Trichlorophenol	-		58-118	20	63-110
8270D	SVOCs	Water	2,4,5-Trichlorophenol	-		64-124	20	67-110
8270D	SVOCs	Water	2-Chloronaphthalene	-		70-130	20	43-110
8270D	SVOCs	Water	2-Nitroaniline	-		70-130	20	56-116
8270D	SVOCs	Water	Dimethyl phthalate	-		70-130	20	61-121
8270D	SVOCs	Water	2,6-Dinitrotoluene	-		70-130	20	58-118
8270D	SVOCs	Water	Acenaphthylene	-		70-130	20	46-110
8270D	SVOCs	Water	3-Nitroaniline	-		70-130	20	47-110
8270D	SVOCs	Water	Acenaphthene	-		70-130	20	84-135
8270D	SVOCs	Water	2,4-Dinitrophenol	-		70-130	20	52-112
8270D	SVOCs	Water	4-Nitrophenol	-		70-130	20	65-125
8270D	SVOCs	Water	Dibenzofuran	-		70-130	20	60-110
8270D	SVOCs	Water	2,4-Dinitrotoluene	-		70-130	20	60-120
8270D	SVOCs	Water	Diethyl phthalate	-		70-130	20	61-121
8270D	SVOCs	Water	Fluorene	-		70-130	20	60-110
8270D	SVOCs	Water	4-Chlorophenyl phenyl ether	-		70-130	20	50-110
8270D	SVOCs	Water	4-Nitroaniline	-		70-130	20	39-110

8270D	SVOCs	Water	4,6-Dinitro-2-methylphenol	-		70-130	20	68-128
8270D	SVOCs	Water	Diphenyl amine	-		70-130	20	29-110
8270D	SVOCs	Water	4-Bromophenyl phenyl ether	-		70-130	20	51-111
8270D	SVOCs	Water	Hexachlorobenzene	-		70-130	20	52-112
8270D	SVOCs	Water	Pentachlorophenol	-		68-128	20	63-112
8270D	SVOCs	Water	Phenanthrene	-		65-125	20	63-110
8270D	SVOCs	Water	Anthracene	-		70-130	20	57-117
8270D	SVOCs	Water	Carbazole	-		70-130	20	20-132
8270D	SVOCs	Water	Di-n-butyl phthalate	-		70-130	20	68-128
8270D	SVOCs	Water	Fluoranthene	-		66-126	20	68-119
8270D	SVOCs	Water	Pyrene	-		65-125	20	65-120
8270D	SVOCs	Water	Butyl benzyl phthalate	-		70-130	20	62-122
8270D	SVOCs	Water	Benzo(a)anthracene	-		60-120	20	67-110
8270D	SVOCs	Water	3,3'-Dichlorobenzidine	-		70-130	20	20-110
8270D	SVOCs	Water	Chrysene	-		60-120	20	67-111
8270D	SVOCs	Water	Bis(2-ethylhexyl) phthalate	-		70-130	20	71-131
8270D	SVOCs	Water	Di-n-octyl phthalate	-		70-130	20	62-122
8270D	SVOCs	Water	Benzo(b)fluoranthene	-		59-119	20	60-110
8270D	SVOCs	Water	Benzo(k)fluoranthene	-		59-119	20	65-117
8270D	SVOCs	Water	Benzo(a)pyrene	-		46-110	20	56-110
8270D	SVOCs	Water	Indeno(1,2,3-cd)pyrene	-		53-113	20	62-110
8270D	SVOCs	Water	Dibenz(a,h)anthracene	-		60-120	20	59-119
8270D	SVOCs	Water	Benzo(g,h,i)perylene	-		55-115	20	64-110
8270D	SVOCs	Water	1,4-Dioxane-d8	46-110		-		-
8270D	SVOCs	Water	2-Fluorophenol	54-110		-		-
8270D	SVOCs	Water	Phenol-d5	54-110		-		-
8270D	SVOCs	Water	2-Chlorophenol-d4	60-110		-		-
8270D	SVOCs	Water	1,2-Dichlorobenzene-d4	38-110		-		-
8270D	SVOCs	Water	Nitrobenzene-d5	26-134		-		-
8270D	SVOCs	Water	2-Fluorobiphenyl	57-110		-		-
8270D	SVOCs	Water	2,4,6-Tribromophenol	46-136		-		-
8270D	SVOCs	Water	Terphenyl-d14	47-130		-		-
8270D	SVOCs	Water	Tentatively Identified Compounds	-		-		-
8015C	TPH - Extractable	Water	TPH - Diesel Range Organics	-		50-126	37	59-109
8015C	TPH - Extractable	Water	TPH - Oil Range Organics	-		-		-
8015C	TPH - Extractable	Water	Hexacosane	47-130		-		-

8015C	TPH - Purgeable	Water	TPH - Gasoline Range Organics	-	5	66-148	5	81-119
8015C	TPH - Purgeable	Water	a,a,a-Trifluorotoluene	87-110		-		-
524.2	VOCs	Water	Dichlorodifluoromethane	-	20	23-150	50	63-136
524.2	VOCs	Water	Chloromethane	-	20	53-150	50	69-129
524.2	VOCs	Water	Vinyl chloride	-	20	58-150	50	70-130
524.2	VOCs	Water	Bromomethane	-	20	43-150	50	53-143
524.2	VOCs	Water	Chloroethane	-	20	69-142	37	83-117
524.2	VOCs	Water	Trichlorofluoromethane	-	20	62-150	49	75-125
524.2	VOCs	Water	1,1-Dichloroethene	-	20	70-143	36	70-130
524.2	VOCs	Water	1,1,2-Trichloro-1,2,2-trifluoroethane	-	20	77-150	40	71-138
524.2	VOCs	Water	Acetone	-	20	38-132	47	56-118
524.2	VOCs	Water	Carbon disulfide	-		-		-
524.2	VOCs	Water	Dichloromethane	-	20	86-111	12	70-130
524.2	VOCs	Water	tert-Butyl alcohol	-		-		-
524.2	VOCs	Water	trans-1,2-Dichloroethene	-	20	75-135	30	70-130
524.2	VOCs	Water	tert-Butyl methyl ether (MTBE)	-	20	75-117	21	67-120
524.2	VOCs	Water	1,1-Dichloroethane	-	20	80-124	22	69-126
524.2	VOCs	Water	Diisopropyl ether	-		-		-
524.2	VOCs	Water	Ethyl tert-butyl ether	-		-		-
524.2	VOCs	Water	2,2-Dichloropropane	-	20	20-150	50	43-144
524.2	VOCs	Water	cis-1,2-Dichloroethene	-	20	71-138	33	70-130
524.2	VOCs	Water	2-Butanone (MEK)	-	20	55-127	36	58-124
524.2	VOCs	Water	Bromochloromethane	-	20	80-129	25	72-126
524.2	VOCs	Water	Chloroform	-	20	72-135	31	70-130
524.2	VOCs	Water	1,1,1-Trichloroethane	-	20	58-133	38	70-130
524.2	VOCs	Water	Carbon tetrachloride	-	20	56-144	44	70-130
524.2	VOCs	Water	1,1-Dichloropropene	-	20	76-121	22	81-110
524.2	VOCs	Water	Benzene	-	20	73-121	24	70-130
524.2	VOCs	Water	1,2-Dichloroethane	-	20	81-110	13	70-130
524.2	VOCs	Water	tert-Amyl methyl ether	-		-		-
524.2	VOCs	Water	Trichloroethene	-	20	84-118	17	70-130
524.2	VOCs	Water	1,2-Dichloropropane	-	20	79-117	19	70-130
524.2	VOCs	Water	Dibromomethane	-	20	82-118	18	77-119
524.2	VOCs	Water	Bromodichloromethane	-	20	84-114	15	70-130
524.2	VOCs	Water	cis-1,3-Dichloropropene	-	20	64-112	24	63-119

524.2	VOCs	Water	4-Methyl-2-pentanone (MIBK)	-		-		-
524.2	VOCs	Water	Toluene	-	20	82-118	18	70-130
524.2	VOCs	Water	trans-1,3-Dichloropropene	-	20	64-110	22	64-119
524.2	VOCs	Water	1,1,2-Trichloroethane	-	20	82-121	20	70-130
524.2	VOCs	Water	Tetrachloroethene	-	20	53-150	50	70-130
524.2	VOCs	Water	1,3-Dichloropropane	-	20	83-118	18	78-121
524.2	VOCs	Water	2-Hexanone	-		-		-
524.2	VOCs	Water	Chlorodibromomethane	-	20	76-126	25	70-130
524.2	VOCs	Water	1,2-Dibromoethane (EDB)	-	20	84-115	15	80-116
524.2	VOCs	Water	Chlorobenzene	-	20	85-114	15	70-130
524.2	VOCs	Water	1,1,1,2-Tetrachloroethane	-	20	82-111	15	77-113
524.2	VOCs	Water	Ethylbenzene	-	20	80-120	20	70-130
524.2	VOCs	Water	m&p-Xylene	-	20	75-124	24	70-130
524.2	VOCs	Water	o-Xylene	-	20	82-114	16	70-130
524.2	VOCs	Water	Styrene	-	20	78-116	19	70-130
524.2	VOCs	Water	Bromoform	-	20	64-131	34	70-130
524.2	VOCs	Water	Isopropylbenzene	-	20	77-125	24	85-112
524.2	VOCs	Water	Bromobenzene	-	20	87-110	11	85-110
524.2	VOCs	Water	1,1,2,2-Tetrachloroethane	-	20	73-132	29	70-129
524.2	VOCs	Water	1,2,3-Trichloropropane	-	20	74-125	25	69-124
524.2	VOCs	Water	Propylbenzene	-	20	76-127	26	86-114
524.2	VOCs	Water	2-Chlorotoluene	-	20	78-117	19	81-113
524.2	VOCs	Water	4-Chlorotoluene	-	20	76-117	21	81-113
524.2	VOCs	Water	1,3,5-Trimethylbenzene	-	20	74-123	25	82-115
524.2	VOCs	Water	tert-Butylbenzene	-	20	70-127	28	85-113
524.2	VOCs	Water	1,2,4-Trimethylbenzene	-	20	76-121	22	79-117
524.2	VOCs	Water	sec-Butylbenzene	-	20	67-139	36	80-124
524.2	VOCs	Water	1,3-Dichlorobenzene	-	20	79-114	18	80-111
524.2	VOCs	Water	p-Isopropyltoluene	-	20	65-136	35	80-121
524.2	VOCs	Water	1,4-Dichlorobenzene	-	20	73-120	24	70-130
524.2	VOCs	Water	1,2-Dichlorobenzene	-	20	81-112	16	70-130
524.2	VOCs	Water	Butylbenzene	-	20	61-141	40	78-124
524.2	VOCs	Water	1,2-Dibromo-3-chloropropane	-	20	56-132	38	64-120
524.2	VOCs	Water	1,2,4-Trichlorobenzene	-	20	68-117	25	70-130
524.2	VOCs	Water	Hexachlorobutadiene	-	20	65-124	29	65-123
524.2	VOCs	Water	Naphthalene	-	20	60-131	35	67-113
524.2	VOCs	Water	1,2,3-Trichlorobenzene	-	20	67-120	27	69-114

524.2	VOCs	Water	1,2-Dichloroethane-d4	77-117		-		-
524.2	VOCs	Water	Toluene-d8	85-110		-		-
524.2	VOCs	Water	4-Bromofluorobenzene	85-110		-		-
524.2	VOCs	Water	1,2-Dichlorobenzene-d4	81-125		-		-
524.2	VOCs	Water	Tentatively Identified Compounds	-		-		-
524.2	VOCs, Low Level, Water	Water	1,2-Dibromoethane (EDB)	-	34	65-133	34	85-128
524.2	VOCs, Low Level, Water	Water	1,2,3-Trichloropropane	-	20	51-147	20	85-123
524.2	VOCs, Low Level, Water	Water	1,2-Dibromo-3-chloropropane	-	30	23-171	30	52-123
524.2	VOCs, Low Level, Water	Water	4-Bromofluorobenzene	80-119		-		-

Attatchment 3- Navy GW Monitoring Workplan

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Attachment 4- EPA Region 9 Lab SOP's

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Attachment 5 – APPL Inc. Lab SOP's

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USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 315
SEMIVOLATILE ORGANIC COMPOUND ANALYSIS

Revision 7
Effective Date: November 15, 2014

Reviewed by: _____ 11/3/14
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This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105037-17464

ED_006532_00005075-00031

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of selected semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS) in extracts prepared from solid or liquid samples by EPA SW-846 extraction and cleanup methods appropriate to the sample matrix. This SOP is based on procedures included in EPA Method SW 846 8270D. Deviations from Method 8270D are described in Appendix A. The scope of this SOP was expanded to include the analysis of 1,4-dioxane. Analytes and quantitation limits (QL) applicable to this analysis are listed in Appendix B.

Sample extracts are prepared using Region 9 SOP 275 *Extraction of Water Samples Using CLLE*, SOP 285 *Soxhlet Extraction of Solid Samples,* SOP 290 *Extraction of Soil Samples Using PFE (Pressurized Fluid Extraction-ASE)*, or SOP 295 *Waste Dilution* for wipe and oil samples.

The applicability of this procedure to specific project data quality objectives must be assessed on a case-by-case basis. The quality control (QC) criteria specified in this procedure do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Sample extracts are injected into a gas chromatograph (GC) with a mass spectrometer (MS) detector. Analytes are separated in a narrow bore fused silica capillary GC column in a temperature-programmed oven and detected by the MS. Each target and surrogate compound is quantitated using the average response factors from the most recent initial calibration.

Target semivolatile organic compounds of interest are identified in the sample extract by comparing the mass spectra to the mass spectra in the National Institute of Standards and Technology (NIST) library and the GC retention times of the target analytes to retention times of standards analyzed under the same conditions as samples.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

CRL – This is a LIMS acronym for contract reporting limit. It is a LIMS QC sample type and is equivalent to the QLS.

4 SAFETY AND HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

4.1.1 Dichloromethane

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals.

Emergency and first aid
Inhalation: immediately remove to fresh air. If not breathing, administer mouth to mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR), contact physician immediately.
Eye contact: rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance.
Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re use, and discard contaminated shoes. Get emergency medical assistance.

Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure.* Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA

Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
SVOC Waste: Glass vials, dichloromethane, 0-2000 ppm semivolatile organic compounds	Hazardous Waste	Toxic

NOTE: N-Nitrosodimethylamine and 3,3'-dichlorobenzidine are listed as known or suspected carcinogens. As such, any sample or sample extract with a combined concentration of these compounds greater than or equal to 1000 mg/kg (wet weight) must be handled as an extremely hazardous waste. Should this concentration be determined, notify the LaSHEM (or designee).

5 SAMPLE HANDLING AND PRESERVATION

5.1 Sample Containers, Required Volume, Preservation, and Holding Time

Refer to EPA Region 9 Laboratory SOP 275, SOP 285, SOP 290, or SOP 295.

5.2 Internal Chain-of-Custody

Sample extracts for GC/MS analysis are received from the extraction lab personnel and custody is transferred to the GC/MS laboratory staff. The GC/MS analyst acknowledges the receipt of the sample extracts by signing the appropriate sections of the completed LIMS bench sheet. Copies of tracking sheets, chain of custody records, and the original LIMS extraction bench sheet should accompany the sample extracts.

The extracts are marked with the EPA Region 9 Laboratory work order number, which can be checked against the tracking sheets and chain of custody record to determine the client sample identification, case number, and sample delivery group (SDG) number. Verify sample IDs and dates and times of collection against the chain-of-custody form.

5.3 Extract Storage

Store sample extracts at $\leq$ -10°C before and after analysis. Retain sample extracts for 60 days after the report is complete (i.e., LIMS status is complete).

5.4 Extract Holding Time

Extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

Method interferences can be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. Phthalates are commonly found as laboratory contaminants. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running a method blank (MB). The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed.

Contamination of the GC system with high boiling material will cause erratic chromatographic behavior for several target analytes: pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, the nitroanilines, and benzyl alcohol.

It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to samples may be affected.

Although not strictly an interference, hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, is photoreactive, and reacts with acetone if this solvent is present in the standard mixture.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

7.1.1 GCMS System

7.1.1.1 Gas Chromatograph (GC): Agilent 6890, 7890, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, splitless injection port, and electronic pressure control (EPC).

7.1.1.2 GC column: 30 m, 0.25 mm ID, 0.50 µm df. A fused silica capillary column with a bonded phase coating of 5% phenyl 95% methyl silicone such as RXI-5SILMS, DB5, DB5MS, RTX 5, HP 5, or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used. The use of a short (5 m) length of a deactivated, uncoated fused silica column (guard column) between the injection port and the analytical column, to trap nonvolatile extract residues, is optional.

7.1.1.3 Mass spectrometer: Agilent 5973, 5975, or equivalent, capable of scanning from 41 to 550 amu or in the SIM mode every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when ≤50 ng of DFTPP is injected through the GC inlet.

7.1.1.4 Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.

7.2 Reagents

Document the receipt of all reagents in the Element database. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

Dichloromethane: High purity pesticide quality or equivalent. Recycled dichloromethane may be used if demonstrated to be suitable for use in this procedure. See Region 9 SOP 239 *Procedures for Recycling used Dichloromethane*.

7.3 Standards

Document the receipt, preparation, and open dates of all standard ampules in the Element database.

All ampulated calibration materials must be maintained in the refrigerator at >0°C to ≤6°C and protected from light. Use the manufacturer's expiration date for ampulated standards.

Open ampules and working standards must be maintained in a freezer at ≤-10 °C and protected from light. The solution is assigned an expiration date which is either 6 months from preparation or open date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Analysts must allow all standard solutions to equilibrate to room temperature before use.

Second Source Calibration Verification Sample (SCV) – Approximately equivalent to the mid-point initial calibration solution but prepared from a source different from the source of the calibration standards. The SCV is used to check the accuracy of the initial calibration solutions. See table below for suggested vendors for SCV standards.

7.3.1 Internal Standard Solution (IS): A solution of acenaphthene-d10, phenanthrene-d10, chrysene-d12, 1,4 dichlorobenzene-d4, perylene-d12, and naphthalene-d8 each at 2000 ug/ml in dichloromethane (Restek 31206 or equivalent). Add 10 µL to 1 mL extract or 5 µL to 0.5 mL extract to attain an extract concentration equivalent to the continuing calibration level.

7.3.2 Calibration Stock Standard: A solution of target analytes and surrogates in dichloromethane at a concentration of 100 ug/mL. The solution is typically prepared from 8270 Mega Mix (Restek 31686), 3,3'-dichlorobenzidine (Restek 31835), N-nitrosodi-n-butylamine (Supelco 48320), 1,4-dioxane (Restek 31853), base/neutral surrogates (Restek 31082), and acid surrogates (Restek 31083). Equivalent solutions may be used in lieu of any of the above mixes.

Add the following solutions to a 10 mL volumetric flask and dilute the solutions to a final volume of 10 mL with dichloromethane.

Stock Standard	Conc. (µg/mL)	Amount (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
8270 Mega Mix	1000	1000	10	100
3,3'-Dichlorobenzidine	2000	500	10	100
1,4-Dioxane	2000	500	10	100
SV B/N Surrogates	5000	200	10	100
SV Acid surrogates	7500	133	10	100

7.3.3 Calibration standards: Target and surrogate compounds are typically prepared at concentrations of 1, 5, 10, 20, 40, 60, 80 and 100 µg/mL by diluting the Calibration Stock Standard solution. Note that the 1 and 5 µg/mL concentrations define the quantitation limit for the method and cannot be excluded from the initial calibration.

7.3.4 Second Source Standard: A solution of target analytes listed in Appendix B and surrogates prepared from a different source (i.e. a separate supplier/manufacturer) from that used to prepare calibration standard. Second Source Standard is typically prepared at a concentration of 20 µg/mL. The solution may be prepared using one or a combination of the following sources, or their equivalent:

Supelco: 1,4-Dioxane- (2000 µg/mL, 48367)

AccuStandard: BASE-NEUTRAL MIX (CLP-HC-BN-SET, 2.0 mg/mL), ACID MIX (CLP-HC-A-R, 2.0 mg/mL), COMP#2 MIX (Z-014E-R, 2.0 mg/mL), Carbazole (M-634-IS, 1.0 mg/mL), 1-Methylnaphthalene (H-001S-D-40X, 2.0 mg/mL), SVOC SURROGATE MIX (CLP-031-R2, 2mg/mL).

7.3.5 GC/MS Tuning Solution (MS tune): A solution of DFTPP, 4,4' DDT, pentachlorophenol, and benzidine at ≤50 ng/µL each in dichloromethane. Restek 31615, 1,000µg/mL each in methylene chloride, or equivalent. The solution is prepared by diluting 250 µL of the mix to 5 mL with dichloromethane.

7.3.6 Instrument Blank: A solution of 1,4-dioxane-d8 at 5 ug/mL and internal standard at 20 ug/mL. The solution is prepared by diluting 25 µL of 1,4-dioxane-d8 and 100 µL of internal standard the mix to 10 mL with dichloromethane.

7.4 Supplies

7.4.1 Syringes: 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, 500 µL, 1 mL.

7.4.2 Helium carrier gas: Ultra-high purity, 99.999%.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound. Refer to Section 8.4 and Appendix F for system maintenance requirements.

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point.

8.1.1 Mass calibration

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions. Use perfluorotributylamine (FC43) to perform mass calibration of the instrument.

Calibrate the Mass Axis of the MS prior to analyzing the DFTPP standard each day that samples are analyzed. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E, and generate a tune report.

Refer to Section 9.2.1 and Appendix C for acceptance criteria and corrective action requirements.

8.1.2 GC/MS System Performance Check (DFTPP analysis)

The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

In the ChemStation data analysis module, load a copy of the most recent ChemStation method from D:\MSDCHEM\Year\Methods\ and associate the newly generated tune file with this method.

Inject 1 µL of the DFTPP solution using the operating parameters provided in Appendix D.

The autofind procedure will automatically find the DFTPP peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Calculate DDT breakdown and generate a tailing factor report for the pentachlorophenol and benzidine peaks.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Save the method as outlined in the "ChemStation File Naming Convention" (see Appendix E) using today's date "mmdd" in the file name under D:\MSDCHEM\Year\Methods\.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (DFTPPand/or manual tune) has been performed. When the instrument is ready for analysis, perform the following steps:

1. In the ChemStation data analysis module, load the current initial calibration method from D:\MSDCHEM\Year\Methods\ and associate the newly generated tune file with this method.
2. Perform an initial calibration using the recommended concentrations listed in Section 7.3.3.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the CCV calibration level.
6. Save the method as outlined in the "ChemStation File Naming Convention"
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
9. Check the time and date to ensure that the correct update is used.
10. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report"
11. Open and immediately close Chemstation Custom Reports. (Note: no Chemstation custom reports are actually used, opening and closing custom reports populates "detail.xls" which is later mined for data.)
12. Open the latest copy of C:\msdchem\custrpt\ "Full_Custom_Report.xls" Make sure automatic updates of links is enabled under options.
13. Go to the "SCV Recovery","ICAL Area", "ICALconc", tabs and print reports. Make sure the SCV passes acceptance criteria (appendix C) and the ICAL areas match what is on the Chemstation quant reports.
14. Verify that the method was updated correctly. Print the Compound List Report from ChemStation. Verify that the average response factor is used. Scrupulously check the elution order and retention times, compare them to an old ICAL if needed.
15. Copy the method to I:\RoomNumber\Instrument\Year\Methods\
16. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
17. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

The analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration

Analyze a calibration verification standard at the beginning of each 12-hour analytical period by performing the following steps:

1. In the ChemStation data analysis module, load today's method from D:\MSDCHEM\Year\Methods.
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. Adjust the electron multiplier (EM) voltage if needed (an increase of 50 volts will typically double the response). If the EM voltage is changed, reanalyze DFTPP and the CCV.
6. Manually calculate the result for one surrogate to insure that the correct RFs are being used. Record the result on the quantitation report.
7. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "QLast Update : Mon Jul 25 08:15:58 2011"), is recorded on each file header.
8. If QLast Update time stamp changes, state the reason, repeat steps 4-7, and include the reports generated in the package.
9. Save a copy of the method to the LAN, when the data are backed up to the LAN the following day.

Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.3 Quantitation Limit Verification Standard (QLS)

Analyze a quantitation limit standard at the concentration of the lowest point of the initial calibration for each 12-hour analytical period. Since there are multiple quantitation limits in the standard BNA list, more than one QLS may have to be analyzed. Typically, 1 and 5 µg/mL QLS standards are run. The 20 µg/mL CCV serves as both a CCV and a QLS for 2,4-dinitrophenol and pentachlorophenol; the most stringent QC criteria will be applied to this combination CCV/QLS. Use the full_custom_report to calculate the QLS recoveries.

Refer to Section 9.2.5 and Appendix C for acceptance criteria and corrective action requirements.

8.3 Analysis

8.3.1 Sample Extract Preparation

Allow the sample extracts and internal standard solutions to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS extraction batch to ensure that the correct sample is being analyzed.

Note: Determine if the sample extract has an unusual color or other physical property. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS "MMO" field.

Add appropriate amount of IS solutions to each field and QC sample extract to attain an extract concentration equivalent to the continuing calibration level.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis using the following steps:

- Obtain a LIMS sequence number by generating an empty LIMS sequence; specify the analysis and instrument, number associated with the samples to be analyzed.

- Enter sample sequence in the instrument software. Include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any, in the "Multiplier" field. Use the LIMS sequence number to name instrument QC as outlined in Appendix D.

- Enter the BNA method name in the "Method" field; analyze all standards and samples with this method. Name the data files according to the data file naming convention outlined in Appendix E.

- Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:
    1. DFTPP
    2. CCV
    3. QLS1 (entered into LIMS as CRL1)
    4. QLS2 (entered into LIMS as CRL2)

5. Samples, sample dilutions, and or QC samples as needed
6. Instrument Blanks, as needed

- Run the sequence

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and ion ratios of the peak must match those of the standard.

The mass spectra used for qualitative identification are from the NIST library. This eliminates the presence of extraneous ions often observed when using spectra generated on the GCMS system using standard mixes that frequently include co-eluting compounds. All ions present in the standard or reference mass spectrum at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectrum. The relative intensities of the ions in the sample mass spectrum must agree within 30% of the relative intensities of those ions in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum. Ions present in the sample mass spectrum at greater than 10 percent abundance but not present in the standard mass spectrum must be reviewed and accounted for by the analyst making the comparison.

If a compound cannot be verified using these criteria but in the technical judgment of the analyst is present, report the analyte and include supporting evidence in the raw data package.

Cross out (with date and initial) all ChemStation results that do not meet qualitative criteria. Review the peak to see if the compound meets reporting the requirement of a TIC. If the compound is to be reported as a TIC, the false positive peak must be deleted (QDEL) in ChemStation.

Review the chromatogram for possible false negatives and edit results as needed.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out ChemStation detailed quantitation reports and chromatograms. Use the average relative response factor from the initial calibration for quantitation.

Analyte concentrations in the sample extracts as shown on the ChemStation quantitation report are calculated as follow:

$$\text{Concentration (ng/mL)} = \frac{Ax \times Cis}{Ais \times \overline{RRF}}$$

Where:

Ax = area of the quantitation ion of the compound
C_{IS} = amount of internal standard in µg/L (20 µg/L)
A_{IS} = area of the quantitation ion of the associated internal standard
$\overline{RRF}$ = analyte average relative response factor from the initial calibration

LIMS calculates the final sample concentration. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

$$\text{Conc. } \mu g / L = \frac{A_x \times C_{is} \times V_t \times V_i \times DF}{A_{is} \times \overline{RRF} \times V_o}$$

Where:

Ax = area of the quantitation ion of the compound
C_{IS} = amount of internal standard in µg/L (20 µg/L)
Vt = volume of concentrated extract in µL
Vi = volume of extract injected in µL
DF = dilution factor
A_{IS} = area of the quantitation ion of the associated internal standard
$\overline{RRF}$ = analyte average relative response factor from the initial calibration
Vo = volume of water extracted in mL

For soil samples, calculate results for target analytes using the following equation:

$$\text{Conc. ug / Kg (dry weight basis)} = \frac{A_x \times C_{is} \times V_t \times V_i \times DF \times GPC}{A_{is} \times \overline{RRF} \times W \times D}$$

Where:

Ax = area of the quantitation ion of the compound
C_{IS} = concentration of Internal Standard in µg/mL (normally 20 µg/L)
Vt = volume of concentrated extract in µL
Vi = volume of extract injected in µL
DF = dilution factor
GPC = GPC factor, normally 1.0 if not used, 2.0 if used

A_{IS} = area of the quantitation ion of the associated internal standard

$\overline{RRF}$ = analyte mean relative response factor from the initial calibration

W = weight of sample in grams

D = dry weight factor (Percent solids/100)

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently or incorrectly, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 Review of Tentatively Identified Compound (TIC)

The analyst must review the library search results for the following:

8.3.4.1 Load the data file of the most concentrated valid analysis of the sample.

8.3.4.2 Examine the spectra for each peak that is not a target, surrogate or internal standard. Report those for which the response is greater than 20% of the closest internal standard and where a tentative identification can be made. If none are identified, so state.

8.3.4.3 Report a maximum of 10 compounds based on total area (largest).

8.3.4.4 Since 1,4-dioxane-d8 is present at a low concentration, it will not be used in TICs calculations or generation. 1,4-dichlorobenzene-d4 will be used for the early eluting TICs.

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

8.3.4.6 The relative intensities of the major ions should agree within 20 percent.

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

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

8.3.4.9 Ions present in the reference spectrum but not within the scan range of the method should not be considered when making a tentative identification.

8.3.4.10 If, in the technical judgment of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown" The analyst shall attempt classification of the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.). The probable molecular weight should be included, if distinguishable.

8.3.4.11 Report the following:

a. Class of compound instead of specific isomers unless the identity of the specific isomer is known. As an example, report dichlorobenzene instead of 1,2-dichlorobenzene. Alternatively, report 1-methylnaphthlene if the calibration standard has 2-methylnaphtalene and the TIC retention time is not that of 2-methylnaphtalene.
b. "Total" of all hydrocarbons as total hydrocarbon m/z 55 and/or total hydrocarbon m/z 57. Calculate the concentration based on ion 55 or 57 as a ratio of the quantitation ion of the closest IS. The IS closest to the center of the "hump" will be selected.

8.3.4.12 Exclude the following compounds from the report:

a. Analytes eluting prior to the first eluting target compound.
b. TICs that were detected in the method blank.
c. Column bleed (i.e. siloxanes).
d. Common laboratory contaminants or aldol condensation products (e.g. hydroxy methyl pentanone).
e. Reagent Preservatives (e.g. amylene hydrate).
f. CO_2/fixed gases peaks.
g. Electronic noise peaks.

8.3.4.13 The concentrations of TICs are estimated. Use the TIC area in Equations in section 8.3.3.2 and assume the RRF is 1. Use the nearest internal standard free of interferences.

If the base peak saturates the detector, document this in the data. Do not dilute a sample extract to get the base peak of a TIC within the detector range. If a sample extract containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC base peak area from the diluted extract to estimate the concentration of the TIC.

8.3.5 Data and QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample

and QC data for compliance with QC limits in Appendix C. If no significant problems are found, perform the following QC reviews for compliance with SOP requirements:

- Check that target analyte results are within range of the initial calibration.
- Process and review the results for the CCV, QLS, and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV, QLS, and instrument QC results are within QC limits. See Section 9.2 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Review the peak to see if the compound meets reporting the requirement of a TIC. If the compound is to be reported as a TIC, the false positive peak must be deleted (QDEL) in ChemStation.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report. All notations must be initialed and dated by the analyst.

8.3.6 Sample Dilution

- The instrument blank solution may be used to make the necessary extract dilutions. As an example if 1:10 dilution is desired, add 900 µL of the instrument blank solution to 100 µL of the sample extract.
- For 1,4-dioxne, the minimum recommended dilution is 1:20 to minimize the effect of 1,4-dioxane-d8 added as a surrogate during the extraction process. Since 1,4-dioxane-d8 is used strictly as an internal standard in this case, do not report 1,4-dioxane-d8 as a surrogate from a diluted run.

8.3.7 Data Export and LIMS Entry

Generate epatemp.txt files for field and QC samples by also printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.

- Edit dilutions in DataTool or LIMS entry table as needed.
- Review results in the LIMS. The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL and values over the calibration range as estimated (J). The analyst must manually add a qualifier flag (C1 or C2) indicating that the reported concentration is estimated because it is less than the quantitation limit or exceeds the calibration range. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems for GC and MS operations. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 GC Maintenance

Symptoms of common problems:

- Carryover
  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.2 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- DFTPP ion 275 ratio is outside acceptance range
- Failing tune checks

Resolution: Clean the source.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability (DOC)

A Demonstration of Capability must be in place prior to using an analytical procedure

and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

Acceptance criteria for QC parameters are listed in Appendix C of this document.

The %RSD and SCV recovery requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. Before continuing with analysis, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.1 Mass calibration

Review the FC43 spectrum for compliance with the criteria list in Appendix C.

If the FC43 spectrum does not meet the criteria, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate FC43 spectra, further maintenance such as cleaning the ion source may be required.

9.2.2 GC/MS System Performance Check (DFTPP analysis)

Review the DFTPP spectrum for compliance with criteria in Appendix C.

Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE. Calculate the breakdown of DDT using peak areas of each quantitation ion (Qion) in the following equation:

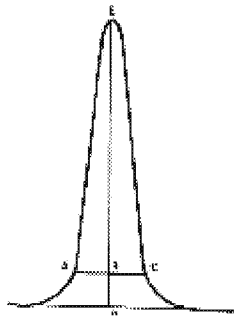
$$\%\ 4,4'\text{-DDT Breakdown} = \frac{\text{Total Qion Area (DDE + DDD)}}{\text{Total Qion Area (DDE + DDD + DDT)}} \times 100$$

Where:

Qions of DDE: 246 Dalton, DDD: 235 Dalton, DDT: 235 Dalton

Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2 given by the following equation:

$$TailingFactor = \frac{BC}{AB}$$



Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and DB is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height.

If the ion abundances, degradation, or tailing fail to meet the criteria, the DFTPP chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.). If the problem is related to poor chromatography, take the necessary corrective action and re-analyze the DFTPP. If the DFTPP continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

9.2.3 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned pairs are benz(a)anthracene/chrysene, phenanthrene/anthracene, and benzo(b)/benzo(k)fluoranthene. Make sure each level of the initial calibration correctly identifies each peak, particularly benzo(b)fluoranthene and benzo(k)fluoranthene.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor ($\overline{RRF}$) for each target compound and surrogate compound using the following equation:

$$\overline{RRF} = (Ax)(Cis) / (Ais)(Cx)$$

Where

Ax	=	Area of quantitation ion of compound x. The quantitation ions and internal standard assignments are listed in Appendix C.
Ais	=	Area of quantitation ion for associated internal standard
Cx	=	Concentration of compound x
Cis	=	Concentration of the associated internal standard

The data system calculates the average RRF (RRFavg) for all analytes and flags the analyte in the calibration summary when the average RRF is less than the minimum response factor criteria.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/ RRF_{avg})*100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{ave})^2}{n-1}}$$

%RSD, minimum response factors, R^2 (coefficient of determination), and SCV recovery requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria in Appendix C are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. If failure persists, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.4 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard changes by more than 50% from the internal standard areas of the continuing calibration level of the most recent initial calibration, the CCV may be re-analyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine the retention times of internal standards in the calibration verification standard. If the retention time for any internal standard changes by more than 0.5 minutes compared to the continuing calibration level of the most recent initial calibration sequence, inspect the chromatographic system for malfunctions and take corrective action as needed and prepare a new calibration curve.

The data system calculates the percent deviation (%D) of the RRF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\ 100$$

Where:

RRF_c = Relative Response Factor of compound from CCV.
RRF_{avg} = Average Relative Response Factor.

If the continuing calibration does not meet the %D criterion in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.2.5 Quantitation Limit Standard (QLS)

A QLS must be analyzed at the beginning of the analytical run, typically just after the CCV. The QLS concentrations match the QL concentrations (at the instrument). The recovery of an analyte in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.
M = measured concentration of the analyte, ug/L.
T = true concentration of the analyte in the ug/L.

Generate a continuing calibration response report using the concentration option. Check that the recoveries meet the criteria specified in Appendix C.

If the QLS recovery does not meet criteria in Appendix C, reanalyze the QLS once to verify. If the reanalysis is unacceptable determine the cause and take corrective action as needed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Laboratory Quality Assurance Manual.

9.3 Batch QC

9.3.1 Method Blank

Extract and analyze a method blank (MB) with each extraction batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system, from extraction through GC/MS analysis, is free of contamination.

If the surrogate recovery exceeds acceptance criteria (high bias) and is ND, narrate the error and continue. If the surrogate recovery fails acceptance criteria low, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, evaluate sample surrogate recoveries to determine acceptability. If samples have acceptable recovery and are ND, report. Otherwise, re-extract any sample that is ND and fails surrogate low or any sample that has a hit. Note that if any samples in the batch are reported, the MB must also be reported and a note placed in the LIMS work order memo field.

Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

Corrective action - If the MB result exceeds QC limits, check the associated samples as follow:

1. If the sample result is less than five times the MB result, re-analyze the MB. If the MB result still exceeds QC limits, the batch may have to be re-extracted. Consult with the Technical Director or designee.
2. If the sample result is greater than five times the MB result or is not detected, report the sample result.

9.3.2 Laboratory Control Sample

Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is extracted and analyzed once per extraction batch. The LCS is an MB spiked with matrix spiking solution.

Calculate the percent recovery (%R) using the following equation:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the LCS.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in the ug/L.

The %R must meet criteria in Appendix C. If acceptable recoveries cannot be achieved, re-analyze the LCS. If the LCS result still exceeds QC limits, re-extract the LCS and all associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed with each SDG of twenty or fewer samples.

Calculate the percent recovery (%R) using the following equation:

$$\% R = [(SSR - SR)/SA] \times 100$$

Where

SSR = Spiked sample result
SR = Unspiked sample result
SA = Spike added

Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

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

Where

MSC	=	Measured concentration of analyte in MS
MSDC	=	Measured concentration of analyte in MSD

See Appendix C for QC limits.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, no further action is required, as long as the LCS is within limits, since the purpose of

these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated.

The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS – = FAIL

CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Extraction batch acceptable.
Case 2: Extraction batch acceptable; matrix effect confirmed.
Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.
Cases 5, 6, 7, & 8: Extraction batch rejected. If additional sample volume is available, the batch should be re-extracted.

9.4 Sample QC

9.4.1 Surrogate Recovery

Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.
2. Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for reanalysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the LIMS work order memo field.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need reanalysis.

If the surrogate recoveries of the reanalysis are within limits, then the problem was within the laboratory's control. Report the results from the reanalysis and submit the data from both analyses. The problem must be documented in the LIMS work order memo field.

If the reanalysis does not solve the problem and additional sample volume is available, re-extract the failing samples unless the sample is ND with a failing high recovery

If sample re-extraction is unfeasible, or surrogate recoveries of the re-extraction are also outside the QC limits, report the results from the first analysis. If re-extraction was performed, submit the data from both analyses and distinguish between the original analysis and the reanalysis by adding the "RE" suffix to the sample ID in the reanalysis. Document the problem in the LIMS work order memo field.

9.4.2 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

1,4-Dioxane-d8 is spiked in the sample during the extraction process as a surrogate. Although the compound serves as an internal standard in calculating 1,4-dioxane concentration, it is exempt from meeting the recovery limits for internal standards since it undergoes the entire extraction process.

Take the following steps if the internal standard areas are not within the limits:

1. Check system performance.
2. Reanalyze the sample if a system performance problem is not evident. The sample may be diluted for reanalysis if examination of the chromatogram so indicates.
3. If a system performance is identified, take corrective action and reanalyze the sample.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

If the sample associated with the MS/MSD analyses does not meet internal standard area criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside limits), then the sample does not need reanalysis.

If the internal standard areas for the reanalysis are within limits, the problem was within the laboratory's control. Report the results from the reanalysis and submit the data from both analyses. Distinguish between the analysis and reanalysis by adding an "RE" suffix to the sample ID on the reanalysis. The problem must be documented in the LIMS work order memo field.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance in the EPA Region 9 Laboratory by matrix.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Addition of internal standard: The amount and concentration of internal standard added is critical. The nominal concentration is used in calculating target analyte concentration.
2. Samples must be stored as outlined in the SOP to minimize analyte degradation and solvent evaporation.
3. Sample temperature: Sample extracts must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
4. Poor column condition may results in inadequate analyte separation and inaccurate integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the Element database. A copy of each Analytical Standard Record associated with sample analysis must be available for printing in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventative or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.6 SOP Read and Understood

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent 6890 Gas Chromatograph Users Manual

Agilent 7890 Gas Chromatograph Users Manual

Agilent 5973 MSD Hardware Manual

Agilent 5975 MSD Hardware Manual

Agilent Environmental Analysis User's Guide

Agilent EnviroQuant ChemStation User's Guide

USEPA Method 525.3, Determination of Semivolatile Organic Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography / Mass Spectrometry, Revision 1.0, February 2012.

USEPA Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

USEPA Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2006.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. SW-846 Method 3500B referenced by Method 8270D specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 100 mg/L.

2. Mass spectra used for target analytes are from the NIST library. The SOP requires that all compounds be included in the calibration standards and thus comparison to spectra generated on the GCMS system where samples are analyzed is possible. However, in order to avoid extraneous peaks due to co-eluting compounds in the standard mixes, it is laboratory practice to use NIST spectra for identification purposes.

3. QC acceptance criteria for LCS, MS/MSD, and surrogates are derived from EPA Region 9 Laboratory performance data as specified in the reference method when possible. Where insufficient data are currently available to calculate QC limits for solid MS/MSD; recovery limits will default to the solid LCS limits and 20 %RSD will be used until sufficient data for solid MS/MSDs are available.

4. Relative Retention Time (RRT) of chromatographic peak is not evaluated in this SOP as documented in the reference method. ChemStation calculates a retention time window and does not calculate RRT window. The retention time window of ± 0.2 min is more stringent than the ± 0.06 RRT units in the reference method.

5. Phenol-d5 is used as a surrogate instead of phenol-d6 as recommended in the reference method.

6. 1,4-Dioxane and carbazole are included as target analytes and 2-chlorophenol-d4, 1,2-dichlorobenzene-d4, and1,4-dioxane-d8 are added surrogates. 1,4-Dioxane and carbazole are not included in the reference method scope.

7. This procedure uses a scan range of 41-550 AMU. The reference method specifies a scan range of 35-500 AMU.

8. Chemstation software monitors the average response factor, not the response factor for each calibration level as required by the method. The EPA Region 9 Laboratory analyzes a QL standard daily to verify adequate response.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following list provides quantitation limits for the semivolatile organic compound target list with associated surrogate compounds.

Compound	CAS Number	Water QL, ug/L	Soil QL, ug/kg	On Column, ng
1,4-Dioxane	123-91-1	1.0	33	1.0
Phenol	108-95-2	5.0	170	5.0
Bis (2-chloroethyl) ether	111-44-4	1.0	33	1.0
2-Chlorophenol*	95-57-8	5.0	170	5.0
1,3-Dichlorobenzene	541-73-1	1.0	33	1.0
1,4-Dichlorobenzene	106-46-7	1.0	33	1.0
Benzyl alcohol	100-51-6	5.0	170	5.0
1,2-Dichlorobenzene	95-50-1	1.0	33	1.0
2-Methylphenol	95-48-7	5.0	170	5.0
Bis(2-chloro-1-methylethyl) ether	108-60-1	1.0	33	1.0
3&4-Methylphenol*	106-44-5	5.0	170	5.0
N-Nitrosodipropylamine	621-64-7	1.0	33	1.0
Hexachloroethane	67-72-1	1.0	33	1.0
Nitrobenzene	98-95-3	1.0	33	1.0
Isophorone	78-59-1	1.0	33	1.0
2-Nitrophenol	88-75-5	5.0	170	5.0
2,4-Dimethylphenol	105-67-9	5.0	170	5.0
Bis(2-chloroethoxy)methane	111-91-1	1.0	33	1.0
2,4-Dichlorophenol*	120-83-2	5.0	170	5.0
1,2,4-Trichlorobenzene	120-82-1	1.0	33	1.0
Naphthalene*	91-20-3	1.0	33	1.0
4-Chloroaniline	106-47-8	5.0	170	5.0
Hexachlorobutadiene	87-68-3	1.0	33	1.0
4-Chloro-3-methylphenol	59-50-7	5.0	170	5.0
2-Methylnaphthalene*	91-57-6	1.0	33	1.0
Hexachlorocyclopentadiene	77-47-4	5.0	170	1.0

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Compound	CAS Number	Water QL, ug/L	Soil QL, ug/kg	On Column, ng
2,4,6-Trichlorophenol*	88-06-2	5.0	170	5.0
2,4,5-Trichlorophenol*	95-95-4	5.0	170	5.0
2-Chloronaphthalene	91-58-7	1.0	33	1.0
2-Nitroaniline	88-74-4	5.0	170	5.0
Dimethyl phthalate	131-11-3	1.0	33	1.0
Acenaphthylene*	208-96-8	1.0	33	1.0
2,6-Dinitrotoluene	606-20-2	1.0	33	1.0
3-Nitroaniline	99-09-2	5.0	170	5.0
Acenaphthene*	83-32-9	1.0	33	1.0
2,4-Dinitrophenol	51-28-5	20	670	20
4-Nitrophenol	100-02-7	5.0	170	5.0
Dibenzofuran	132-64-9	1.0	33	1.0
2,4-Dinitrotoluene	121-14-2	1.0	33	1.0
Diethyl phthalate	84-66-2	1.0	33	1.0
Fluorene*	86-73-7	1.0	33	1.0
4-Chlorophenyl phenyl ether	7005-72-3	1.0	33	1.0
4-Nitroaniline	100-01-6	5.0	170	5.0
4,6-Dinitro-2-methyphenol	534-52-1	5.0	170	5.0
Diphenylamine	122-39-4	1.0	33	1.0
4-Bromophenyl phenyl ether	101-55-3	1.0	33	1.0
Hexachlorobenzene	118-74-1	1.0	33	1.0
Pentachlorophenol*	87-86-5	20	670	20
Phenanthrene	85-01-8	1.0	33	1.0
Anthracene	120-12-7	1.0	33	1.0
Carbazole	86-74-8	1.0	33	1.0
Di-n-butyl phthalate	84-74-2	1.0	33	1.0
Fluoranthene*	206-44-0	1.0	33	1.0
Pyrene*	129-00-0	1.0	33	1.0
Butyl benzyl phthalate	85-68-7	1.0	33	1.0
Benz(a)anthracene*	56-55-3	1.0	33	1.0
3,3'-Dichlorobenzidine	91-94-1	1.0	33	1.0

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Compound	CAS Number	Water QL, ug/L	Soil QL, ug/kg	On Column, ng
Chrysene*	218-01-9	1.0	33	1.0
Bis(2-ethylhexyl)phthalate	117-81-7	1.0	33	1.0
Di-n-octyl phthalate	117-84-0	1.0	33	1.0
Benzo(b)fluoranthene*	205-99-2	1.0	33	1.0
Benzo(k)fluoranthene*	207-08-9	1.0	33	1.0
Benzo(a)pyrene*	50-32-8	1.0	33	1.0
Indeno(1,2,3-cd)pyrene*	193-39-5	1.0	33	1.0
Dibenzo(a,h)anthracene*	53-70-3	1.0	33	1.0
Benzo(g,h,i)perylene*	191-24-2	1.0	33	1.0
Surrogates				
Phenol-d5	4165-62-2			
2-Fluorophenol	367-12-4			
2,4,6-Tribromophenol	118-79-6			
Nitrobenzene-d5	4165-60-0			
2-Fluorobiphenyl	321-60-8			
Terphenyl-d14	1718-51-0			
2-Chlorophenol-d4	NA			
1, 2-Dichlorobenzene-d4	2199-69-1			
1,4-Dioxane-d8	17647-74-4			

* A lower quanitation limit for these compounds may be achieved through the use of a separate SIM analysis. See SOP 375 for applicability.

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APPENDIX C.
QUALITY CONTROL PARAMETERS AND CRITERIA

ANALYSIS	SUMMARY	Frequency
MS Calibration	<table><tr><th>Mass</th><th>Target % of Mass 69</th></tr><tr><td>50</td><td>0.3-5</td></tr><tr><td>69</td><td>100</td></tr><tr><td>131</td><td>20-120</td></tr><tr><td>219</td><td>20-120</td></tr><tr><td>414</td><td>0.3-10</td></tr><tr><td>502</td><td>0.3-10</td></tr></table>	With Every ICAL
MS Mass Axis	Calibrate the Mass Axis of the MS prior to analyzing the DFTPP standard. Adjust the EM voltage as necessary.	Each day that samples are analyzed
GC/MS System Performance Check (DFTPP analysis)	The ion abundance ratios must meet the following criteria. <table><tr><th>Mass (m/z)</th><th>Relative Ion Abundance Criteria</th></tr><tr><td>51</td><td>10-80% of Base Peak</td></tr><tr><td>68</td><td>< 2% of mass 69</td></tr><tr><td>70</td><td>< 2% of mass 69</td></tr><tr><td>127</td><td>10-80% of Base Peak</td></tr><tr><td>197</td><td>< 2% of mass 198</td></tr><tr><td>198</td><td>Base peak, or > 50% of Mass 442</td></tr><tr><td>199</td><td>5-9% of mass 198</td></tr><tr><td>275</td><td>10-60% of Base Peak</td></tr><tr><td>365</td><td>> 1% of mass 198</td></tr><tr><td>441</td><td>present but < 24% of mass 442</td></tr><tr><td>442</td><td>Base Peak, or > 50% of mass 198</td></tr><tr><td>443</td><td>15-24% of mass 442</td></tr></table> Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and the peak-tailing factor must be less than 2. Breakdown of DDT is less than 20%.	Once every 12-hours
Initial Calibration	90% of reported analytes should meet the maximum %RSD of 20. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met: The %RSD of the reported analytes that exceed the limit is ≤30. The average RRF must meet the minimum response factor criteria listed in the table below.	As Needed

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ANALYSIS	SUMMARY	Frequency
Second Source Calibration Verification	Recovery for 90% of reported analytes must be within 70-130%. Data must be flagged as failing initial calibration criteria for analytes not within the acceptance limits.	With Every ICAL
Continuing Instrument Calibration Verification	The absolute value of the %D of all reported analytes should be ≤ 20%. If one or more reported analytes exceed the %D limit, the calibration verification may still be acceptable if the following conditions are met: 90% of reported analytes meet the criteria The absolute value of the %D of the reported analytes that exceed the limit is ≤ 30%. The CCV standard must meet the minimum response factor criteria listed in the table below. Internal standard retention time should be within 30 seconds from that in the mid-point standard level of the most recent initial calibration. EICP area for any of the internal standards should be within (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence.	Once every 12-hours
Quantitation Limit Verification	The percent recovery for 90% of the reported analytes should be between 60 to 140 percent of the actual concentration.	Once every 12-hours
Method Blank (MB)	The MB is acceptable if it contains less than one-half the quantitation limit (QL) of all target compounds.	One per extraction batch
Target Analytes	All ions present in the standard or reference mass spectrum at a relative intensity of 20 % of the most abundant ion should be present in the sample spectrum. The relative intensities of the ions in the sample mass spectrum should agree within 30% of the relative intensities of those ions in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum.	NA

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ANALYSIS	SUMMARY	Frequency
Internal Standards (covering reported analytes)	Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. The retention time for any internal standard should be within 0.5 minute and the total area of internal standard should be recovered within -50% to +100% from the mid-point standard of the most recent initial calibration. Compare the IS retention times and areas in the field and QC samples analyzed within the 12-hour analytical period to the associated 12-hour CCV standard. The retention time for any internal standard should be within 0.5 minute and the total area of internal standard should be recovered within -50% to +100% from the associated 12-hour CCV standard. 1,4-Dioxane-d8 is exempt from meeting internal standard criteria.	NA
LCS	90% of reported analytes should meet the acceptance criteria or the batch may require re-extraction. Refer to the tables below for control limits.	One per extraction batch or every 20 samples, whichever is more frequent.
MS/MSD	Refer to the tables below for control limits. Flag outliers.	One per extraction batch or every 20 samples, whichever is more frequent.

Quantitation Ions, Surrogates, Internal Standards, and Minimum Response Factors

Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
1,2,4-Trichlorobenzene	180	182, 145	2	4	0.01
1,2-Dichlorobenzene	146	148, 111	1	8	0.01
1,3-Dichlorobenzene	146	148, 111	1	8	0.01
1,4-Dichlorobenzene	146	148, 111	1	1	0.01
1,4-Dioxane	88	58	7	9	0.01
2,4,5-Trichlorophenol	196	198, 200	3	7	0.2
2,4,6-Trichlorophenol	196	198, 200	3	7	0.2
2,4-Dichlorophenol	162	164, 98	2	7	0.2
2,4-Dimethylphenol	122	107, 121	2	1	0.2

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Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
2,4-Dinitrophenol	184	63, 107	3	3	0.01
2,4-Dinitrotoluene	165	63, 89	3	5	0.2
2,6-Dinitrotoluene	165	63, 89	3	5	0.2
2-Chloronaphthalene	162	127, 164	3	5	0.8
2-Chlorophenol	128	64, 130	1	7	0.8
2-Methylnaphthalene	142	141	2	5	0.4
2-Methylphenol	107	108,	1	1	0.7
2-Nitroaniline	65	92, 138	3	5	0.01
2-Nitrophenol	139	109, 65	2	7	0.1
3&4-Methylphenol	107	108,	1	7	0.6
3,3'-Dichlorobenzidine	252	254, 126	5	6	0.01
3-Nitroaniline	138	108, 92	3	5	0.01
4,6-Dinitro-2-methyphenol	198	105	4	3	0.01
4-Bromophenyl phenyl ether	248	250, 141	4	6	0.1
4-Chloro-3-methylphenol	107	144, 142	2	7	0.2
4-Chloroaniline	127	129,	2	4	0.01
4-Chlorophenyl phenyl ether	204	206, 141	3	5	0.4
4-Nitroaniline	138	108, 92,	3	6	0.01
4-Nitrophenol	109	139, 65	3	3	0.01
Acenaphthene	154	153, 152	3	5	0.9
Acenaphthylene	152	151, 153	3	5	0.9
Anthracene	178	176, 179	4	6	0.7
Benz(a)anthracene	228	229, 226	5	6	0.8
Benzo(a)pyrene	252	253, 125	6	6	0.7
Benzo(b)fluoranthene	252	253, 125	6	6	0.7
Benzo(g,h,i)perylene	276	138, 277	6	6	0.5
Benzo(k)fluoranthene	252	253, 125	6	6	0.7
Benzyl alcohol	108	79, 77	1	8	0.01
Bis (2-chloroethyl) ether	93	63, 95	1	8	0.7
Bis(2-chloro-1-methylethyl) ether	45	77, 121	1	4	0.01
Bis(2-chloroethoxy)methane	93	95, 123	2	4	0.3

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Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
Bis(2-ethylhexyl)phthalate	149	167, 279	5	6	0.01
Butyl benzyl phthalate	149	91, 206	5	6	0.01
Carbazole	167	166, 139	4	6	0.01
Chrysene	228	226, 229	5	6	0.7
Dibenz(a,h)anthracene	278	139, 279	6	6	0.4
Dibenzofuran	168	139	3	5	0.8
Diethyl phthalate	149	177, 150	3	5	0.01
Dimethyl phthalate	163	194, 164	3	5	0.01
Di-n-butyl phthalate	149	150, 104	4	6	0.01
Di-n-octyl phthalate	149	167, 279	6	6	0.01
Diphenylamine	169	168, 167	4	6	0.01
Fluoranthene	202	101, 203	4	6	0.6
Fluorene	166	165, 167	3	5	0.9
Hexachlorobenzene	284	142, 249	4	6	0.1
Hexachlorobutadiene	225	223, 227	2	5	0.01
Hexachlorocyclopentadiene	237	235, 272	3	5	0.05
Hexachloroethane	117	201, 199	1	8	0.3
Indeno(1,2,3-cd)pyrene	276	138, 227	6	6	0.5
Isophorone	82	95, 138	2	4	0.4
Naphthalene	128	129, 127	2	5	0.7
Nitrobenzene	77	123, 65	2	4	0.2
N-Nitrosodipropylamine	70	42, 101, 130	1	4	0.5
Pentachlorophenol	266	264, 268	4	3	0.05
Phenanthrene	178	179, 176	4	6	0.7
Phenol	94	65, 66	1	1	0.8
Pyrene	202	200, 203	5	6	0.6
Surrogates					
1, 2-Dichlorobenzene-d4	152	115, 150	1	8	
1,4-Dioxane-d8	64	96	1	9	
2,4,6-Tribromophenol	330	332, 141	3	3	
2-Chlorophenol-d4	132	68, 134	1	7	

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Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
2-Fluorobiphenyl	172	171	3	5	
2-Fluorophenol	112	64	1	2	
Nitrobenzene-d5	82	128, 54	2	4	
Phenol-d5	99	42, 71	1	1	
Terphenyl-d14	244	122, 212	5	6	
Internal Standards					
1,4-Dichlorobenzene-d4	152	115	1		
1,4-Dioxane-d8	64	96	7		
Acenaphthene-d10	164	162, 160	3		
Chrysene-d12	240	120, 236	5		
Naphthalene-d8	136	68	2		
Perylene-d12	264	260, 265	6		
Phenanthrene-d10	188	94, 80	4		

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Water LCS and MS/MSD QC Criteria:

Water LCS and MS/MSD criteria are based on results obtained from January 4, 2012 to December 4, 2013. Minimum recovery criteria of 20% will be used for LCS and MS/MSD.

	LCS		Matrix Spike		
Analyte	**Lower**	**Upper**	**Lower**	**Upper**	**RPD**
1,4-Dioxane	66	126	70	130	20
Phenol	48	110	70	130	20
Bis(2-chloroethyl)ether	53	113	70	130	20
2-Chlorophenol	64	110	50	110	20
1,3-Dichlorobenzene	28	110	70	130	20
1,4-Dichlorobenzene	29	110	70	130	20
Benzyl alcohol	49	110	70	130	20
1,2-Dichlorobenzene	32	110	70	130	20
2-Methylphenol	47	110	70	130	20
Bis(2-chloro-1-methylethyl) ether	51	111	70	130	20
3&4-Methylphenol	68	110	52	112	20
N-Nitrosodipropylamine	48	110	70	130	20
Hexachloroethane	22	110	70	130	20
Nitrobenzene	54	114	70	130	20
Isophorone	53	113	70	130	20
2-Nitrophenol	49	110	70	130	20
2,4-Dimethylphenol	45	110	70	130	20
Bis(2-chloroethoxy)methane	52	112	70	130	20
2,4-Dichlorophenol	65	110	60	120	20
3&4-Chlorophenol	51	111	37	110	20
1,2,4-Trichlorobenzene	33	110	70	130	20
Naphthalene	52	110	70	130	20
4-Chloroaniline	43	110	70	130	20
Hexachlorobutadiene	22	110	70	130	20
4-Chloro-3-methylphenol	53	113	70	130	20
2-Methylnaphthalene	49	110	70	130	20
Hexachlorocyclopentadiene	20	110	70	130	20
2,4,6-Trichlorophenol	63	110	58	118	20
2,4,5-Trichlorophenol	67	110	64	124	20
3,5-Dichlorophenol	54	114	61	121	20
2-Chloronaphthalene	43	110	70	130	20
3,4-Dichlorophenol	59	119	65	125	20
2-Nitroaniline	56	116	70	130	20
Dimethyl phthalate	61	121	70	130	20
2,6-Dinitrotoluene	58	118	70	130	20
Acenaphthylene	46	110	70	130	20
3-Nitroaniline	47	110	70	130	20
Acenaphthene	84	135	70	130	20
2,4-Dinitrophenol	52	112	70	130	20
4-Nitrophenol	65	125	70	130	20

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	LCS		Matrix Spike		
Analyte	**Lower**	**Upper**	**Lower**	**Upper**	**RPD**
Dibenzofuran	60	110	70	130	20
2,4-Dinitrotoluene	60	120	70	130	20
2,3,4,6-Tetrachlorophenol	57	117	63	123	20
Diethyl phthalate	61	121	70	130	20
Fluorene	60	110	70	130	20
4-Chlorophenyl phenyl ether	50	110	70	130	20
4-Nitroaniline	39	110	70	130	20
3,4,5-Trichlorophenol	62	122	70	130	20
4,6-Dinitro-2-methylphenol	68	128	70	130	20
Diphenyl amine	29	110	70	130	20
4-Bromophenyl phenyl ether	51	111	70	130	20
Hexachlorobenzene	52	112	70	130	20
Pentachlorophenol	63	112	68	128	20
Phenanthrene	63	110	65	125	20
Anthracene	57	117	70	130	20
Carbazole	20	132	70	130	20
Di-n-butyl phthalate	68	128	70	130	20
Fluoranthene	68	119	66	126	20
Pyrene	65	120	65	125	20
Butyl benzyl phthalate	62	122	70	130	20
Benzo(a)anthracene	67	110	60	120	20
3,3'-Dichlorobenzidine	20	110	70	130	20
Chrysene	67	111	60	120	20
Bis(2-ethylhexyl) phthalate	71	131	70	130	20
Di-n-octyl phthalate	62	122	70	130	20
Benzo(b)fluoranthene	60	110	59	119	20
Benzo(k)fluoranthene	65	117	59	119	20
Benzo(a)pyrene	56	110	46	110	20
Indeno(1,2,3-cd)pyrene	62	110	53	113	20
Dibenz(a,h)anthracene	59	119	60	120	20
Benzo(g,h,i)perylene	64	110	55	115	20

Water Surrogate Recovery

Water surrogate criteria are based on sample results obtained from January 4, 2012 to December 4, 2013.

Water Surrogate	**Lower Percent**	**Upper Percent**
1,2-Dichlorobenzene-d4	38	110
1,4-Dioxane-d8	46	110
2,4,6-Tribromophenol	46	136
2-Chlorophenol-d4	60	110
2-Fluorobiphenyl	57	110
2-Fluorophenol	54	110
Nitrobenzene-d5	26	134

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Water Surrogate	Lower Percent	Upper Percent
Phenol-d5	54	110
Terphenyl-d14	47	130

Soil LCS and MS/MSD QC Criteria:

Soil LCS and MS/MSD recovery criteria are based on results obtained from February 29, 2012 to December 4, 2013. Not enough data points are available to assess performance for MS/MSD, the LCS limits are used for the MS/MSD. Minimum recovery criteria of 20% will be used for LCS and MS/MSD.

	LCS		Matrix Spike (use LCS)		
Analyte	Lower	Upper	Lower	Upper	RPD
1,4-Dioxane	63	123			20
Phenol	43	110			20
Bis(2-chloroethyl)ether	47	110			20
2-Chlorophenol	42	110			20
1,3-Dichlorobenzene	37	110			20
1,4-Dichlorobenzene	39	110			20
Benzyl alcohol	31	110			20
1,2-Dichlorobenzene	40	110			20
2-Methylphenol	42	110			20
Bis(2-chloro-1-methylethyl) ether	44	110			20
3&4-Methylphenol	49	110			20
N-Nitrosodipropylamine	42	110			20
Hexachloroethane	38	110			20
Nitrobenzene	48	110			20
Isophorone	43	110			20
2-Nitrophenol	44	110			20
2,4-Dimethylphenol	24	110			20
Bis(2-chloroethoxy)methane	45	110			20
2,4-Dichlorophenol	48	110			20
1,2,4-Trichlorobenzene	43	110			20
Naphthalene	45	110			20
4-Chloroaniline	20	110			20
Hexachlorobutadiene	42	110			20
4-Chloro-3-methylphenol	50	110			20
2-Methylnaphthalene	45	110			20
Hexachlorocyclopentadiene	32	110			20
2,4,6-Trichlorophenol	47	110			20
2,4,5-Trichlorophenol	52	112			20
2-Chloronaphthalene	47	110			20
2-Nitroaniline	58	118			20
Dimethyl phthalate	63	123			20
2,6-Dinitrotoluene	56	116			20

	LCS		Matrix Spike (use LCS)		
Analyte	**Lower**	**Upper**	**Lower**	**Upper**	**RPD**
Acenaphthylene	49	110			20
3-Nitroaniline	29	110			20
Acenaphthene	72	132			20
2,4-Dinitrophenol	30	110			20
4-Nitrophenol	67	127			20
Dibenzofuran	52	112			20
2,4-Dinitrotoluene	63	123			20
Fluorene	54	114			20
4-Chlorophenyl phenyl ether	53	113			20
4-Nitroaniline	56	116			20
4,6-Dinitro-2-methylphenol	50	110			20
Diphenyl amine	39	110			20
4-Bromophenyl phenyl ether	52	112			20
Hexachlorobenzene	52	112			20
Pentachlorophenol	49	110			20
Phenanthrene	55	115			20
Anthracene	57	117			20
Carbazole	53	113			20
Di-n-butyl phthalate	72	132			20
Fluoranthene	63	123			20
Pyrene	60	120			20
Butyl benzyl phthalate	64	124			20
Benzo(a)anthracene	60	120			20
3,3'-Dichlorobenzidine	20	110			20
Chrysene	61	121			20
Bis(2-ethylhexyl) phthalate	76	136			20
Di-n-octyl phthalate	70	130			20
Benzo(b)fluoranthene	60	120			20
Benzo(k)fluoranthene	64	124			20
Benzo(a)pyrene	57	117			20
Indeno(1,2,3-cd)pyrene	62	122			20
Dibenz(a,h)anthracene	64	124			20
Benzo(g,h,i)perylene	58	118			20

Soil Surrogate recovery

Soil surrogate criteria are based on sample results obtained from February 29, 2012 to December 4, 2013.

Surrogate	**Lower Percent**	**Upper Percent**
1,2-Dichlorobenzene-d4	20	136
1,4-Dioxane-d8	32	110
2,4,6-Tribromophenol	20	146
2-Chlorophenol-d4	20	121
2-Fluorobiphenyl	20	121
2-Fluorophenol	20	111
Nitrobenzene-d5	20	125

Surrogate	Lower Percent	Upper Percent
Phenol-d5	20	111
Terphenyl-d14	20	131

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APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

BNA Method

INSTRUMENT CONTROL PARAMETERS: AG5975B

D:\MSDCHEM\2011\METHODS\110211BB.M
Wed Nov 02 08:59:07 2011

Control Information
--- ---

Sample Inlet : GC
Injection Source : GC ALS
Mass Spectrometer : Enabled

No Sample Prep method has been assigned to this method.

Oven
Equilibration Time 0.5 min
Max Temperature 340 degrees C
Slow Fan Disabled
Oven Program On
40 °C for 2 min
then 15 °C/min to 330 °C for 6 min
Run Time 27.333 min

Front Injector
Syringe Size 10 µL
Injection Volume 1 µL
Injection Repetitions 1
Injection Delay 0 sec
Solvent A Washes (PreInj) 1
Solvent A Washes (PostInj) 3
Solvent A Volume 8 µL
Solvent B Washes (PreInj) 1
Solvent B Washes (PostInj) 3
Solvent B Volume 8 µL
Sample Washes 0
Sample Wash Volume 8 µL
Sample Pumps 3
Dwell Time (PreInj) 0 min

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Dwell Time (PostInj) 0 min
Solvent Wash Draw Speed 300 µL/min
Solvent Wash Dispense Speed 6000 µL/min
Sample Wash Draw Speed 300 µL/min
Sample Wash Dispense Speed 6000 µL/min
Injection Dispense Speed 6000 µL/min
Viscosity Delay 1 sec
Sample Depth Disabled

Sample Overlap
Sample overlap is not enabled

Front SS Inlet He
Mode Pulsed Splitless
Heater On 280 °C
Pressure On 7.1574 psi
Total Flow On 44 mL/min
Septum Purge Flow On 3 mL/min
Gas Saver On 20 mL/min After 2 min
Injection Pulse Pressure 30 psi Until 0.5 min
Purge Flow to Split Vent 40 mL/min at 0.4 min

Thermal Aux 2 {MSD Transfer Line}
Heater On
Temperature Program On
280 °C for 0 min
Run Time 27.333 min

Column #1
Restek Rxi-5Sil MS: 851017
Cat# 13638
350 °C: 30 m x 250 µm x 0.5 µm
In: Front SS Inlet He
Out: Vacuum

(Initial) 40 °C
Pressure 7.1574 psi
Flow 1 mL/min
Average Velocity 36.262 cm/sec
Holdup Time 1.3789 min
Flow Program On
1 mL/min for 0 min
Run Time 27.333 min

ED_006532_00005075-00079

Aux EPC 1 He
Pressure Program Off
2.2 psi for 0 min
Run Time 27.333 min

Aux EPC 2 He
Pressure Program Off
10 psi for 0 min
Run Time 27.333 min

Aux EPC 3 He
Pressure Program Off
10 psi for 0 min
Run Time 27.333 min

Signals
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz

MS ACQUISITION PARAMETERS

General Information
--- ---

Tune File : DF110211B.u
Acquistion Mode : Scan

MS Information
-- ---

Solvent Delay : 3.60 min

EMV Mode : Gain Factor
Gain Factor : 0.60
Resulting EM Voltage : 1318

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[Scan Parameters]

Low Mass : 41.0
High Mass : 550.0
Threshold : 150
Sample # : 2 A/D Samples 4

[MSZones]

MS Source : 230 C maximum 250 C
MS Quad : 150 C maximum 200 C

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS for SN: US81829666

Trace Ion Detection is OFF.

EMISSION : 34.610
ENERGY : 69.922
REPELLER : 23.757
IONFOCUS : 90.157
ENTRANCE_LE : 0.000
EMVOLTS : 1329.412
Actual EMV : 1329.41
GAIN FACTOR : 0.64
AMUGAIN : 2251.000
AMUOFFSET : 121.875
FILAMENT : 1.000
DCPOLARITY : 0.000
ENTLENSOFFS : 19.325@ 3 19.325@ 50 14.808@ 69 14.808@131 15.561@219 14.557@414 15.310@502 15.310@1049
MASSGAIN : -410.830
MASSOFFSET : -45.042

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS
--- ---

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA
BFB	BFB

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DFTPP DFT

C: Channel (use when applicable):
Front A
Back B
Both AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

YY: Year i.e. 12 for 2012

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Split vent trap	Annually	Replace.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As needed and with each ICAL	Remove ½-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.). It may be necessary to decrease the column flow (e.g. from 1.0 to 0.9 mL/min) to reflect the change in column length.
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
EM voltage	As needed	If an overall change in sensitivity (area counts in CCV in comparison to most recent ICAL), the EM voltage may need adjusting.

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MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check the calibration vials		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

ED_006532_00005075-00085

APPENDIX G.
METHOD PERFORMANCE

Semivolatile Organic Compound Analysis
Water: January 4, 2012 to December 4, 2013

Analyte	Number of Points	Mean	StdDev	Lower Performance	Upper Performance
1,4-Dioxane	18	96.00	13.00	70	122
Phenol	15	78.00	5.28	62	94
Bis(2-chloroethyl)ether	15	82.60	3.46	72	93
2-Chlorophenol	30	79.10	5.18	64	95
1,3-Dichlorobenzene	15	57.70	8.47	41	75
1,4-Dichlorobenzene	15	59.10	8.62	42	76
Benzyl alcohol	15	78.70	10.00	49	109
1,2-Dichlorobenzene	15	61.50	8.55	44	79
2-Methylphenol	15	77.10	4.17	65	90
Bis(2-chloro-1-methylethyl) ether	15	80.70	6.06	63	99
3&4-Methylphenol	30	84.60	5.50	68	101
N-Nitrosodipropylamine	15	77.50	4.32	65	90
Hexachloroethane	15	51.50	6.95	31	72
Nitrobenzene	15	84.10	6.31	65	103
Isophorone	15	82.50	5.17	67	98
2-Nitrophenol	15	79.10	5.13	64	95
2,4-Dimethylphenol	15	75.40	6.36	63	88
Bis(2-chloroethoxy)methane	15	81.70	6.16	63	100
2,4-Dichlorophenol	30	80.80	5.20	70	91
3&4-Chlorophenol	13	80.70	7.67	58	104
1,2,4-Trichlorobenzene	15	63.20	8.65	46	81
Naphthalene	30	77.50	8.59	52	103
4-Chloroaniline	15	72.50	16.70	22	123
Hexachlorobutadiene	15	52.30	6.63	32	72
4-Chloro-3-methylphenol	15	82.90	6.14	64	101
2-Methylnaphthalene	30	75.50	8.94	49	102
Hexachlorocyclopentadiene	16	34.50	8.41	9	60
2,4,6-Trichlorophenol	30	80.10	5.68	69	91
2,4,5-Trichlorophenol	30	86.90	6.76	73	100
3,5-Dichlorophenol	14	83.90	6.53	64	104
2-Chloronaphthalene	15	73.30	8.54	48	99
3,4-Dichlorophenol	14	89.40	7.53	67	112
2-Nitroaniline	15	86.40	7.50	64	109

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Analyte	Number of Points	Mean	StdDev	Lower Performance	Upper Performance
Dimethyl phthalate	15	90.70	9.85	61	120
2,6-Dinitrotoluene	15	87.50	7.08	66	109
Acenaphthylene	15	76.30	9.17	49	104
3-Nitroaniline	15	76.90	17.20	25	129
Acenaphthene	30	110.00	8.48	84	135
2,4-Dinitrophenol	15	82.10	12.90	43	121
4-Nitrophenol	15	94.80	10.90	62	127
Dibenzofuran	30	82.60	7.60	60	105
2,4-Dinitrotoluene	15	89.70	7.49	67	112
2,3,4,6-Tetrachlorophenol	14	87.40	7.04	73	101
Diethyl phthalate	15	90.60	9.11	63	118
Fluorene	30	84.50	8.19	60	109
4-Chlorophenyl phenyl ether	15	79.90	8.81	53	106
4-Nitroaniline	15	68.70	27.90	-15	153
3,4,5-Trichlorophenol	14	92.00	7.42	70	114
4,6-Dinitro-2-methylphenol	15	97.70	8.04	74	122
Diphenyl amine	15	59.20	22.10	-7	126
4-Bromophenyl phenyl ether	15	81.30	7.80	58	105
Hexachlorobenzene	16	81.70	8.14	57	106
Pentachlorophenol	30	87.60	8.06	63	112
Phenanthrene	30	86.60	7.83	63	110
Anthracene	15	86.90	8.26	62	112
Carbazole	30	72.50	19.80	13	132
Di-n-butyl phthalate	15	97.50	9.23	70	125
Fluoranthene	30	93.30	8.56	68	119
Pyrene	30	92.70	9.17	65	120
Butyl benzyl phthalate	15	91.60	8.19	67	116
Benzo(a)anthracene	32	87.10	6.77	67	107
3,3'-Dichlorobenzidine	14	49.00	23.20	-21	119
Chrysene	32	89.10	7.34	67	111
Bis(2-ethylhexyl) phthalate	18	101.00	16.00	53	149
Di-n-octyl phthalate	15	92.10	11.40	58	126
Benzo(b)fluoranthene	32	84.90	8.19	60	109
Benzo(k)fluoranthene	32	90.70	8.67	65	117
Benzo(a)pyrene	32	75.60	6.53	56	95
Indeno(1,2,3-cd)pyrene	30	84.60	7.45	62	107
Dibenz(a,h)anthracene	32	88.60	10.00	59	119
Benzo(g,h,i)perylene	30	87.30	7.65	64	110

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Semivolatile Organic Compound Analysis
Soil: February 29, 2012 to December 4, 2013

Analyte	Number of Points	Mean	StdDev	Lower Performance	Upper Performance
1,4-Dioxane	14	92.70	8.79	75	110
Phenol	16	73.30	6.75	53	94
Bis(2-chloroethyl)ether	16	77.00	10.70	45	109
2-Chlorophenol	16	72.30	6.86	52	93
1,3-Dichlorobenzene	16	67.40	7.59	52	83
1,4-Dichlorobenzene	16	68.60	7.67	53	84
Benzyl alcohol	16	60.70	18.00	7	115
1,2-Dichlorobenzene	16	69.50	7.49	55	85
2-Methylphenol	16	72.30	6.99	51	93
Bis(2-chloro-1-methylethyl) ether	16	73.70	10.40	42	105
3&4-Methylphenol	16	79.40	8.42	54	105
N-Nitrosodipropylamine	16	71.50	7.33	50	94
Hexachloroethane	16	68.10	9.38	40	96
Nitrobenzene	16	78.10	7.97	54	102
Isophorone	16	73.40	6.76	53	94
2-Nitrophenol	16	73.80	7.57	51	97
2,4-Dimethylphenol	16	53.80	18.30	17	90
Bis(2-chloroethoxy)methane	16	74.80	6.81	54	95
2,4-Dichlorophenol	16	77.80	7.88	62	94
1,2,4-Trichlorobenzene	16	73.20	7.52	58	88
Naphthalene	17	74.60	6.96	54	96
4-Chloroaniline	16	43.90	21.90	-22	109
Hexachlorobutadiene	16	72.10	9.08	45	99
4-Chloro-3-methylphenol	16	80.30	7.73	57	103
2-Methylnaphthalene	17	75.30	7.82	52	99
Hexachlorocyclopentadiene	16	62.40	15.20	17	108
2,4,6-Trichlorophenol	16	77.10	7.93	61	93
2,4,5-Trichlorophenol	16	81.70	8.49	65	99
2-Chloronaphthalene	16	77.10	6.97	56	98
2-Nitroaniline	16	87.90	9.57	59	117
Dimethyl phthalate	16	93.20	10.80	61	126
2,6-Dinitrotoluene	16	86.30	7.82	63	110

ED_006532_00005075-00088

Analyte	Number of Points	Mean	StdDev	Lower Performance	Upper Performance
Acenaphthylene	17	78.50	8.28	54	103
3-Nitroaniline	16	59.40	16.70	9	110
Acenaphthene	17	102.00	12.80	64	141
2,4-Dinitrophenol	16	59.60	15.10	14	105
4-Nitrophenol	16	96.90	17.30	45	149
Dibenzofuran	16	82.40	7.68	59	105
2,4-Dinitrotoluene	16	92.60	10.10	62	123
Diethyl phthalate	16	91.90	9.41	64	120
Fluorene	17	84.10	8.54	58	110
4-Chlorophenyl phenyl ether	16	83.40	7.59	61	106
4-Nitroaniline	17	85.90	19.10	29	143
4,6-Dinitro-2-methylphenol	16	80.40	11.30	47	114
Diphenyl amine	16	68.90	15.10	24	114
4-Bromophenyl phenyl ether	16	82.40	6.52	63	102
Hexachlorobenzene	16	81.60	6.26	63	100
Pentachlorophenol	16	78.90	12.00	43	115
Phenanthrene	17	84.80	8.61	59	111
Anthracene	17	87.00	9.38	59	115
Carbazole	16	82.60	29.90	-7	172
Di-n-butyl phthalate	16	102.00	11.90	66	138
Fluoranthene	17	92.90	10.30	62	124
Pyrene	17	90.10	11.90	54	126
Butyl benzyl phthalate	16	93.90	10.70	62	126
Benzo(a)anthracene	16	90.00	9.71	61	119
3,3'-Dichlorobenzidine	16	39.40	16.70	-11	90
Chrysene	17	90.80	10.00	61	121
Bis(2-ethylhexyl) phthalate	16	106.00	16.90	56	157
Di-n-octyl phthalate	16	100.00	12.50	63	138
Benzo(b)fluoranthene	17	89.80	10.50	58	121
Benzo(k)fluoranthene	17	94.00	9.30	66	122
Benzo(a)pyrene	17	86.50	8.95	60	113
Indeno(1,2,3-cd)pyrene	17	92.20	10.80	60	125
Dibenz(a,h)anthracene	17	94.00	11.50	59	129
Benzo(g,h,i)perylene	17	88.20	15.90	41	136

ED_006532_00005075-00089

APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 315
Revision: 7, Effective: 11/15/14

SEMIVOLATILE ORGANIC COMPOUND ANALYSIS

Revision	Effective Date	Description
5	06/30/09	1. Revisions throughout document. 2. Replaced Method Performance and QC Limits with recent data. 3. Updated instrumentation and methods.
6	02/01/12	1. Replaced Method Performance and QC Limits with recent data. 2. Updated tune criteria to Method 8270D recommendations. 3. Masses used for quantitation changed to recommended masses in Method 8270D for several compounds. 4. Miscellaneous edits throughout for consistency with EPA Region 9 Laboratory practices (internal COC, waste labeling, etc.).
7	11/15/14	1. Replaced Method Performance and QC Limits with recent data. 2. Changed surrogate assignments for 2-chlorophenol and 3&4-methylphenol. 3. Raised the quantitation limit for pentachlorophenol. 4. Miscellaneous edits throughout for consistency with EPA Region 9 Laboratory practices.

ED_006532_00005075-00090

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 353
LOW LEVEL VOLATILES

Revision 3
Effective Date: October 17, 2016

Reviewed by: _____ 10/3/16
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: _____ October 3, 2016
Barbara Bates, Laboratory QA Officer — Date

Approved by: _____ 10/3/16
Peter Husby, Laboratory Director — Date

Periodic Review:

Signature	Title	Date

This SOP was prepared by ICF for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105086-19311

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the analysis of selected volatile organic compounds at low concentrations using gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM) in aqueous samples. Samples with concentrations expected to exceed 500 ng/L should be analyzed by USEPA Region 9 Laboratory SOP 354 *Volatile Organic Compound Analysis in Water*. This SOP is based on procedures contained in EPA Method 524.2, Revision 4.1, 1995 as modified for low concentration analysis by the California Department of Health Services in *Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry*, February 2002. Deviations from Method 524.2 are described in Appendix A. Analytes and Quantitation Limits (QLs) are listed in Appendix B. Extension of the procedures to include additional VOCs must be arranged on a project basis.

The quality control (QC) criteria specified in this procedure do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Volatile organic compounds (VOCs) are purged from a 25-mL aqueous sample in a fritted sparge cell. The samples are fortified with internal standard (IS) and surrogate compounds (SURR) before they are purged. An inert gas (nitrogen) is bubbled through the sample in the sparge cell, which causes the purgeable VOCs to be transferred from the aqueous sample to the vapor phase. The vapor phase is swept through a trap containing an adsorbent material at ambient temperature where the VOCs are adsorbed. After the purging of the sample is completed, the adsorbent trap is heated and back flushed with helium which desorbs the VOCs onto a capillary column in a gas chromatograph (GC). The VOCs are separated in the GC column and detected by a mass spectrometer (MS).

Target VOCs are identified in the sample by comparing the characteristic ion(s) and GC retention time in the sample to the characteristic ion(s) and retention time of compounds in the standards analyzed under identical conditions. Each target and surrogate compound is quantitated by comparing the responses of the target and surrogate compound responses to the internal standard responses, using the average relative response factors from the most recent initial calibration.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the USEPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

GC/MS Tuning Solution (MS tune): Bromofluorobenzene (BFB) used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

FC43: Perfluorotributylamine. Compound used to tune the MS.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the USEPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

Methanol is the primary solvent used for the preparation of standards in this procedure. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing and shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly. Use methanol in laboratory fume hood. The analyst must wear appropriate personal protective

equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammables storage cabinet away from oxidizers and sources of ignition.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The USEPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *USEPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The USEPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with USEPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA

Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Aqueous acidic VOC waste (wastewater, hydrochloric acid, trace halogenated volatile compounds)	Hazardous Waste	Corrosive
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Waste pump oil (trace halogenated volatile compounds)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples must be received in pre-cleaned 40-mL VOA vials with Teflon-lined septa. No headspace or bubbles are acceptable. Three vials is adequate volume to complete the analysis and allow for reanalysis if required.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

Samples should be preserved with hydrochloric acid to a pH of ≤ 2 at the time of sampling. The analyst must document unacceptable preservation in the work order memo field in LIMS and use the appropriate flag for data qualification (see Appendix R of the

USEPA Region 9 Laboratory Quality Assurance Plan). Preservation is not verified until sample analysis is complete.

5.4 Sample Storage

Samples must be stored at >0 and ≤ 6 °C in the refrigerators designated for sample storage in Rooms 201or 209. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within 14 days from collection. If samples were not preserved at the time of collection, analyze within 7 days of collection.

6 INTERFERENCES

6.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 9.3.1. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during storage and handling.

6.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

7.1.1 Gas Chromatograph (GC): Hewlett Packard/Agilent 6890 or 6890N, Agilent 7890A or, equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, split/splitless injection port, and Electronic Pressure Control (EPC).

7.1.2 Column: Hewlett Packard HP-624 25M x 0.20 mm, 1.12 micron film or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

7.1.3 Mass spectrometer: Hewlett Packard/Agilent 5973 or 5973N, Agilent 5975C, or equivalent, capable of scanning from 35 to 300 amu every two seconds or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 25 ng of BFB is injected through the GC inlet.

7.1.4 Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window and selectively scan specified masses (see Appendix B). The software must also allow integration of the ion abundance of any specific ion between specified times or scan number limits and to calculate the relative response factors (RRFs) and concentrations of analytes in samples.

7.1.5 Purge and Trap Concentrator: Tekmar 3000, Tekmar 3100, Teledyne Tekmar Stratum, OI Eclipse, or equivalent.

7.1.6 Autosampler: Varian Archon, OI Analytical Model 4552, or equivalent.

7.2 Reagents

Document the receipt of all reagents in the LIMS. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

7.2.1 Methanol (Purge & Trap grade).

7.2.2 Organic-free method blank water (prepared following USEPA Region 9 Laboratory SOP 205 *Preparation of Organic-free Method Blank Water*).

7.2.3 Hydrochloric acid, 6N HCl - Slowly add 50 mL of reagent grade concentrated HCl to 50 mL of organic-free method blank water. Prepare as needed. Also known as 1:1 or 1+1 HCl.

7.3 Standards

Document the receipt, preparation, and ampule open dates of all standards in the LIMS. Print and attach a LIMS standard label to all standard vials.

All ampulated calibration materials must be maintained in the refrigerator at >0°C to ≤6°C and protected from light. Use the manufacturer's expiration date for ampulated standards.

Open stock ampules and working standards must be maintained in a freezer at ≤-10 °C and protected from light. Open ampules are assigned an expiration date which is either six month from opening date, or the manufacturer expiration date, whichever is earlier. Working standards are assigned an expiration date which is either one month from preparation date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Analysts must allow all standard solutions to equilibrate to room temperature before use. Replace standards sooner if analysis indicates that the solution has degraded. Dispose of any remaining solution in the correct waste container.

7.3.1 BFB, 5000 µg/mL: 4-Bromofluorobenzene VOA Tuning Compound solution, Restek catalog #30003 or equivalent.

7.3.2 1,2,3-Trichloropropane-d5 (TCP-d5): 2000 µg/mL, CPI catalog #Z020596-01, or equivalent.

7.3.3 1,2,3-Trichloropropane: 2000 µg/mL, Restek catalog #30429, or equivalent.

7.3.4 8011 Calibration Mix (EDB/DBCP): 2000 µg/mL, Restek catalog #30062, or equivalent

7.3.5 1,2-Dibromo-3-chloropropane (DBCP): 2000 µg/mL, Restek catalog #30270, or equivalent.

7.3.6 1,2,3-Trichloropropane: 200 µg/mL, Supelco catalog #48355, or equivalent.

7.3.7 Calibration Standards: EPA EDB/DBCP Mix: 2000 µg/mL, Supelco catalog #48225-U, or equivalent.

7.3.8 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/µL): Add 1.5 mL of purge and trap grade methanol to a clean, dry, 2-mL volumetric flask using a gas tight syringe.

Add 20 µL of a BFB stock solution (5000 µg/mL) to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Pour the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve. (Do not use pipettes to transfer VOA solutions because the vacuum used to draw the solutions up into the pipettes can cause some volatile compounds to come out of solution).

7.3.9 Internal standard and surrogate solution (TCP_ISSUR 1.25 µg/mL)

Add 8 mL of purge and trap grade methanol to a clean, dry, 10-mL volumetric flask.

Add the stock standard solutions in the amounts indicated in the table below to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixtures.

Bring the volume up to 10 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. µg/mL
TCP-d5	Restek	2000	6.25	10	1.25
BFB	Restek	5000	2.5	10	1.25

Pour the contents of the volumetric flask into a clean 5-mL standard reservoir vial and immediately install the standard reservoir in the appropriate standard position on the autosampler. Print and attach a LIMS standard label to the standard vial or the back panel of the autosampler adjacent to the vial.

7.3.10 Calibration mix (5/10 µg/mL)

Add 1.5 mL of purge and trap grade methanol to a clean and dry 2-mL volumetric flask using a 5 mL syringe.

Add the stock standards to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol in the amounts indicated in the table below. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixes.

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. µg/mL
8011 Cal Mix EDB/DBCP	Restek	2000	5	2	5*
1,2,3-Trichloropropane	Restek	2000	5	2	5
DBCP	Restek	2000	5	2	5*

*DBCP concentration is 10 µg/mL in the calibration mix as a total from two sources.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial.

7.3.11 Calibration mix (0.25/0.50 µg/mL)

Add 1.5 mL of purge and trap grade methanol to a clean and dry 2-mL volumetric flask using a gas tight syringe.

Add 0.1 mL of the 5 µg/mL Calibration mix to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol.
Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial.

7.3.12 Second Source Verification (SCV) solution (EDB/DBCP//TCP_SCV-1 µg/mL)

Add 4 mL of purge and trap grade methanol to a clean and dry 5-mL volumetric flask using a gas tight syringe.

Add the stock standards to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol in the amounts indicated in the table below. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixes.

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. ug/mL
EPA EDB/DBCP Mix	Supelco	2000	2.5	5	1
1,2,3-Trichloropropane	Supelco	200	25	5	1

Bring the volume up to 5 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 5-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial.

7.4 Supplies

7.4.1 Gas-tight syringes (5-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 10-mL, 25-mL and 50 mL).

7.4.2 25-mL fritted sparge vessels.

7.4.3 Disposable Pasteur pipettes.

7.4.4 pH paper (pH 0-14 range).

7.4.5 Trap K (VOCARB 3000, or equivalent).

7.4.6 40-mL VOC vials for standards with screw-hollow cap lined with 22 mm PTFE-faced silicone septa.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix E as a starting point. Parameters for the autosampler and concentrator are found in Appendix D.

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound. Refer to Section 8.4.1 and Appendix F for system maintenance requirements.

Ensure that waste containers are properly connected and labeled and have sufficient empty volume for the waste that will be generated during instrument operation.

8.1.1 Mass calibration

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions (Appendix E). Use perfluorotributylamine (FC43) to perform mass calibration of the instrument.

Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.1.2 GC/MS tuning

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to at the beginning of each analytical period. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Inject or purge 0.5 µL of the BFB solution using the operating parameters provided in Appendix D.

The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (auto-tune and/or manual tune) has been performed (refer to Appendices E and F).

Perform an initial calibration using six calibration standards. The recommended concentrations are listed in the following table.

Analysis Type	Calibration Levels					
	1 (CRL)	2	3	4 (CCV)	5	6
EDB/DBCP/TCP*, ng/L	5	10	25	50	100	500
Standard Amounts (µL) for each calibration level added to 50 mL Acidified Water						
Calibration mix 0.25/0.50 µg/mL	1	2	5	10		
Calibration mix 5.0/10 µg/mL					1	5
1.0 µg/mL SCV Standard				2.5		

*DBCP concentrations are twice the listed concentrations.

Update the initial calibration response factors for the method by associating the current data file with each calibration level and save the method.

Print the raw area report for an internal standard or the target analyte for single analyte analysis. From the ChemStation menu, select initial calibration → edit compound → view → page 3. Verify that the method was updated correctly. Print analyte list from the ChemStation menu by selecting initial calibration → list compound, to verify that the average response factor is used.

Analyze an SCV standard at calibration level 4 to verify the accuracy of the calibration materials and preparation used in the initial calibration.

Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration

Prior to analyzing a continuing calibration, ensure that proper system maintenance and GC/MS tuning (mass axis calibration) has been performed (Appendices E and F).

8.2.2.1 Continuing Calibration Verification (may also serve as the LCS)

Analyze a calibration verification standard following the BFB tune check.

Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Note that CCV and LCS/BS are the same and that one analysis can serve both functions (i.e. instrument calibration verification and batch accuracy QC).

8.2.2.2 Quantitation Limit Verification Standard (CRL)

Analyze a CRL standard at the reporting limit (the concentration of the lowest point of the initial calibration).

Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS batch to ensure that the correct sample is being analyzed.

Note if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS "MMO" field.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log and the LIMS sequence page.

Prepare instrument and batch QC samples in acidified organic-free method blank water.

Prepare the samples to be analyzed. The following table represents the spike levels recommended for most projects:

Spike Amounts, Autosampler, 25 mL Purge

Sample	TCP_ISSUR Mix 1.25 µg/mL, µL	Calibration Mix 0.25/0.50 µg/mL, µL
Blanks	1.0	NA
Samples	1.0	NA
BS/LCS*	1.0	10.0
MS/MSD#	1.0	8.0

* Prepare 50 mL and transfer to 40-mL vial. Also the CCV.
\# 40-mL Sample vial spiked with Calibration Mix
NA = Not Applicable

Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:

1. BFB
2. CCV/LCS
3. CRL (QLS)
4. Method Blank
5. Samples, sample dilutions, and/or QC samples as needed.
6. Instrument blanks, as needed

Enter sample sequence in the instrument software. Include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any in the "Multiplier" field.

Name the data files according to the data file naming convention outlined in Appendix G.

Program the autosampler to use the appropriate locations for the analysis.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and the characteristic ions of the peak must match those of the standard.

For relative retention time, the peak must elute within 0.06 relative retention time units of the analyte in the continuing calibration standard. The relative retention time is the retention time of the target divided by the retention time of the associated IS. If the relative retention time for the target analyte in the CCAL is 0.82 then the peak in the sample must have a relative retention time of 0.76 to 0.88.

The relative intensities of the characteristic ions must agree within 20% between the standard and sample spectra.

If a compound cannot be verified using these criteria but in the technical judgment of the analyst is present, report the analyte and include supporting evidence in the raw data package.

Cross out all reported hits that do not meet qualitative criteria. Date and initial the change.

Review the chromatogram for possible false negatives and edit results as needed.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out quantitation reports and chromatograms. Use the average relative response factor from the initial calibration for quantitation.

Calculate results for target analytes using the following equation:

Conc. (ng/L) = Ax * AMTIS * DF / (AIS * RRF)

Where:

Ax	=	area of the characteristic ion of the compound
AMTIS	=	amount of internal standard in ng/L (200 ng/L)
DF	=	dilution factor
AIS	=	area of the characteristic ion of the associated internal standard
RRF	=	analyte average relative response factor from the initial calibration

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow USEPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 QC Review

8.3.4.1 Process and review the results for the IB/MB, CCV/LCS/BS, and CRL, samples and QC samples (MS/MSD). Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and CRL (QLS) QC sample results are within QC limits. See Section 9.2 for instrument QC requirements; see Section 9.3 for Batch QC requirements.

8.3.4.2 Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.

8.3.4.3 Review all sample results:

8.3.4.3.1 Determine if any samples contain target analytes at concentrations exceeding the calibration range. If so, determine if dilution is required, or if the analyte will be quantitated using the full scan procedures (EPA Region 9 Laboratory SOP 354).

8.3.4.3.2 Review the chromatogram for possible false negatives.

8.3.4.3.3 Manually cross out all compounds that do not meet the qualitative criteria and document the reason on the quantitation report.

8.3.4.3.4 If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.4.4 Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the USEPA Region 9 Laboratory Quality Assurance Plan.

8.3.5 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J) and provide the C1 qualifier.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems for GC and MS operations. Refer to Appendix E for routine preventative maintenance procedures and schedule.

8.4.1 GC Maintenance

Symptoms of common problems:

- Carryover
  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.2 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio

- Failing tune checks

Resolution: Clean the source.

9 QUALITY CONTROL

The USEPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in USEPA Region 9 Laboratory SOP 880 *Demonstration of Capability* for more details.

9.2 Instrument QC

9.2.1 Mass calibration

Review the FC43 spectrum for compliance with the criteria list in Appendix C.

If the FC43 spectrum does not meet the criteria, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate FC43 spectra, further maintenance such as cleaning the ion source may be required.

9.2.2 GC/MS Tune

Review the BFB spectrum for compliance with the criteria list in Appendix C.

If the ion abundances, degradation, or tailing fail to meet the criteria, the BFB chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.). If the problem is related to poor chromatography, take the necessary corrective action and reanalyze the BFB. If the BFB continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

Reanalyze samples injected after the 12-hour time period has elapsed.

9.2.3 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound using the following equation:

$$RRF = (Ax)(Cis) / (Ais)(Cx)$$

Where

Ax	=	Area of quantitation ion of compound x. The quantitation ions and internal standard assignments are listed in Appendix B.
Ais	=	Area of quantitation ion for associated internal standard
Cx	=	Concentration of compound x
Cis	=	Concentration of the associated internal standard

The data system calculates the average RRF (RRFavg) for all analytes.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/\ RRF_{avg})*100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{ave})^2}{n-1}}$$

The %RSD and SCV accuracy requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria (see Appendix C) are not met, the SCV must be reanalyzed. If it fails again, prepare a fresh solution. If failure persists, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration, if necessary.

9.2.4 Continuing Calibration Verification (may also be evaluated as the LCS)

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard changes by more than 50% from the internal standard areas of the continuing calibration level of the most recent initial calibration, the CCV may be reanalyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine the retention times of internal standards in the calibration verification standard. If the retention time for any internal standard changes by more than 0.5 minutes compared to the continuing calibration level of the most recent initial calibration sequence, inspect the chromatographic system for malfunctions and take corrective action as needed and prepare a new calibration curve.

The data system calculates the percent deviation (%D) of the RRF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\,100$$

Where:

RRF_c = Relative Response Factor of compound c.
RRF_{avg} = Average Relative Response Factor.

If the continuing calibration does not meet %D criterion listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

9.2.5 Quantitation Limit Standard (CRL or QLS)

CRL must be analyzed at the beginning of the analytical run, typically just after the CCV. The concentrations match the QL concentration (at the instrument). The recovery of analytes in the CRL is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.
M = measured concentration of the analyte, ng/L.
T = true concentration of the analyte in the ng/L.

Check that the recoveries meet the criteria specified in Appendix C.

If the CRL recovery does not meet criteria provided in Appendix C, rerun the CRL once to verify. If still unacceptable determine the cause, take corrective action.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix R of the Region 9 Laboratory Quality Assurance Plan.

9.3 Batch QC

9.3.1 Method Blank (equivalent to an instrument blank in this procedure)

- Analyze a method blank (MB) to demonstrate that the entire analytical system is free of contamination.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action - If the MB result exceeds QC limits, check the associated samples as follow:

  1. If the sample result is less than five times the MB result, reanalyze the MB. If the MB result still exceeds QC limits, qualify the data as described in the Region 9 Lab QA Plan, Appendix R for each analyte found in the MB.
  2. If the sample result is greater than five times the MB result or is not detected, report the sample result.

- If the surrogate recovery does not meet acceptance criteria, reanalyze the MB. If the surrogate recovery still does not meet acceptance criteria, the batch should be reanalyzed.

9.3.2 Laboratory Control Sample (equivalent to the CCV in this procedure – one analysis serves both functions)

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is analyzed once per batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with matrix spiking solution.

- Calculate the percent recovery (%R) using the following equation:

$$\% R = [(SSR - SR)/SA] \times 100$$

Where,
SSR = Spiked sample result
SR = Unspiked sample result
SA = Spike added

- The %R must be within the QC limits in Appendix C. If acceptable recoveries cannot be achieved, reanalyze the LCS. If the LCS result still exceeds QC limits, correct the error (which may include maintenance or repair and recalibration of the instrument) and reanalyze the LCS and all associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are analyzed for each batch of twenty or fewer samples analyzed as a group.

- Calculate the recovery of each analyte.

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

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

Where,
MSC = Measured concentration of analyte in MS
MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

  The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS – = FAIL

CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Analysis batch acceptable.
Case 2: Analysis batch acceptable; matrix effect confirmed.
Cases 3 & 4: Analysis batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.
Cases 5, 6, 7, & 8: Analysis batch rejected. If additional sample volume is available, the batch should be reanalyzed.

9.4 Sample QC

9.4.1 Surrogate Recovery

Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.

2. Reanalyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for reanalysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

Do not reanalyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be reanalyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need reanalysis.
If the surrogate recoveries of the reanalysis are within limits, then the problem was within the laboratory's control. Report the results from the reanalysis and submit the data from both analyses. The problem must be documented in the LIMS MMO field.

- If the reanalysis does not solve the problem and additional sample volume is available, the failing samples should be re-analyzed.

- If sample re-analyses is unfeasible, or surrogate recoveries of the re-analyses are also outside the QC limits, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis. The problem must be documented in the LIMS MMO field.

9.4.2 Internal Standard Area:

- Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.
Take the following steps if the internal standard areas are not within the limits:

1. Check the system performance.

2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

Do not reanalyze the MS/MSD samples, even if internal standard areas are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be reanalyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need reanalysis.
If the internal standard areas of the reanalysis are within limits, then, the problem was within the laboratory's control. Report the results from the reanalysis and submit the data from both analyses. Distinguish between the analysis and reanalysis by adding an "RE" suffix to the sample ID on the reanalysis. The problem must be documented in the LIMS MMO field.

9.5 Method Performance

The following table summarizes method performance from LCS data (water matrix) for the period March 1, 2016 to August 30, 2016.

Method Performance

Analyte	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
1,2,3-Trichloropropane	41	104	91.2-116
1,2-Dibromoethane	41	107	92.4-121
1,2-Dibromo-3-chloropropane	41	87.5	63.7-111

Functional areas of the SOP that may be significant sources of analytical error are:

1. Addition of internal standard: The amount and concentration of internal standard

added is critical. The nominal concentration is used in calculating target analyte concentration.

2. Samples must be stored as outlined in the SOP to minimize analyte degradation and solvent evaporation.

3. Sample temperature: Samples must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.

4. Poor column condition may results in inadequate analyte separation and inaccurate integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis is included in the data package, if required.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades

- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.6 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on the local area network, LIMS, or the Lab QA SharePoint site for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies/HP 5975C GC/MS User's Manual.

California Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch, Berkeley, CA 94704; *Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry,* February 2002.

OI Analytical Model 4552 Autosampler User's Manual.

Teledyne Tekmar Stratum Purge & Trap User Manual.

USEPA Method 524.2, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry* Revision 4.1, 1995.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP, following the Region 9 QA Plan, specifies preservation and storage temperatures of > 0° to ≤ 6°C, while the reference method specifies < 4°C.

2. Method 524.2 describes using the spectra generated by the analytical system as reference spectra for target analyte identification. This SOP specifies the use of selected ion monitoring (SIM) which relies on the presence of specific ions at the retention time of the standard. A full spectrum is not available for comparison, but lower detection limits are obtained.

3. Method 524.2 uses fluorobenzene as the internal standard; this procedures follows recommendations in the California Department of Health Services method and uses deuterated 1,2,3-trichloropropane.

4. Method 524.2 indicates that "The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture." The retention time window of ± 0.2 min used in this procedure prevents false negatives due to retention time shifts that may result from instrument changes or chromatographic anomalies caused by sample matrix. All peaks identified by the data system are reviewed by the analyst to confirm qualification.

Note: the California Department of Health Services method for 1,2,3-trichloropropane uses a heated purge; this procedures does not heat the sample while purging.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	Water Quantitation Limit, ng/L
1,2,3-Trichloropropane	96-18-4	5
1,2-Dibromoethane	106-93-4	5
1,2-Dibromo-3-chloropropane	96-12-8	10

SIM Ions, System Monitoring Compounds, and Internal Standards

Compound Name	IS	SMC Reference	SIM Primary Ion, m/z	SIM Secondary Ion m/z
1,2-Dibromoethane	TCP-d5	BFB	107	109
1,2,3-Trichloropropane	TCP-d5	BFB	75	61, 110
1,2-Dibromo-3-chloropropane	TCP-d5	BFB	157	75, 155
Bromofluorobenzene (BFB)	TCP-d5	-----	95	174, 176
1,2,3-Trichloropropane -d5 (TCP-d5)	-----	-----	79	114

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
BFB	Every 12 hrs.	See below
IC %RSD	As needed	≤ 20%
SCV %D	As part of IC	≤ 30%
CCV %D	Every 12 hrs.	≤ 30%
CCV IS/SURR Area	Every 12 hrs.	±30% of IC
CCV Ret Time Drift	Every 12 hrs.	±30 sec of IC
LCS Recovery*	Every 12 hrs.	
1,2,3-Trichloropropane	85-123 %	
1,2-Dibromoethane	85-128 %	
1,2-Dibromo-3-chloropropane	52-123 %	
QLS Recovery	Every 12 hrs.	60 – 140%
MB, SB	Every 12 hrs.	< ½ QL
MS/MSD*	Each Batch of 20 samples or less	
1,2,3-Trichloropropane	51-147 % Recovery	≤ 20 RPD
1,2-Dibromoethane	65-133 % Recovery	≤ 34 RPD
1,2-Dibromo-3-chloropropane	23-171 % Recovery	≤ 30 RPD
Surrogate Recovery	Each Sample	80-119%
Sample IS Area	Each Sample	±30% of CCV1

* Limits calculated from historical data from March 01, 2016 to August 31, 2016.

BFB ion abundance ratios must meet the following criteria:

Mass (m/z)	Relative Ion Abundance Criteria
50	15 - 40 % of mass 95
75	30 - 60 % of mass 95
95	Base peak, 100 % relative abundance
96	5 - 9 % of mass 95
173	< 2 % of mass 174
174	>50 % of mass 95 (Mass 95 must be base peak)
175	5 - 9 % of mass 174
176	> 95 but < 101 % of mass 174
177	5 - 9 % of mass 176

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The Agilent ChemStation software requires that the FC43 spectrum meet the following criteria:

Mass	Target % of Mass 69
50	0.3-5
69	100
131	20-120
219	20-120
414	0.3-10
502	0.3-10

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APPENDIX D.
INSTRUMENT INFORMATION

PURGE & TRAP CONCENTRATOR/AUTOSAMPLER PARAMETERS

Recommended Purge and Trap Concentrator Operating Parameters

The operating parameters for the purge & trap concentrators. These parameters may vary slightly to optimize instrument responses.

PARAMETER	SETTING
Standby temperature	35°C
Preheat temperature	N/A
Prepurge time	0.5 min
Sample temperature	Ambient
Purge Time	11 minutes
Dry purge	2 minutes
Dry purge flow	100 mL/min
Purge Flow	40 mL/min
Desorb preheat temperature	245°C
Desorb	2.00 minutes @ 250°C
Desorb flow	150 mL/min
Bake	15 minutes @ 260°C
Auto drain	Off (controlled by Autosampler)
Bake gas bypass	Off
Valve temperature	150°C
Mount temperature	100°C
Line temperature	150°C

OI Analytical Model 4552 Autosampler or Varian Archon

The Autosampler delivers an aliquot of the water sample directly from the 40 mL sample vial into the sparge vessel on the concentrator. The Autosampler can be programmed to add the internal standard and surrogate into the sample during the transfer process. In water analysis mode, the settings for the Autosampler method are equivalent to the settings on the concentrator. The following parameters must be established on the Autosampler: sample volume, dilution, standard addition, purge time (same as concentrator), and number of vials to be analyzed.

Standards loading:

1. Prepare standards and blank spikes in a 50-mL volumetric flask with acidified method blank water.
2. Gently invert three times.
3. Gently pour the standard solution into the 40-mL vial (pre-label with information about the standard), down the side of the vial, without any agitation. Overfill the vial to form an inverted meniscus. Cap the vial. Invert the vial to ensure that there

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are no air bubbles present.

4. Gently place the vial in the appropriate autosampler position.
5. The autosampler will analyze a 25 mL aliquot and add 1 µL of the 5 µg/mL VOA IS solution. The amount used results in the analytical equivalent of 200 ng/L.

Sample Loading:

1 Equilibrate the sample to room temperature.
2 Remove the custody seal if present and place the vial in the appropriate position of the autosampler.
3 For MS/MSD sample inject the specified amount of the standard through the septum and place the vial in the autosampler.

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APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

RECOMMENDED GC/MSD PARAMETERS

MSD Parameters

The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

BFB analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	100°C
Initial Oven Time	0.5 minutes
Temperature Ramp	25°C/minute for 3.6 minutes
Final Oven Temp	190°C
Final Hold Time	1.5 minutes
Inlet mode:	Split
Split vent flow:	2 mL/min
Column Flow rate	0.97 mL/min at constant flow mode
Electron Energy	70 volts (nominal)
MS Scan range	35-260 amu

VOA analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.25 minutes
Column Flow rate	0.92 mL/min at constant flow mode.
Initial Oven Temp	35°C
Initial Oven Time	4.0 minutes
Temperature Ramp	8°C/minute to 180°C for 0 minutes; 25°C/minute to 220°C
Final Oven Temp	220°C
Final Hold Time	7.0 minutes
Inlet mode:	Split, Split Ratio 2:1
Split flow:	2 mL/min.
MS Quad	150°C
MS Source	230°C
Electron Energy	70 volts (nominal)
MS Scan	SIM Mode
Ions	61, 75, 79, 95, 107, 109, 110, 114, 155, 157, 174, 176
Dwell time	100 for each ion

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Analytical system preparation:

Leak Checking
From the ChemStation Instrument Control panel of the Agilent 5975C MSD select View, Tune and Vacuum control.
Select Spectrum scan. Check the nitrogen (m/z 28), water (m/z 18), to FC43 (m/z 69) ratio. Ratios for ions 28 and 18 should not exceed 20% of ion 69. Values higher than indicated above are indicative of large leaks and must be corrected.

Auto Tuning
Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned.

Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

Preparation for an Initial Calibration
Perform an autotune of the analytical system prior to an initial calibration.

1. The system should be reset to default parameters as follow:
   a. From the ChemStation Instrument Control panel of the MSD select View, Tune and Vacuum control. Select File, Reset to Default, Autotune.
   b. If the DC polarity for the system is normally set to negative for the system, resetting the tune parameter will set it to positive. Set the parameter to negative by selecting Parameters, Manual tune, DC polarity and slide the polarity selector to negative.
2. Save the default parameters by selecting save tune, Autotune.u.
3. Autotune the system by selecting Tune, Autotune.
4. The system will generate an Autotune report.
5. Save the resulting tune file by selecting File, Save tune Value
6. The tune file name is selected as outlined in the "ChemStation File Naming Convention".
7. Generate the tuning report by selecting File, Generate report.

Preparation for a Continuing Calibration

1. Perform a mass axis calibration of the analytical system prior to continuing calibration. By selecting calibrate, Mass axis.
2. Save the resulting tune file by selecting File, Save tune Value.
3. The tune file name is selected as outlined in the "ChemStation File Naming Convention".
4. Generate the tuning report by selecting File, Generate report.

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Manual tuning

If the system fails to meet the tuning criteria, the source may need to be cleaned or manual tuning may be required. BFB or DFTPP tuning routines may be used to correct ions ratios.

To manually tune the system, select Manual Tune from View menu in Instrument Control view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Incorporate the new tune parameters and generate today's method

1. Load a copy of the last initial calibration from C:\HPCHEM\1\Methods\Initial.
2. From the ChemStation Instrument Control panel of the Agilent 5975C MSD click on Select MS Tune File icon, click on the name of tune file generated today.
3. Select MS/SIM San Parameters. If necessary, adjust the EM voltage by adding or subtracting voltage relative "REL" to today's tune voltage.
4. Save the resulting method file as outlined in the as outlined in the "ChemStation File Naming Convention" by selecting File, Save method.

Mass Calibration

Perform mass calibration of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Replacement	Annually or as needed	When trimming no longer returns chromatographic performance.
Ferrules	As needed	Replace ferrules when changing columns and inlet/detector parts.
Purge/Sample Lines	Annually or as needed	Bake out and purge. Clean with organic free water if necessary.
Trap	Every 6 months or as needed	Replace with loss of performance/low response.

MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check FC43 level		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

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APPENDIX G.
CHEMSTATION FILENAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA
BFB	BFB

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DFTPP DFT

C: Channel (use when applicable):
Front A
Back B
Both AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

YY: Year i.e. 13 for 2013

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APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 353
Revision: 3, Effective: 10/17/2016

Low Level Volatiles

Revision	Effective Date	Description
0	10/31/2008	1. New SOP.
1	06/06/2011	1. Changed internal standard and surrogate to 1,2,3-trichloropropane-d5 and bromofluorobenzene, respectively. 2. Updated target analyte list to include 1,2,3-trichloropropane, 1,2-dibromoethane (EDB), and 1,2-dibromo-3-chloropropane (DBCP) and remove 1,2-dichloropropane. 3. Added provision for alternative analytical systems. 4. Minor edits throughout. 5. Appendix F, updated maintenance schedule.
2	08/05/2013	1. Combined CCV and LCS into one analysis. 2. Updated sections 3 and 11 to current format. 3. Minor edits throughout for clarity.
3	10/17/2016	Limited revision to address the following: 1. Removed preparation of standards in 50-mL syringe in Section 8.3.2 and Appendix D. 2. Corrected volumetric flask size for BFB solution in Section 7.3.2. 3. Removed typical data package format (Appendix H). 4. Updated control limits for BS/MS/Surrogate and method performance data. 5. Minor edits throughout.

ED_006532_00005075-00131

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 354
VOLATILE ORGANIC COMPOUND ANALYSIS IN WATER

Revision 12
Effective Date: October 17, 2016

Reviewed by: _____ 10/3/16
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: Barbara Bates 10/3/2016
Barbara Bates, Laboratory QA Officer — Date

Approved by: _____ 10/3/16
Peter Husby, Laboratory Director — Date

Periodic Review:

Signature	Title	Date

This SOP was prepared by ICF for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105086-19312

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the analysis of volatile organic compounds (VOCs) in water by gas chromatography/mass spectrometry (GC/MS). This SOP is based on EPA Method 524.2, Revision 4.1, 1995. Deviations from the reference methods are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

This SOP is applicable to the analysis of surface water, ground water, and drinking water for VOCs, including SDWA compliance samples. It is not appropriate for NPDES compliance samples. The quality control (QC) criteria specified in this SOP meet compliance criteria for drinking water monitoring projects.

2 METHOD SUMMARY

VOCs are purged from a 25-mL sample in a fritted sparge cell, separated in a narrow bore fused silica GC column, and detected by a mass spectrometer. Target volatile organic compounds are identified in the sample by comparing the mass spectra to the mass spectra in the National Institute of Standards and Technology (NIST) library and the GC retention times of the target analytes to retention times of standards analyzed under the same conditions as samples. Each compound is quantitated using average response factors from the most recent initial calibration.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

Calibration Standard (CAL) –The CAL solutions are used to calibrate instrument response with respect to analyte concentration. CAL solutions are prepared in the laboratory by diluting vendor supplied materials (pure material or solutions of analytes at certified concentrations).

Mass to charge ratio (m/z) – equals ion mass (in u) divided by number of unit charge for the ion.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan (CHP) and the Region 9

Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the CHP for further information and the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional chemical-specific information.

4.1.1 Methanol

Methanol is the primary solvent used for the preparation of standards in these procedures. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing, and shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly. Use methanol in a laboratory fume hood with appropriate personal protective equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammable storage cabinet away from oxidizers and sources of ignition.

4.1.2 Hydrochloric acid

Hydrochloric acid is a corrosive poison. Liquid and mist cause severe burns to all body tissues and may be fatal if swallowed or inhaled. Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms of exposure by inhalation may include irritation of the nose and throat, and labored breathing. Do not get acid in eyes, on skin, or on clothing. Skin contact can cause redness, pain, and severe skin burns. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes.

When diluting an acid, the acid should always be added slowly to water and in small amounts. Never use hot water and never add water to the acid. Water added to acid can cause uncontrolled boiling and splashing. Concentrated hydrochloric acid is incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates and other alkaline materials. Acids are incompatible with materials such as cyanides, sulfides, sulfites, and formaldehyde.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration standards, lower concentration reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases

from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Aqueous acidic VOC waste (wastewater, hydrochloric acid, trace halogenated volatile compounds)	Hazardous Waste	Corrosive
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Waste pump oil (trace halogenated volatile compounds)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned 40-mL screw cap vials equipped with Teflon-faced silicone septum. Volume collected should be sufficient to allow for replicate analysis yet minimize waste disposal. Three 40-mL vials should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form. If discrepancies are noted, inform the sample custodian.

Update the LIMS internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS using the “return to home

location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

Samples for VOC analysis are delivered by the Sample Custodian to Room 201, logged into the Laboratory Information Management System (LIMS), and transferred to the sample refrigerator (or freezer, as applicable).

5.3 Preservation Verification

Unless specified otherwise in project plans or the COC, samples should be preserved at the time of sampling to a pH < 2 with hydrochloric acid. Drinking water compliance samples must be dechlorinated with ascorbic acid or sodium thiosulfate and preserved with hydrochloric acid to pH < 2 at the time of sampling. Drinking water compliance samples that are not preserved must be re-sampled and preserved before a valid analysis can be performed. If an unpreserved drinking water compliance sample is received, inform the Chemistry Technical Director immediately so that the proper notifications can be made.

5.4 Sample Storage

Samples must be stored at >0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Acid preserved samples must be analyzed within 14 days from the date of sample collection; unpreserved samples must be analyzed within 7 days from the date of sample collection. See Section 5.3 regarding additional requirements for drinking water compliance samples.

Sort samples according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times.

6 INTERFERENCES

Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, or solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Sections 8.3.2.1 and 8.3.2.2. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and dichloromethane) through the septum seal into the sample during storage and handling.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

Solvents and other compounds, which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Dichloromethane, acetone and other common laboratory chemicals are target analytes under this SOP and must be excluded from Room 201. Particular attention must be paid to the possibility of transport of solvent vapors on individuals. Analysts should never enter Room 201 after being in the extraction laboratories or glassware washing area.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- GCMS System

  Gas Chromatograph (GC): Hewlett Packard/Agilent 6890, 6890N, or 7890, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, split/splitless injection port, and electronic pressure control (EPC).

  Mass spectrometer: Hewlett Packard/Agilent 5973, 5973N, or 5975, or equivalent, capable of scanning from 35 to 300 amu every two second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 25 ng of BFB is injected through the GC inlet.

  Column: Hewlett Packard HP-624 25M x 0.20 mm, 1.12 micron film, or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

- Data system: ChemStation (Agilent), or equivalent, able to control the GC/MS

system and to acquire, store, and reduce mass spectral data. The software must be able to process a GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.

- Purge and Trap Concentrator: Tekmar 3000, 3100, Stratum, EST Encon Evolution, or equivalent.
- Autosampler: Varian Archon, EST Centurion, or equivalent.

Other GC/MS systems with similar configurations can be used to analyze samples following this SOP as long as the instrumentation meets the requirements of this SOP.

7.2 Reagents

All chemicals must be entered into the Environmental Management System (EMS) upon receipt. Analysts must enter all reagents except organic-free method blank water into the LIMS.

Reagents may contain impurities that affect analytical data. Only materials that conform to the American Chemical Society (ACS) reagent grade specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

- Methanol (Purge and Trap grade).
- Reagent water: water in which method analytes or other interferences are at less than one-half the QL of the analytes of interest. Reagent water is prepared by bubbling contaminant-free inert gas through EPA Region 9 Laboratory deionized water. (Refer to EPA Region 9 Laboratory SOP 205 *Preparation of Organic-free Method Blank Water*.)
- Hydrochloric acid, (HCl) - analytical reagent grade
- Hydrochloric acid 1:1 (v/v), 1:1 HCl – carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water and mix.

7.3 Standards

Standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials.

All standards must be entered into the Environmental Management System (EMS) upon receipt. The analyst must enter all standards into the LIMS. Standards are stored in designated refrigerators or freezers. Standards are not to be stored with samples. Protect all standards from light when stored.

Store ampulated standard solutions in the designated Room 201 refrigerator at >0° to ≤ 6°C. Follow manufacturer's recommendations for solution expiration date. Store all working standard solutions in glass bottles or vials with Teflon lined screw caps at ≤-10°C.

Several standard solutions contain peroxide-forming compounds such as acrylonitrile, diisopropyl ether, 1,1-dichloroethene, 1,4-dioxane, 4-methyl-2-pentanone, styrene, tetrahydrofuran, and vinyl chloride. Containers should be labeled with a peroxide-forming compound precautionary label. Discard dates and disposal instructions specified in USEPA Region 9 Laboratory SOP 785 *Procedures for Storage, Monitoring & Handling Peroxide forming Chemicals* must be followed.

7.3.1 General guidelines for preparation of diluted standards:

- All working standards must be prepared in clean, dry, volumetric flasks – see the tables in Section 7.3.2 for appropriate volumes.
- Add a volume of purge and trap grade methanol equal to at least one-half the total volume of the flask leaving sufficient volume to add all the solutions in the preparation.
- Use only gas-tight syringes in the volatiles laboratory. Triple rinse syringes with purge and trap grade methanol both prior to and after each use.
- Syringes should be selected to minimize measurement error. The percent error is high at the low end and it may be difficult to handle the syringe and plunger if it is used at full volume.
- Add the appropriate volume of each standard to the volumetric flask with the syringe needle beneath the surface of the methanol. Place the ground glass stopper on the flask between additions of standards.
- After adding the solutions indicated in the table, bring the volume to the mark with purge and trap grade methanol.
- Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).
- Pour the contents of the volumetric flask into a screw cap vial the same volume as the flask used for preparation, (or several smaller vials, but minimize headspace) equipped with a Teflon-lined screw cap and a Mininert valve.
- Do not use pipettes to transfer solutions containing volatile compounds because the vacuum used to draw the solutions up into the pipettes can cause some volatile compounds to come out of solution.
- All standards must be labeled with LIMS Standard ID, expiration date, analyst initials, and description.
- Expired or otherwise unusable standard solutions must be disposed in an appropriate waste container.

7.3.2 Working Standards:

- 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/µL)

  Dilute 20 µL of a 5,000 ug/mL solution of 4-Bromofluorobenzene (VOA Tuning Compound solution, Restek catalog #30003 or equivalent) to 2 mL with purge and trap grade methanol.

  Replace the solution after 6 months, or sooner if analysis indicates that the tuning solution has degraded.

- Internal Standard / Surrogate solution (VOA IS/SS, 125 ng/µL)

  Dilute VOA IS/SS custom mix, Restek catalog #566692 or equivalent, as outlined in the following table.

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. ng/µL
Custom IS Mix	Restek	10,000	125	10	125

  Fill a clean 5-mL standard reservoir and immediately install the standard reservoir in the appropriate standard position on the autosampler.

  Replace the solution after 14 days, or sooner if analysis indicates that the standard solution has degraded.

- Calibration mix (DW Mix, 25 - 200 ng/µL)

  Dilute the following standards, or equivalent, as outlined in the following table.

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
502.2 Cal. Mix #1	Restek 30042	2,000	25	2	25
1,1,2-Trichloro-1,2,2-trifluoroethane	Restek 30462	2,000	25	2	25
VOA Calibration Mix 1 (ketones)	Restek 30006	5,000	80	2	200
1,2-Dibromo-3-chloropropane*	Restek 30270	2,000	75	2	100

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
Carbon Disulfide	Restek 30258	2,000	25	2	25
Custom Ether/ THF Mix	Restek 30465	2,000	100	2	100
Restek Mega	Restek 30431	2,000	25	2	25

*1,2-Dibromo-3-chloropropane concentration includes 25 ng/µL from the 502.2 Cal Mix or the Mega Mix and 75 ng/µL from this standard.

Replace the solution after 7 days, or sooner if analysis indicates that the standard solution has degraded.

- Second Source Verification (SCV) Solution (DWLF solution, 25 - 500 ng/µL)

  Dilute the following standards, or equivalent, as outlined in the following table.

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
502/524 VOC MIX	Supelco 5-02111	2,000	25	2	25
VOC MIX 6	Supelco 48799-U	2,000	25	2	25
VOA Calif. Oxygenates Mix	Supelco 4M6872-U	2,000-10,000	100	2	100-500
1,1,2-Trichloro-1,2,2-trifluoroethane	Supelco 4-7944	2,000	25	2	25
8240 Standard Mix 2	Supelco 47364	2,000	200	2	200
Carbon Disulfide	Supelco 40363	5,000	10	2	25

Replace the solution after 7 days, or sooner if analysis indicates that the standard solution has degraded.

7.4 Supplies

- Gas-tight syringes (5-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 25-mL and 50-mL).

- 25-mL fritted sparge vessels.
- Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers
- pH paper (pH 0-14 range).
- Trap K (VOCARB 3000, EST EV1, or equivalent).
- VOA vials – pre-cleaned 40-mL glass vials equipped with screw-hollow caps lined with 22 mm PTFE-faced silicone septa.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point.

Set-up the purge and trap following the operating parameters provided in Appendix D.

Ensure that appropriate waste containers are present and properly labeled.

Check the mass spectrometer for leaks on a daily basis prior to the analysis of the tuning check compound using the instructions provided in Appendix D.

8.1.1 Mass calibration

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions. Use perfluorotributylamine (FC43) to perform mass calibration of the instrument. Include the mass calibration printout with ICAL data.

Calibrate the mass axis of the MS prior to analyzing the BFB solution each day that samples are analyzed. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E, and generate a tune report. Include the mass calibration printout with analysis data.

8.1.2 GC/MS Tuning Check

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Inject 0.5 µL of a 50 ng/µL BFB solution using the operating parameters provided in Appendix D. Optionally, purge BFB in water solution. Prepare this solution by

adding 1 µL of a 50 ng /µL BFB solution to a 50-mL syringe filled with acidified reagent water and decant into a 40-mL vial as shown in Appendix D.

Evaluate BFB in Chemstation by selecting "Tuner", "Evaluate BFB". The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances. Follow requirements and take corrective action as described in Section 9.2.1.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration. Prepare standards at the following recommended concentrations:

Calibration Standard Amounts for 50 mL Final Volume

Calibration Level	Concentration, µg/L	VOA IS/SS* Mix 125 µg/mL, µL	DW Mix 25 µg/mL, µL
1	25	1	50
2	10	1	20
3**	5	1	10
4	2	1	4
5	1	1	2
6***	0.5	1	1

* Added by the autosampler.
** CCV, LCS, MS, MSD concentrations except as noted below.
*** LCV/MRL/QLS concentrations except as noted below. Do not vary the concentration.

NOTE: Since ketones, ethers, and 1,2-dibromo-3-choropropane purge poorly from aqueous samples, they are analyzed at higher concentration ranges. See Section 7.3.2 for recommended concentrations.

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned compounds are the 1,3- and 1,4-dichlorobenzenes.

No quantitation ion may saturate the detector; review the 25 µg/L calibration standard (or the highest concentration included in the initial calibration) to confirm that this criterion is met.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound for all calibration standards using the following equation. The quantitation ions and internal standard assignments are listed in Appendix C.

$$RRF = (Ax)(Cis) / (Ais)(Cx)$$

Where

Ax = Area of quantitation ion of compound x
Ais = Area of quantitation ion for associated internal standard
Cx = Concentration of compound x
Cis = Concentration of the associated internal standard

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/ RRF_{avg})*100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{ave})^2}{n-1}}$$

RRF_{avg} = Average Relative Response Factor from the ICAL

Analyze a SCV at standard level 3 outlined in Section 8.2.1. The SCV is prepared in the same manner as the CCV except it is spiked with the Second Source Verification (SCV) Solution (DWLF solution, 25 ng/µL, ketones 200 ng/µL).

Refer to Appendix D for ChemStation calculation and calibration instructions.

Refer to Section 9.2.2 and Appendix C for acceptance criteria and corrective action requirements.

8.2.2 Continuing Calibration Verification (CCV)

Perform continuing calibration using the recommended concentration outlined in Section 8.2.1.

The data system calculates the percent deviation (%D) of the RF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\ 100$$

Where:
RRF_C: Relative Response Factor of compound in the CCV.
RRF_{avg}: Average Relative Response Factor from the ICAL.

Refer to Appendix D for ChemStation calculation and calibration instructions.

Refer to Section 9.2.3 and Appendix C for acceptance criteria and corrective action requirements.

8.2.3 Closing Calibration Verification

When analyzing drinking water compliance samples, analyze a closing calibration verification using the recommended continuing calibration concentration level outlined in Section 8.2.1.

Refer to Section 9.2.4 and Appendix C for acceptance criteria and corrective action requirements.

8.2.4 Low Level Calibration Verification (LCV) or Quantitation Limit Standard (QLS)

Analyze the low level calibration verification using the recommended concentration outlined in Section 8.2.1.

The LCV concentrations match the QL concentration (at the instrument). The recovery of analytes in the LCV is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in the ug/L.

Refer to Section 9.2.5 and Appendix C for acceptance criteria and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample to reach ambient temperature before analysis.

Verify that the sample identification on the vials coincides with the sample identification on the COC and the LIMS to ensure that the correct sample is being analyzed.

Check if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the sample to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS work order memo field.

Note: After the analysis is complete, check the pH for each sample using pH 0-14 range pH paper. If samples are drinking water compliance, check the residual chlorine in each sample using chlorine test strips. Record the results in LIMS. If any sample has a pH greater than 2 or if a drinking water sample has residual chlorine, make a note in the LIMS work order memo field. Contact the Chemistry Team Leader who will follow up to determine if resampling is required.

8.3.2 Sample Analysis and Analytical Sequence

This section describes preparing the analytical sequence and analyzing the samples.

Make a LIMS batch containing the samples to be analyzed and an empty LIMS sequence to obtain LIMS assigned IDs for the instrument and batch QC samples.

Document sample dilutions by entering the initial/final volumes in the LIMS bench sheet.

Prepare all instrument and batch QC samples in acidified reagent water.

To spike the MS and MSD, quickly remove the 40-mL sample vial cap from each vial and spike directly in the field sample vial and recap the vial.

Prepare the samples to be analyzed. The following table represents the spike levels recommended for most projects:

Spike Amounts

Sample	VOA IS/SS Mix* 125 µg/mL, µL*	DW Mix 25 µg/mL, µL
Blanks	1.0	NA
Samples	1.0	NA
BS/LCS	1.0	10.0

MS/MSD	1.0	8.0

Prepare LCS in 50-mL volumetric flask and transfer to 40-mL vial.
NA = Not Applicable
* IS/SS is added by autosampler.

Load the samples in the autosampler according to their designated positions in the sequence file. The following represents a recommended analysis sequence:

1. BFB
2. CCV/LCS*
3. LCV (QLS)
4. MB
5. Samples
6. MS/MSD, as needed**
7. Sample dilutions, as needed
8. Storage Blanks and Instrument Blanks, as needed

* CCV and LCS requirements may be satisfied in one analysis.
** When included, analyze MS/MSD and source sample early in the sequence to allow QC review prior to completion of the sequence, if possible.

Gently place the vial in the appropriate autosampler position.

Enter sample sequence in the instrument software. Include the LIMS sample number (WO-sample number) in the "Sample" field.

Name the data files according to the data file naming convention outlined in Appendix E.

8.3.2.1 Method Blank

Prepare method blanks by filling a 40-mL screw-capped volatile vial fitted with a PTFE-faced silicone septum with acidified organic-free method blank water.

See Section 9.3.1 for frequency, acceptance criteria, and corrective action requirements.

The method blank is acceptable if it meets criteria listed in Appendix C.

8.3.2.2 Instrument Blank

As needed, prepare instrument blanks in the same manner as method blanks.

See Section 9.3.2 for acceptance criteria and corrective action requirements.

Note: The instrument blanks may be analyzed beyond the 12 hour tune time period.

8.3.2.3 Storage Blank

Prepare storage blanks as described in Section 9.3.3.

See Section 9.3.3 for frequency, acceptance criteria, and corrective action.

Note: The storage blanks may be analyzed beyond the 12 hour tune time period.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

For a target analyte to be identified as present in a sample both the retention time and the mass spectra of the peak must match those of the standard.

This SOP specifies the use of NIST library spectra as reference spectra to prevent confusion due to co-elution of compounds in the calibration standards. Therefore, do not update the reference spectra in the method.

All ions present in the NIST mass spectra at a relative intensity of 10 % of the most abundant ion must be present in the sample spectra.

The relative intensities of the ions must agree within 20 % between sample spectra and the CCV level spectra of the most recent ICAL.

Ions present in the sample but not present in the standard spectra should be reviewed for possible coelution.

If a compound cannot be verified consistent with these criteria but, in the technical judgment of the analyst, is present, the analyte is reported and supporting evidence must be noted on the raw data.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out a quantitation report and chromatogram for each sample. Use the average relative response factor from the initial calibration for quantitation.

8.3.4 Calculations

Target analyte concentrations as shown on the ChemStation quantitation report are calculated using the following equation:

Conc. (µg/L) = Ax * AMTIS * DF / (AIS * RRF)

Where:

Ax	= area of the quantitation ion of the compound
AMTIS	= amount of internal standard in µg/L (5 µg/L)
DF	= dilution factor
AIS	= area of the characteristic ion of the associated internal standard
RRF	= analyte average relative response factor from the initial calibration

LIMS calculates the final analyte concentration in samples from the result in the ChemStation quantitation report and the initial and final volumes in the LIMS bench sheet.

8.3.4.1 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow EPA Region 9 Laboratory SOP 835 *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.5 Review of Tentatively Identified Compounds:

The TICs reporting requirement is determined by the Technical Director on a project by project basis and noted in the LIMS project or work order memo fields. Check project requirements before reviewing data.

Load the data file of the most concentrated valid analysis of the sample.

Review the library search results for the following:

Check that each significant peak in the LSC Report has been reported either in the ChemStation quantitation report or the LSC report.

Report those TICs for which the response is greater than 20% of the closest internal standard.

Use the nearest internal standard free of interferences for quantitation.

Report up to 10 TICs based on largest total area.

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

The relative intensities of the major ions should agree within 20 %.

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

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

Ions present in the reference spectrum but not within the scan range of the method should not be considered when making a tentative identification.

If, in the technical judgment of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown"; attempt to classify the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.).

Report the following:

a. Class of compound instead of specific isomers unless the identity of the specific isomer is known. As an example, report dichlorobenzene instead of 1,2-dichlorobenzene. Alternatively, report 1-methylnaphthlene if the calibration standard has 2-methylnaphtalene and the TIC retention time is not that of 2-methylnaphtalene. Edit the TIC name to correct errors and remove extraneous punctuation.

b. Total of all hydrocarbons as "Total Hydrocarbon", if required, is determine as follows:
   - Click "Int" and make sure that "integrate a peak" option is not selected.
   - Click and hold the left mouse button and drag the cursor across the entire hydrocarbon peak range; this will generate an average spectrum of the range.
   - Determine whether m/z 55 or 57 is larger in the spectrum. Click "Int", "Ion Chromatogram" and enter the larger of the two ions (55 or 57).
   - Click "Int" and select "integrate a peak" then integrate the hydrocarbon peak range.

- Click "File", "Print Trace + spectrum". Click "Int", "Integration Results", "Print"; this prints the area for the total hydrocarbon peak.
- Calculate the estimated total hydrocarbon concentration by dividing the area of the total hydrocarbon peak determined above by the area of the closest IS to the center of the total hydrocarbon peak from the quantitation report (not the LSC report) then multiplying this result by the concentration of the IS.
- Click "LSC", "LSC for current scan"; this adds the peak to the LSC report.
- Click "LSC", "Edit LSC Results". Select "unknown hydrocarbon" and change name to "Total Hydrocarbon" then enter the concentration of the total hydrocarbon peak determined above.

Exclude the following compounds from the report:

a. Analytes eluting prior to the first eluting target compound in the CCV.
b. TICs that were detected in the method blank.
c. Column bleed (i.e. siloxanes).
d. CO2/fixed gases peak.
e. Electronic noise peaks.

If the base peak saturates the detector, document this in the data. Do not dilute a sample to get the base peak of a TIC within the detector range. If a sample containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC base peak area from the diluted analysis to estimate the concentration of the TIC.

8.3.6 Data and QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, perform the following QC reviews for compliance with SOP requirements:

- Process and review the results for the CCV and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and LCV (QLS) results are within QC limits. See Section 9.2 for instrument QC requirements.

- Process and review the results for the MB, LCS, and MS/MSD and batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.

- Print a ChemStation QA-QC Check Report after processing all the samples.

- Check the sample's surrogate and internal standard recoveries with criteria in Appendix C.
- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out and initial all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Delete the compound (Qdel) in ChemStation.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.7 Data Export and LIMS Entry

Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table and to populate the empty LIMS sequence.

Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using DataTool.

Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See the LIMS manual for detailed procedure.

Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

8.4 Maintenance:

The analyst should observe trends in the data such as declining response, erratic relative

response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Routine maintenance procedures and frequency are listed in Appendix F.

8.4.1 Purge and trap maintenance

Symptom:

- Decline in chloromethane, bromomethane, chloroethane, bromoform, and / or 1,2-dibromo-3-chloropropane responses.

  Cause: purge flow rate or trap problem.
  Corrective action: Check purge flow; replace trap if necessary.

- Carryover of naphthalene and/or 1,2,3-trichlorobenzene

  Possible causes: Cold spot in system, especially the transfer lines between the sparge unit and the concentrator or between the concentrator and the GC or analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

  Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.

  Possible cause: Degradation of trap.
  Corrective action: Replace trap.

- Loss of all purged analytes.

  Possible cause: Leak in system.

Corrective action: Leak check purge and trap system. Inspect sparge ferrules and replace them when worn or distorted.

8.4.2 GC Maintenance

Symptom

- Carryover

Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

  Possible cause: column flow rate problem.

  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution or tailing.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.3 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- Failing tune checks

Corrective action: Clean the source.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists

of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A demonstration of capability (DOC) must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 GC/MS System Performance Check (BFB analysis):

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to analysis.

If the ion abundances fail to meet criteria listed in Appendix C, the BFB chromatogram should be examined for any obvious chromatographic problems (e.g. bad injection leading to poor response etc.). If the problem is determined to be related to poor chromatography take the necessary corrective action and re-analyze the BFB. If the BFB continues to fail the ion abundance criteria retune the mass spectrometer, it may be necessary to clean the ion source, or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the BFB time period has elapsed it must be re-analyzed.

9.2.2 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed once and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that criteria are satisfied.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

If the calibration does not meet the SCV criteria listed in Appendix C, the SCV may be re-analyzed once. If the failure is repeated, terminate the analysis, correct the problem, and prepare a new calibration curve.

9.2.3 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard.

Examine the retention time of the internal standards in the calibration verification standard.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

If the continuing calibration does not meet %D criteria listed in Appendix C, the CCV may be re-analyzed once. If the failure is repeated, the analysis shall be terminated, the problem corrected, documented, and two consecutive successful CCVs or a new initial calibration analyzed.

9.2.4 Closing Continuing Calibration Verification – required when analyzing drinking water compliance samples

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard.

Examine the retention time of the internal standards in the calibration verification standard.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

If the continuing calibration does not meet %D criteria listed in Appendix C, the closing CCV may be re-analyzed once. If the failure is repeated, drinking water compliance samples must be reanalyzed in a sequence with an acceptable closing CCV.

9.2.5 Low Level Calibration Verification (Quantitation Limit Standard)

A LCV (QLS) must be analyzed at the beginning of the analytical sequence (typically after the CCV/LCS).

Generate a LCV (QLS) report and check that the recoveries meet criteria specified in Appendix C.
Qualify and flag results in the LIMS Data Entry/Review table following

Appendix R of the Region 9 Quality Assurance Manual.

If the LCV (QLS) recovery does not meet criteria provided in Appendix C, rerun the LCV (QLS) once to verify. If still unacceptable, determine the cause and take corrective action.

9.3 Batch QC

9.3.1 Method Blank

A method blank must be analyzed at the beginning of the analytical sequence (typically before samples are analyzed).

If a method blank fails to meet criteria, use the following guidelines to determine when samples must be re-analyzed:

a) If the MB analyte value ≥½ QL and the sample result is less than five times the MB analyte amount, all associated samples containing less than five times the MB analyte amount may have to be re-analyzed. Consult with the Chemistry Technical Director or designee. Common laboratory contaminants (acetone, dichloromethane) are excluded; flag the results for these analytes following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

b) If the MB analyte value ≥½ QL and the sample result is greater than five times the MB analyte concentration or is non-detected, report sample result.

9.3.2 Instrument Blank and high concentration samples

In the event that a known high concentration sample containing analytes which exceed the calibration range of the instrument is analyzed, analyze an instrument blank to demonstrate that the system is free of carryover contamination. If a high concentration sample was analyzed in the absence of an IB, the analyst must evaluate any sample that is analyzed immediately following the overrange sample to determine if carryover may have occurred.

Use the following guidelines when instrument blank data is available:

a) If the IB analyte value ≥½ QL and the sample result is less than five times the IB analyte amount, re-analyze the sample if an additional aliquot is available. If re-analysis is not possible, flag sample result following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

b) If the IB analyte value ≥½ QL and the sample result is greater than five times the IB analyte concentration, report sample result.

In the absence of an instrument blank, the subsequent sample result must be evaluated for potential contribution by the overrange sample. If the analyte value ≥½ QL, re-analyze the sample if an additional aliquot is available. If re-analysis is not possible, flag sample result following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

9.3.3 Storage Blank (SB)

Every Monday morning, or the first work day of the week, fill two 40-mL screw-cap volatile vials with PTFE-faced silicone septa with acidified organic-free method blank water and store them with the samples in the sample storage refrigerator in Room 201.

Analyze the storage blank, prepared and stored last week, on the first workday of the week.

Use the following guidelines if contamination is present:

a) If the SB analyte value ≥½ QL and the sample result is ≥½ QL but less than five times the SB analyte amount, flag sample result.

b) If the SB analyte value ≥½ QL and the sample result is non-detected or greater than five times the SB analyte concentration, report sample result unflagged.

9.3.4 LCS

Since the CCV and LCS are prepared from the same source and at the same concentration, one analysis serves both purposes. However, LCS acceptance criteria are determined from historical data.

Using the same file as the passing CCV, calculate LCS recovery:

$$\%R = \frac{C_m}{C_t} \times 100$$

Where

$\%R$ = percent recovery.
C_m = measured analyte concentration in the LCS.
C_t = true analyte concentration in the LCS.

Generate an LCS report and check that the recoveries meet criteria specified in Appendix C.

If the LCS recovery does not meet criteria provided in Appendix C, rerun the LCS

once to verify. If still unacceptable determine the cause, take corrective action and document these actions. Samples may not be analyzed without an acceptable LCS unless an approved discrepancy is obtained prior to continuing the analysis (see EPA Region 9 Laboratory SOP 820 *Laboratory Discrepancies and Corrective Actions*).

In the LIMS Data Entry/Review table, qualify and flag results associated with outliers following Appendix R of the Region 9 Laboratory Quality Assurance Plan.

9.3.5 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the affect of sample matrix on the measurement system. One set of MS/MSD samples must be analyzed for each SDG. Do not evaluate MS/MSD recovery for any analyte whose concentration in the MS/MSD source sample is more than four times the MS/MSD spike level. Do not evaluate MS/MSD recovery for any analyte exceeding the calibration range of the instrument.

Samples identified as field blanks or trip blanks cannot be used for MS/MSD sample analysis.

MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$	=	percent recovery.
C_{ms}	=	measured concentration of analyte in the MS, corrected for sample preparation and any dilutions.
C	=	measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions.
s	=	expected analyte concentration in the MS, corrected for sample preparation and any dilutions.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where

RPD = relative percent difference.

C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions.

C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the MS/MSD analytes do not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS accuracy or precision is likely to be matrix-related.

Flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Laboratory Quality Assurance Plan.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS ! = FAIL

CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Batch acceptable.
Case 2: Batch acceptable; matrix effect confirmed.
Cases 3 & 4: Batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS work order memo field.
Cases 5, 6, 7, & 8: Batch rejected. If additional sample volume is available, the batch should be re-analyzed.

9.4 Sample QC

9.4.1 Surrogate Recovery

Check the surrogate recovery in all field and QC samples immediately after analysis.

ChemStation calculates the surrogate recovery using the following formula:

Equation 9:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

The surrogate recovery must be within QC limits outlined in Appendix C.

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.
2. Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the runlog.

Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries meet criteria. If the sample and spikes show the same pattern (i.e., outside the limits), then sample reanalysis is not required.

If surrogate recoveries of the re-analysis are within limits, the problem is assumed to have been within the laboratory's control. Report the results from the re-analysis and submit data for both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS work order memo field.

If the re-analysis fails to meet criteria, report the results from the first analysis and submit the data for both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.4.2 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

Take the following steps if the internal standard areas do not meet criteria:

1. Check the system performance.
2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

Do not re-analyze the MS/MSD samples, even if internal standard areas are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

If the internal standard areas are of the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS work order memo field.

If the re-analysis does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance at the 95% confidence level (2σ). Data are from the Region 9 Laboratory for water samples analyzed from September 7, 2012 to February 11, 2013.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Sample handling. Loss of volatile compounds due to excessive sample handling.
2. Sample volatilization and degradation. Samples must be stored as outlined in the SOP to minimize losses.
3. Sample temperature: Samples must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
4. Poor column condition may results in inadequate analyte separation and inaccurate integration.
5. Trap condition.
6. Leaks in sample transfer and GC/MS systems.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, SCV, CCV/LCS, LCV (QLS), and MS/MSD) are recorded in the

LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS and on the benchsheet.

10.3 Analytical Sequence

The analytical sequence is documented in the Element database or in the instrument Run Log, date of analysis, QC solution IDs, analyst initials, lab sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes, laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies/HP 5973 GC/MS Users Manual.

Agilent Technologies 5975 GC/MS Users Manual.

EST Analytical Manuals (Centurion, Cobra L-S, Encon Evolution, HS9000, LC-241 Plus, and LGX50).

Varian Archon Autosampler and HP/Archon/Tekmar Concentrator Operator's Manuals.

U.S. Environmental Protection Agency, 1995. Method 524.2, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1.*

USEPA Method 5035A, *Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*; Draft Revision 1, July 2002.

USEPA Method 8000C, *Determinative Chromatographic Separations*; Revision 3, March 2003.

USEPA Method 8260B, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique*; Revision 2, December 1996.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP follows the Region 9 Laboratory Quality Assurance Plan which specifies preservation and storage temperatures of >0° to ≤ 6°C, while the reference method specifies < 4°C.

2. The reference method specifies using m/z ion 95 as the quantitation ion for 4-bromofluorobenzene. The Region 9 Laboratory uses m/z ion 174 for quantitation of 4-bromofluorobenzene to avoid possible interference from a target analyte.

3. Section 11.6 of Method 524.2 describes using the spectra generated by the analytical system as reference spectra for target analyte identification. This SOP specifies the use of NIST library spectra as reference spectra to prevent confusion due to co-elution of compounds in the calibration standards.

3. This procedure uses QC limits generated from Region 9 Laboratory data. Deviations are allowed for up to 10% of these limits. This allowance is not included in the reference method.

4. The three standard deviations of the mean retention time is not evaluated in this SOP as discussed in Method 524.2. ChemStation calculates an absolute retention time difference for sample components, not SD difference. A retention time window of ± 0.5 min is used in this SOP.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table contains target compounds and quantitation limits covered by this SOP. Routinely reported analytes are indicated; other listed compounds may be added on a project-specific basis. When required, lower quantitation limits may be reported when supported by method detection limit studies and appropriate QC and calibrations are performed. Analytes regulated under the Safe Drinking Water Act are identified.

Compound Name	CAS No.	QL, ug/L	Regulated	Routinely Report
Dichlorodifluoromethane	75-71-8	0.5		X
Chloromethane	74-87-3	0.5		X
Vinyl chloride	75-01-4	0.5	X	X
Bromomethane	74-83-9	0.5		X
Chloroethane	75-00-3	0.5		X
Trichlorofluoromethane	75-69-4	0.5		X
1,1-Dichloroethene	75-35-4	0.5	X	X
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	0.5		X
Acetone	67-64-1	4.0		X
Carbon disulfide	75-15-0	0.5		
Dichloromethane	75-09-2	0.5	X	X
tert-Butyl alcohol	75-65-0	10		
trans-1,2-Dichloroethene	156-60-5	0.5	X	X
tert-Butyl methyl ether (MTBE)	1634-04-4	2.0		X
1,1-Dichloroethane	75-34-3	0.5		X
Diisopropyl ether	108-20-3	2.0		
Ethyl *tert*-butyl ether	637-92-3	2.0		
2,2-Dichloropropane	594-20-7	0.5		X
cis-1,2-Dichloroethene	156-59-2	0.5	X	X
2-Butanone (MEK)	78-93-3	4.0		X
Bromochloromethane	74-97-5	0.5		X
Chloroform*	67-66-3	0.5	X	X
1,1,1-Trichloroethane	71-55-6	0.5	X	X
tert-Amyl methyl ether	994-05-8	2.0		
1,1-Dichloropropene	563-58-6	0.5		X
Benzene	71-43-2	0.5	X	X
1,2-Dichloroethane	107-06-2	0.5	X	X
Carbon tetrachloride	56-23-5	0.5	X	X
Trichloroethene	79-01-6	0.5	X	X
1,2-Dichloropropane	78-87-5	0.5	X	X
Dibromomethane	74-95-3	0.5		X
Bromodichloromethane*	75-27-4	0.5	X	X
cis-1,3-Dichloropropene	10061-01-5	0.5		X
4-Methyl-2-pentanone (MIBK)	108-10-1	4.0		
trans-1,3-Dichloropropene	10061-02-6	0.5		X
1,1,2-Trichloroethane	79-00-5	0.5	X	X
Toluene	108-88-3	0.5	X	X
2-Hexanone	591-78-6	4.0		
Tetrachloroethene	127-18-4	0.5	X	X
1,3-Dichloropropane	142-28-9	0.5		X

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Compound Name	CAS No.	QL, ug/L	Regulated	Routinely Report
Chlorodibromomethane*	124-48-1	0.5	X	X
1,2-Dibromoethane (EDB)	106-93-4	0.5		X
Chlorobenzene	108-90-7	0.5	X	X
1,1,1,2-Tetrachloroethane	630-20-6	0.5		X
Ethylbenzene	100-41-4	0.5	X	X
m&p-Xylene	106-42-3	1.0	X	X
o-Xylene	95-47-6	0.5	X	X
Styrene	100-42-5	0.5	X	X
Bromoform*	75-25-2	0.5	X	X
Isopropylbenzene	98-82-8	0.5		X
Bromobenzene	108-86-1	0.5		X
1,1,2,2-Tetrachloroethane	79-34-5	0.5		X
1,2,3-Trichloropropane	96-18-4	0.5		X
Propylbenzene	103-65-1	0.5		X
2-Chlorotoluene	95-49-8	0.5		X
4-Chlorotoluene	106-43-4	0.5		X
1,3,5-Trimethylbenzene	108-67-8	0.5		X
tert-Butylbenzene	98-06-6	0.5		X
1,2,4-Trimethylbenzene	95-63-6	0.5		X
sec-Butylbenzene	135-98-8	0.5		X
1,3-Dichlorobenzene	541-73-1	0.5		X
1,4-Dichlorobenzene	106-46-7	0.5	X	X
p-Isopropyltoluene	99-87-6	0.5		X
1,2-Dichlorobenzene	95-50-1	0.5	X	X
Butylbenzene	104-51-8	0.5		X
1,2-Dibromo-3-chloropropane	96-12-8	2.0		X
1,2,4-Trichlorobenzene	120-82-1	0.5	X	X
Hexachlorobutadiene	87-68-3	0.5		X
Naphthalene	91-20-3	0.5		X
1,2,3-Trichlorobenzene	87-61-6	0.5		X
Surrogate Compounds				
1,2-Dichloroethane-d4				
Toluene-d8				
4-Bromofluorobenzene				
1,2-Dichlorobenzene-d4				
Internal Standards				
Dichloromethane-d2				
Fluorobenzene				
Chlorobenzene-d5				

* Trihalomethanes

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

ANALYSIS	CRITERIA	Frequency
MS Calibration	Mass / Target % of Mass 69 50 / 0.3-5 69 / 100 131 / 20-120 219 / 20-120 414 / 0.3-10 502 / 0.3-10	With Every ICAL
MS Mass Axis	Calibrate the Mass Axis of the MS prior to analyzing the BFB standard. Adjust the EM voltage as necessary.	Each day that samples are analyzed
GC/MS System Performance Check (BFB analysis)	The ion abundance ratios must meet the following criteria. Mass / Relative Ion Abundance 50 / 15 - 40 % of mass 95 75 / 30 - 60 % of mass 95 95 / Base peak, 100 % relative abundance 96 / 5 - 9 % of mass 95 173 / < 2 % of mass 174 174 / >50 % of mass 95 (Mass 95 must be base peak) 175 / 5 - 9 % of mass 174 176 / > 95 but < 101 % of mass 174 177 / 5 - 9 % of mass 176 All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be greater than that of m/z 95.	Once every 12-hours
Initial Calibration (1)	Reported analytes should meet the maximum %RSD of 20. Data must be flagged for analytes not within the acceptance limits. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.	As Needed
Second Source Calibration Verification (1)	Recovery for of reported analytes must be within 70-130%. Data must be flagged as failing initial calibration criteria for analytes not within the acceptance limits. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.	With Every ICAL

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Continuing Instrument Calibration Verification (1)	The absolute value of the %D of all reported analytes should be ≤ 30%. Internal standard retention time should be within 30 seconds from that in the mid-point standard level of the most recent initial calibration. EICP area for any of the internal standards should be within (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria. Data must be flagged for analytes not within the acceptance limits.	Once every 12-hours
Low Level Calibration Verification (also QLS) (1)	The percent recovery for the reported analytes should be between 60 to 140 percent of the actual concentration. Data must be flagged for analytes not within the acceptance limits.	Once every 12-hours
Method Blank (MB)	The MB is acceptable if it contains less than one-half the quantitation limit (QL) of all target compounds. Data must be flagged for analytes not within the acceptance limits.	Once every 12-hours
Target Analytes	All ions present in the standard or reference mass spectrum at a relative intensity of 20 % of the most abundant ion should be present in the sample spectrum. The relative intensities of the ions in the sample mass spectrum should agree within 30% of the relative intensities of those ions in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum.	NA
Sample Internal Standards	Compare the IS retention times and areas in the field and QC samples analyzed within the 12-hour analytical period to the associated 12-hour CCV standard. The retention time for any internal standard should be within 0.5 minute. The total area of internal standard should be recovered within 30% from the associated 12-hour CCV standard. Data must be flagged for analytes not within the acceptance limits.	NA
Surrogates	See Table Below. Data must be flagged for analytes not within the acceptance limits.	NA

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LCS [1]	Reported analytes should meet the acceptance criteria or the batch may require re-extraction. Refer to the tables below for control limits. Data must be flagged for analytes not within the acceptance limits. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.	Once every 12-hours
MS/MSD [1]	Refer to the tables below for control limits. Flag outliers. Data must be flagged for analytes not within the acceptance limits.	One per SDG

[1] Up to 10 % of the compounds may fail to meet these criteria, but if the samples are for drinking water compliance, all regulated compounds must meet all QC criteria.

Quantitation Ions, Surrogates, and Internal

Compound Name	IS Reference	Surrogate Reference	Primary Ion, m/z
Dichlorodifluoromethane	1	1	85
Chloromethane	1	1	50
Vinyl chloride	1	1	62
Bromomethane	1	1	94
Chloroethane	1	1	64
Trichlorofluoromethane	1	1	101
1,1-Dichloroethene	1	1	96
1,1,2-Trichloro-1,2,2-trifluoroethane	1	1	101
Acetone	1	1	43
Carbon disulfide	1	1	76
Dichloromethane	1	1	84
tert-Butyl alcohol	1	1	59
trans-1,2-Dichloroethene	1	1	96
tert-Butyl methyl ether (MTBE)	1	1	73
1,1-Dichloroethane	1	1	63
Diisopropyl ether	1	1	45
Ethyl *tert*-butyl ether	1	1	59
2,2-Dichloropropane	1	1	77
cis-1,2-Dichloroethene	1	1	96
2-Butanone (MEK)	1	1	43
Bromochloromethane	1	1	128
Chloroform	1	1	83
1,1,1-Trichloroethane	2	1	97
Tert-Amyl methyl ether	2	1	73
1,1-Dichloropropene	2	1	75
Benzene	2	2	78
1,2-Dichloroethane	2	1	62
Carbon tetrachloride	2	1	117
Trichloroethene	2	1	95
1,2-Dichloropropane	2	1	63
Dibromomethane	2	3	93
Bromodichloromethane	2	1	83

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Compound Name	IS Reference	Surrogate Reference	Primary Ion, m/z
cis-1,3-Dichloropropene	2	1	75
4-Methyl-2-pentanone (MIBK)	3	3	43
trans-1,3-Dichloropropene	2	1	75
1,1,2-Trichloroethane	2	3	83
Toluene	3	2	92
2-Hexanone	3	3	43
Tetrachloroethene	3	3	166
1,3-Dichloropropane	3	3	76
Chlorodibromomethane	3	3	129
1,2-Dibromoethane (EDB)	3	3	107
Chlorobenzene	3	3	112
1,1,1,2-Tetrachloroethane	3	3	131
Ethylbenzene	3	2	91
m&p-Xylene	3	2	106
o-Xylene	3	2	106
Styrene	3	2	104
Bromoform	3	3	173
Isopropylbenzene	3	2	105
Bromobenzene	3	2	156
1,1,2,2-Tetrachloroethane	3	3	83
1,2,3-Trichloropropane	3	3	75
Propylbenzene	3	2	91
2-Chlorotoluene	3	3	91
4-Chlorotoluene	3	3	91
1,3,5-Trimethylbenzene	3	2	105
tert-Butylbenzene	3	2	119
1,2,4-Trimethylbenzene	3	2	105
sec-Butylbenzene	3	2	105
1,3-Dichlorobenzene	3	3	146
1,4-Dichlorobenzene	3	3	146
p-Isopropyltoluene	3	2	119
1,2-Dichlorobenzene	3	3	146
Butylbenzene	3	2	91
1,2-Dibromo-3-chloropropane	3	3	75
1,2,4-Trichlorobenzene	3	3	180
Hexachlorobutadiene	3	3	225
Naphthalene	3	2	128
1,2,3-Trichlorobenzene	3	3	180
Surrogate Compounds			
1,2-Dichloroethane-d4	2	1	65
Toluene-d8	3	2	98
4-Bromofluorobenzene	3	3	174
1,2-Dichlorobenzene-d4	3	4	152
Internal Standards			
Dichloromethane-d2	1	-	53
Fluorobenzene	2	-	96
Chlorobenzene-d5	3	-	117

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LCS and MS/MSD QC Criteria (based on laboratory historical data from June 20, 2016 to September 8, 2016 at 99% confidence)[1]

Analyte	LCS Recovery, %		MS/MSD Recovery, %		MS/MSD, RPD
Dichlorodifluoromethane	63	136	23	150	50
Chloromethane	69	129	53	150	50
Vinyl chloride	70	130	58	150	50
Bromomethane	53	143	43	150	50
Chloroethane	83	117	69	142	37
Trichlorofluoromethane	75	125	62	150	49
1,1-Dichloroethene	70	130	70	143	36
1,1,2-Trichloro-1,2,2-trifluoroethane	71	138	77	150	40
Acetone	56	118	38	132	47
Carbon disulfide					
Dichloromethane	70	130	86	111	12
tert-Butyl alcohol					
trans-1,2-Dichloroethene	70	130	75	135	30
tert-Butyl methyl ether (MTBE)	67	120	75	117	21
1,1-Dichloroethane	69	126	80	124	22
Diisopropyl ether					
Ethyl tert-butyl ether					
2,2-Dichloropropane	43	144	20	150	50
cis-1,2-Dichloroethene	70	130	71	138	33
2-Butanone (MEK)	58	124	55	127	36
Bromochloromethane	72	126	80	129	25
Chloroform	70	130	72	135	31
1,1,1-Trichloroethane	70	130	58	133	38
Carbon tetrachloride	70	130	56	144	44
1,1-Dichloropropene	81	110	76	121	22
Benzene	70	130	73	121	24
1,2-Dichloroethane	70	130	81	110	13
tert-Amyl methyl ether					
Trichloroethene	70	130	84	118	17
1,2-Dichloropropane	70	130	79	117	19
Dibromomethane	77	119	82	118	18
Bromodichloromethane	70	130	84	114	15
cis-1,3-Dichloropropene	63	119	64	112	24
4-Methyl-2-pentanone (MIBK)					
Toluene	70	130	82	118	18
trans-1,3-Dichloropropene	64	119	64	110	22
1,1,2-Trichloroethane	70	130	82	121	20
Tetrachloroethene	70	130	53	150	50
1,3-Dichloropropane	78	121	83	118	18
2-Hexanone					
Chlorodibromomethane	70	130	76	126	25
1,2-Dibromoethane (EDB)	80	116	84	115	15
Chlorobenzene	70	130	85	114	15
1,1,1,2-Tetrachloroethane	77	113	82	111	15

1. Regulated compounds, shown in bold, have LCS acceptance limits of 70-130% recovery per Method 524.2.

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Analyte	LCS Recovery, %		MS/MSD Recovery, %		MS/MSD, RPD
Ethylbenzene	70	130	80	120	20
m&p-Xylene	70	130	75	124	24
o-Xylene	70	130	82	114	16
Styrene	70	130	78	116	19
Bromoform	70	130	64	131	34
Isopropylbenzene	85	112	77	125	24
Bromobenzene	85	110	87	110	11
1,1,2,2-Tetrachloroethane	70	129	73	132	29
1,2,3-Trichloropropane	69	124	74	125	25
Propylbenzene	86	114	76	127	26
2-Chlorotoluene	81	113	78	117	19
4-Chlorotoluene	81	113	76	117	21
1,3,5-Trimethylbenzene	82	115	74	123	25
tert-Butylbenzene	85	113	70	127	28
1,2,4-Trimethylbenzene	79	117	76	121	22
sec-Butylbenzene	80	124	67	139	36
1,3-Dichlorobenzene	80	111	79	114	18
p-Isopropyltoluene	80	121	65	136	35
1,4-Dichlorobenzene	70	130	73	120	24
1,2-Dichlorobenzene	70	130	81	112	16
Butylbenzene	78	124	61	141	40
1,2-Dibromo-3-chloropropane	64	120	56	132	38
1,2,4-Trichlorobenzene	70	130	68	117	25
Hexachlorobutadiene	65	123	65	124	29
Naphthalene	67	113	60	131	35
1,2,3-Trichlorobenzene	69	114	67	120	27

Surrogate QC Criteria

Compound Name	Recovery, %	
1,2-Dichloroethane-d4	77	117
Toluene-d8	85	110
4-Bromofluorobenzene	85	110
1,2-Dichlorobenzene-d4	81	125

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APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

PURGE & TRAP CONCENTRATOR/AUTOSAMPLER PARAMETERS

Purge and Trap Concentrator operating parameters

The operating parameters for the purge & trap concentrators. These parameters may vary slightly to optimize instrument responses except Purge Time, Purge Flow, and Desorb Time cannot be altered from the method required settings.

PARAMETER	SETTING
	Concentrator
Standby temperature	38°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient (off)
Purge Time*	11 minutes
Dry purge	1 minute
Purge Flow*	40 mL/min
Desorb preheat temperature	245°C
Desorb Time*	4.00 minutes @ 250°C
Bake	11 minutes @ 260°C
Auto drain	On (controlled by Autosampler)
Bake gas bypass	Off
Valve temperature	150°C
Mount temperature	40°C
Line temperature	150°C

*Do not optimize these settings.

Autosampler

The Autosampler delivers an aliquot of the water sample directly from the 40 mL sample vial into the sparge vessel on the concentrator. The Autosampler is programmed to add the internal standard and surrogate into the sample during the transfer process.

Standard loading:

1. Prepare standards and blank spikes in a 50-mL volumetric flask with acidified method blank water.
2. Gently invert three times.
3. Gently pour the standard solution into the 40-mL vial (pre-label with information about the standard), down the side of the vial, without any agitation. Overfill the vial to form an inverted meniscus. Cap the vial. Invert the vial to ensure that there are no

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air bubbles present.

4. Gently place the vial in the appropriate autosampler position.
5. The autosampler will analyze a 25 mL aliquot and add 1 µL of the 125 ng/µL VOA IS/SS solution. The amount used results in the analytical equivalent of 5 µg/L.

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HP/Agilent 6890 GC & HP/Agilent 5973MSD

The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

BFB analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	110°C
Initial Oven Time	0.5 minutes
Temperature Ramp	25°C/minute for 3.6 minutes
Final Oven Temp	190°C
Final Hold Time	1.9 minutes
Inlet mode:	Split
Split vent flow:	20 mL/min
Column Flow rate	0.8 mL/min at constant flow mode
Electron Energy	70 volts (nominal)
MS Scan range	35-260 amu

VOA analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	35°C
Initial Oven Time	3.0 minutes
Temperature Ramp	8°C/minute to 120°C for 2 minutes; 25°C/minute to 195°C for 2.2 minutes
Final Oven Temp	200°C
Final Hold Time	2.0/* 5.0 minutes
Inlet mode:	Split
Split vent flow:	20 mL/min.
Column Flow rate	0.8 mL/min at constant flow mode.
Electron Energy	70 volts (nominal)
MS Scan Range	35-260 amu

Analytical system preparation:

Leak Checking

From the ChemStation Instrument Control panel of the HP 5973 MSD select View, Tune and Vacuum control.

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Select Spectrum scan. Check the nitrogen (m/z 28), water (m/z 18), to FC43 (m/z 69) ratio. Ratios for ions 28 and 18 should not exceed 20% of ion 69. Values higher than indicated above are indicative of large leaks and must be corrected.

Auto Tuning

Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned.

Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

The Agilent ChemStation software requires that the FC43 spectrum meet the Criteria listed in Appendix C.

Preparation for an Initial Calibration

Perform an autotune of the analytical system prior to an initial calibration.

1. The system should be reset to default parameters as follow:
   a. From the ChemStation Instrument Control panel of the HP 5973 MSD select View, Tune and Vacuum control. Select File, Reset to Default, Autotune.
   b. If the DC polarity for the system is normally set to negative for the system, resetting the tune parameter will set it to positive. Set the parameter to negative by selecting Parameters, Manual tune, DC polarity and slide the polarity selector to negative.
2. Save the default parameters by selecting save tune, Autotune.u.
3. Autotune the system by selecting Tune, Autotune.
4. The system will generate an Autotune report.
5. Save the resulting tune file by selecting File, Save tune Value
6. The tune file name is selected as outlined in Appendix E.
7. Generate the tuning report by selecting File, Generate report.

Preparation for a Continuing Calibration

1. Perform a mass axis calibration of the analytical system prior to continuing calibration. By selecting calibrate, Mass axis.
2. Save the resulting tune file by selecting File, Save tune Value.
3. The tune file name is selected as outlined in Appendix E.
4. Generate the tuning report by selecting File, Generate report.

Manual tuning

If the system fails to meet the tuning criteria, the source may need to be cleaned or manual tuning may be required. BFB or DFTPP tuning routines may be used to correct ions ratios.

To manually tune the system, select Manual Tune from View menu in Instrument Control

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view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Incorporate the new tune parameters and generate today's method

1. Load a copy of the last initial calibration from C:\HPCHEM\1\Methods\Initial.
2. From the ChemStation Instrument Control panel of the HP 5973 MSD click on Select MS Tune File icon, click on the name of tune file generated today.
3. Select MS/SIM San Parameters. If necessary, adjust the EM voltage by adding or subtracting voltage relative "REL" to today's tune voltage.
4. Save the resulting method file as outlined in the as outlined in Appendix E by selecting File, Save method.

Mass Calibration:

Perform mass calibration of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

Initial Calibration:

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (BFB and/or manual tune) has been performed. When the instrument is ready for analysis, perform the following steps:

1. In the ChemStation data analysis module, load the current initial calibration method from D:\MSDCHEM\Year\Methods\
2. Perform an initial calibration using the recommended concentrations listed in Section 8.2.1.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the CCV calibration level.
6. Save the method as outlined in Appendix E.
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
9. Check the time and date to ensure that the correct update is used.
10. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report"
11. Open and immediately close Chemstation Custom Reports. (Note: no Chemstation custom reports are actually used, opening and closing custom reports populates "detail.xls" which is later mined for data.)
12. Open the latest copy of C:\msdchem\custrpt\ "Full_Custom_Report.xls" Make sure automatic updates of links is enabled under options.
13. Go to the "SCV Recovery", "ICAL Area", "ICAL conc", tabs and print reports. Make sure the SCV passes acceptance criteria (Appendix C) and the ICAL areas match what is on the

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Chemstation quant reports.

14. Verify that the method was updated correctly. Print the Compound List Report from ChemStation. Verify that the average response factor is used. Scrupulously check the elution order and retention times, compare them to an old ICAL if needed.
15. Copy the method to I:\RoomNumber\Instrument\Year\Methods\
16. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
17. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

The analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Continuing Calibration

Analyze a calibration verification standard at the beginning of each 12-hour analytical period by performing the following steps:

1. In the ChemStation data analysis module, load today's method from D:\MSDCHEM\Year\Methods.
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. Adjust the electron multiplier (EM) voltage if needed (an increase of 50 volts will typically double the response). If the EM voltage is changed, reanalyze BFB and the CCV.
6. Manually calculate the result for one surrogate to insure that the correct RFs are being used. Record the result on the quantitation report.
7. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "QLast Update : Mon Jul 25 08:15:58 2011"), is recorded on each file header.
8. If QLast Update time stamp changes, state the reason, repeat steps 4-7, and include the reports generated in the package.
9. Save a copy of the method to the LAN, when the data are backed up to the LAN the following day.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

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APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA
BFB	BFB

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DFTPP DFT

C: Channel (use when applicable):
Front A
Back B
Both AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

YY: Year i.e. 12 for 2012

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Check often. Replace with liner or with signs of wear.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Replacement	As needed	When trimming no longer returns chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
Archon/Purge System Lines	As needed	Bake out transfer and purge system line. Clean with organic free water if necessary.
Trap	As needed	Replace with loss of performance.
EM voltage	As needed	If an overall change in sensitivity (area counts in CCV in comparison to most recent ICAL), the EM voltage may need adjusting.

MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check FC43 level		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

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APPENDIX G.
METHOD PERFORMANCE

Volatile Organic Compound Analysis in Water
June 20, 2016 to September 8, 2016

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
Dichlorodifluoromethane	37	99.3	12.1	63	136
Chloromethane	37	99.0	9.9	69	129
Vinyl chloride	37	99.1	6.1	81	117
Ethylbenzene	37	97.4	3.2	88	107
Bromomethane	37	97.9	15.0	53	143
Chloroethane	37	99.9	5.6	83	117
Trichlorofluoromethane	37	100.2	8.3	75	125
1,1-Dichloroethene	37	97.5	7.0	77	118
1,1,2-Trichloro-1,2,2-trifluoroethane	37	104.6	11.2	71	138
Acetone	37	87.1	10.3	56	118
Carbon disulfide					
Dichloromethane	37	95.1	5.1	80	110
tert-Butyl alcohol					
trans-1,2-Dichloroethene	37	98.3	7.3	76	120
tert-Butyl methyl ether (MTBE)	37	93.1	8.8	67	120
1,1-Dichloroethane	37	97.2	9.4	69	126
Diisopropyl ether					
Ethyl tert-butyl ether					
2,2-Dichloropropane	36	93.3	16.9	43	144
cis-1,2-Dichloroethene	36	98.9	8.2	74	124
2-Butanone (MEK)	37	90.6	11.0	58	124
Bromochloromethane	37	99.2	8.9	72	126
Chloroform	37	98.6	7.6	76	121
1,1,1-Trichloroethane	37	93.3	6.4	74	113
Carbon tetrachloride	37	94.8	7.4	73	117
1,1-Dichloropropene	37	94.4	4.4	81	108
Benzene	37	96.4	3.9	85	108
1,2-Dichloroethane	37	94.3	6.1	76	113
tert-Amyl methyl ether					200
Trichloroethene	37	96.1	3.3	86	106
1,2-Dichloropropane	37	97.0	5.5	81	113
Dibromomethane	37	97.8	6.9	77	119
cis-1,3-Dichloropropene	37	90.9	9.3	63	119
Bromodichloromethane	37	97.2	6.1	79	115
4-Methyl-2-pentanone (MIBK)					
Toluene	37	97.5	3.5	87	108
Tetrachloroethene	37	95.2	4.4	82	109
trans-1,3-Dichloropropene	37	91.7	9.2	64	119
1,1,2-Trichloroethane	37	100.4	7.2	79	122
1,2-Dibromoethane (EDB)	37	97.8	6.0	80	116

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Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
1,3-Dichloropropane	37	99.1	7.2	78	121
2-Hexanone					
Chlorodibromomethane	37	99.6	9.2	72	127
Chlorobenzene	37	97.2	3.2	88	107
1,1,1,2-Tetrachloroethane	37	95.2	5.9	77	113
m&p-Xylene	37	97.4	4.9	83	112
o-Xylene	37	96.1	3.8	85	108
Styrene	37	98.2	4.9	84	113
Bromoform	37	98.7	11.2	65	132
Isopropylbenzene	37	98.4	4.4	85	112
Bromobenzene	37	96.0	3.7	85	107
1,1,2,2-Tetrachloroethane	37	99.8	9.8	70	129
1,2,3-Trichloropropane	37	96.7	9.2	69	124
Propylbenzene	37	99.8	4.7	86	114
2-Chlorotoluene	37	97.1	5.3	81	113
4-Chlorotoluene	37	96.6	5.3	81	113
1,3,5-Trimethylbenzene	37	98.2	5.5	82	115
tert-Butylbenzene	37	98.8	4.7	85	113
1,2,4-Trimethylbenzene	37	98.0	6.3	79	117
sec-Butylbenzene	37	102.1	7.4	80	124
1,3-Dichlorobenzene	37	95.5	5.1	80	111
1,4-Dichlorobenzene	37	95.0	5.8	78	112
p-Isopropyltoluene	37	100.5	6.9	80	121
1,2-Dichlorobenzene	37	94.9	6.0	77	113
Butylbenzene	37	101.1	7.8	78	124
1,2-Dibromo-3-chloropropane	37	91.9	9.3	64	120
1,2,4-Trichlorobenzene	37	91.1	6.6	71	111
Hexachlorobutadiene	37	94.1	9.7	65	123
Naphthalene	37	89.8	7.6	67	113
1,2,3-Trichlorobenzene	37	91.4	7.5	69	114

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APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 354
Revision: 12, Effective: 10/17/2016

Volatile Organic Compound Analysis in Water

Revision	Effective Date	Description
8	04/21/08	1. Added Method 8260B as a reference method. 2. Added requirement that all equipment, standards, reagents, and supplies must meet technical & QC requirements of the reference method. 3. Added requirement to prepare standards and instrument and batch QC samples in acidified organic-free water. 4. Changed LCS %R QC Limits to 70 – 130% for regulated compounds. 5. Added option to purge BFB. 6. Changed RRT criteria for analyte identification from relative to absolute. 7. Deleted requirement to re-analyze samples containing < 5 times MB amount for common laboratory contaminants. 8. Revised Sections 8.2.1 and 8.2.2 and Appendix D to clarify and reflect current practice.
9	11/27/09	1. Revised Appendix D to require adherence to instrument operating conditions specified in the reference method. 2. Minor changes throughout to update SOP to current requirements of SOP 850 for format.
10	03/01/13	1. Revised Appendix C to require adherence to drinking water criteria. 2. Moved ChemStation specific instructions to Appendix D to improve readability. 3. Minor changes throughout to update SOP to current requirements of SOP 850 for format.
11	02/03/14	Limited revision to address the following: 1. Added EST purge and trap and EST trap to equipment list. 2. Added previously omitted 10% allowance for CCV outliers to Appendix C. 3. Added purge and trap parameters to Appendix D and EST operating parameters to Appendix D. 4. General edits throughout to comply with current SOP format.
12	10/17/16	Limited revision to address the following: 1. Removed preparation of standards in 50-mL syringe in Section 8.2.1, Section 8.3.2, and Appendix D. 2. Added instructions regarding peroxide-forming chemicals

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	and reference to SOP 785. 3. Removed run log example and references to it. 4. Updated method performance and QC limits. 5. Minor changes throughout.

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USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 375

LOW LEVEL SEMIVOLATILE ORGANICS ANALYSIS

Revision 5
Effective Date: May 9, 2014

Reviewed by: _____ 4/28/14
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: _____ 4-28-2014
Lucrina Jones, Laboratory QA Officer — Date

Approved by: _____ 5/1/14
Duane James, Acting Laboratory Director — Date

Periodic Review:

Signature	Title	Date

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105028-16903

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used for the low level analysis of selected semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM) in extracts prepared from solid or liquid samples by EPA SW-846 extraction and cleanup methods appropriate to the sample matrix. This SOP is based on procedures contained in EPA Method SW 846 8270D. Deviations from Method 8270 are described in Appendix A. Analytes and Quantitation Limits (QLs) for this analysis are listed in Appendix B.

Sample extracts are prepared using EPA Region 9 Lab SOP 290 *Extraction of Soil Samples Using Pressurized Fluid* or SOP 265 *Extraction of Low Level Phenols and Polycyclic Aromatic Hydrocarbons from Water*.

The applicability of this procedure to specific project data quality objectives must be assessed on a case-by-case basis. The quality control (QC) criteria specified in this procedure do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Sample extracts are injected into a gas chromatograph (GC) with a mass spectrometer (MS) detector. Analytes are separated in a narrow bore fused silica capillary GC column in a temperature-controlled oven and detected by the MS in selected ion monitoring (SIM) mode. Each target and surrogate analyte is quantitated using the average response factors from the most recent initial calibration.

Target analytes of interest are identified in the sample extract by comparing the selected characteristic ion(s) and GC retention time of the analyte to the characteristic ion(s) and retention time of standards analyzed under the same conditions.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

There are no terms or definitions specific to this procedure.

4 SAFETY AND HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals.

Emergency and first aid:

- Inhalation: immediately remove to fresh air. If not breathing, administer mouth to mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR), contact physician immediately.
- Eye contact: rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance.
- Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re use, and discard contaminated shoes. Get emergency medical assistance.
- Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated

with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, does not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure.* Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste

streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
SVOC Waste: Glass vials, dichloromethane, 0-2000 ppm semivolatile organic compounds	Hazardous Waste	Toxic

NOTE: N-Nitrosodimethylamine and 3,3'-dichlorobenzidine are listed as known or suspected carcinogens. As such, any sample or sample extract with a combined concentration of these compounds greater than or equal to 1000 mg/kg (wet weight) must be handled as an extremely hazardous waste. Should this concentration be determined, notify the LaSHEM (or designee).

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Refer to EPA Region 9 Lab SOP 290 *Extraction of Soil Samples Using Pressurized Fluid* or SOP 265 *Extraction of Low Level Phenols and Polycyclic Aromatic Hydrocarbons from Water*.

5.2 Internal Chain-of-Custody

Sample extracts for GC/MS analysis are received from the extraction lab personnel and custody is transferred to the GC/MS laboratory staff. The GC/MS analyst acknowledges the receipt of the sample extracts by signing the appropriate sections of the completed LIMS bench sheet. Copies of tracking sheets, chain of custody records, and the original LIMS extraction bench sheet should accompany the sample extracts.

5.3 Sample Storage

Store extracts in the freezer in Room 402 or 406 at $\leq$ -10° C before and after analysis. Retain samples extracts until holding time has expired.

5.4 Holding Time

Extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

Method interferences can be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. Phthalates are commonly found as laboratory contaminants. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running a method blank (MB). The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed.

It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to samples may be affected.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

7.1.1 GCMS System

7.1.1.1 Gas Chromatograph (GC): Agilent 6890, 6890N, 7890A, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, splitless injection port, and electronic pressure control (EPC).

7.1.1.2 GC column: 30 m, 0.25 mm ID, 0.5 µm DF. A fused silica capillary column with a bonded phase coating of 5% diphenyl 95% methyl silicone such as DB5, DB5MS, RTX 5, RXI-5Sil MS, HP 5, or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

7.1.1.3 Mass spectrometer: Agilent 5973, 5973N, 5975, or equivalent, capable of continuous scanning and selective ion monitoring from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when ≤50 ng of DFTPP is injected through the GC inlet.

7.1.1.4 Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.

7.2 Reagents

Document the receipt of all reagents in the LIMS. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

Dichloromethane: High purity pesticide quality or equivalent. Recycled dichloromethane may be used if demonstrated to be suitable for use in this procedure.

7.3 Standards

Prepare standard solutions to include the project specific analytes of interest over the required concentration range. Document the receipt, preparation, and ampule open dates of all standards in the LIMS.

Store all ampulated calibration materials in the refrigerator at >0°C to ≤6°C protected from light. Use the manufacturer's expiration date for ampulated standards.

Store open stock ampules and working standards in a freezer at ≤-10 °C protected from light. The solution is assigned an expiration date which is either 6 months from preparation date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Allow all standard solutions to equilibrate to room temperature before use.

7.3.1 Internal Standard Solution (IS): A solution of acenaphthene-d10, phenanthrene-d10, chrysene-d12, 1,4 dichlorobenzene-d4, perylene-d12, and naphthalene-d8 each in dichloromethane. Prepare by diluting purchased solutions to attain an extract concentration equivalent to the continuing calibration verification level. Restek 31206 or equivalent.

7.3.2 Surrogate solution: A solution of 2-fluorobiphenyl, nitrobenzene-d5, p-terphenyl-d14, and 1,2-dichlorobenzene-d4 (base/neutral surrogates); 2-fluorophenol, phenol-d5, 2,4,6-tribromophenol, and 2-chlorophenol-d4 (acid surrogates). Base/neutral surrogates - Restek 31072 or equivalent; acid surrogates - Restek 31073 or equivalent.

7.3.3 Calibration Stock Standard, Phenols: A solution of project-specific target analytes in dichloromethane.

- Restek 8270 Mega Mix Restek 31850,
- 4-Chlorophenol AccuStandard AS-E0183,
- 3,5-dichlorophenol Supelco 44-2378,
- 3,4-dichlorophenol Supelco 44-2375,
- 3,4,5-Trichlorophenol Accustandard M-1653-IS.

7.3.4 Calibration Stock Standard PAH: A solution of project-specific target analytes in dichloromethane. Restek 8270 Mega Mix Restek 31850.

7.3.5 Calibration standards: A solution of target analytes listed in Appendix B prepared by diluting the calibration stock standard and mixing it with the appropriate amount of IS solution to attain the project specific concentration range. The suggested target analyte concentrations are listed in the following table:

Analysis Type	Calibration Levels (ng/L)					
	1 (QLS)	2	3 (CCV)	4	5	6
PAH	50	100	500	1,000	5,000	8,000
Phenols	1,000	2,000	5,000	10,000	15,000	20,000

7.3.6 Second Source Standard (SCV): A solution of target analytes listed in Appendix B and surrogates prepared from a source different from the calibration standard. The SCV is used to check the accuracy of the initial calibration solutions.

- PAH: Supelco 47543-U, EPA 8310 Polynuclear Aromatic Hydrocarbons Mix, 2000 µg/mL) or equivalent.
- Phenols: Accustandard ACID MIX (CLP-HC-A-R, 2000 µg/mL) or equivalent.

Note: Some phenolic compounds are extremely difficult to obtain. Consequently, not every target analyte will necessarily be in the phenol SCV. For the phenol analysis at least one of each type of phenolic compound will be represented in the SCV (i.e., one di-chlorophenol, one tri-chlorophenol etc.). The PAH SCV will have every compound present.

7.3.7 GC/MS Tuning Solution (MS tune). A solution of DFTPP, 4,4'-DDT, pentachlorophenol, and benzidine at ≤50 ng/µL each in dichloromethane. Restek 31615 or equivalent.

7.4 Supplies

7.4.1 Syringes: 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, 500 µL, 1 mL.

7.4.2 Helium carrier gas: Ultra-high purity, 99.999%.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound. Refer to Section 8.4 and Appendix F for system maintenance requirements.

Set-up the GC/MS following operating instructions provided by the manufacturer. Use the method provided in Appendix D as a starting point.

8.1.1 Mass axis calibration

Calibrate the Mass Axis of the MS prior to analyzing the DFTPP standard each day that samples are analyzed. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E and generate a tune report.

Since DFTPP is analyzed in the full scan mode, the most recent BNA method will be used for the analysis of DFTPP. Select the most recent BNA method and associate the newly generated tune file with this method; name the method using the naming convention in Appendix E and save it. Use this method for all subsequent DFTPP analyses.

Select the most recent low level SIM method (phenols or PAH, depending upon the procedure used) and associate the newly generated tune file with this method; name the method using the naming convention in Appendix E and save it. Use this method for all subsequent SIM analyses.

Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.1.2 GC/MS tuning

The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Inject 1 µL of the DFTPP solution using the BNA method provided in Appendix D.

Quantitate the DFTPP solution data and generate a DFTPP report using the Autofind DFTPP to printer menu item from the Tuner → Evaluate DFTPP menu.

The autofind procedure will automatically find the DFTPP peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Generate a tailing factor report for the pentachlorophenol and benzidine peaks.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (DFTPPand/or manual tune) has been performed.

Since retention times may drift due to column maintenance or condition, it is necessary to verify the retention times for all compounds. To verify retention times, analyze a calibration standard in the full scan mode using the BNA method used for DFTPP analysis prior to analyzing the initial calibration. Adjust SIM groups' retention time windows accordingly.

When the instrument is ready for analysis, perform the following steps:

1. In the ChemStation data analysis module, load the current initial calibration method from D:\MSDCHEM\Year\Methods\
2. Perform an initial calibration using the recommended concentrations listed in Section 7.3.5.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the continuing calibration level.

6. Save the method as outlined in the "ChemStation File Naming Convention"
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
9. Check the time and date to ensure that the correct update is used.
10. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report"
11. Open and immediately close Chemsation Custom Reports. (note: no Chemstation custom reports are actually used, opening and closing custom reports populates "detail.xls" which is later mined for data.)
12. Open the latest copy of C:\msdchem\custrpt\ "Full_Custom_Report.xls" Make sure automatic updates of links is enabled under options.
13. Go to the "SCV Recovery","ICAL Area", "ICALconc", tabs and print reports. Make sure the SCV passes acceptance criteria (appendix C) and the ICAL areas match what is on the Chemstation quant reports.
14. Verify that the method was updated correctly. Print the Compound List Report from ChemStation. Verify that the average response factor is used. Scrupulously check the elution order and retention times, compare them to an old ICAL if needed.
15. Copy the method to I:\RoomNumber\Instrument\Year\Methods\
16. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
17. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration Verification

Analyze a calibration verification standard at the beginning of each analytical sequence by performing the following steps:

1. In the ChemStation data analysis module, load today's method from D:\MSDCHEM\Year\Methods\
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration verification file.
4. Generate "Evaluate Continuing Calibration Report".
5. Manually calculate a result for one surrogate to insure that the correct RFs are being used and write the results on the quantitation report.
6. As each run is quantitated during the day, make sure that the same date and time stamp (example: "QLast Update : Mon Jul 25 08:15:58 2011") is reflected on each file header.

7. If QLast Update time stamp changes, state the reason, repeat steps 4-6, and include the reports generated in the package.

Save a copy of the method to the LAN, when the data is backed up to the LAN the following day.

Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.3 Quantitation Limit Verification Standard (CRL)

Analyze a quantitation limit standard at the concentration of the lowest point of the initial calibration for each analytical sequence.

Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample extracts to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS extraction batch to ensure that the correct sample is being analyzed.

Note if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS work order memo .

Add appropriate amount of IS solutions to each field and QC sample extract to attain an IS extract concentration equivalent to the continuing calibration verification level.

8.3.2 Sample Analysis and Analytical Sequence

Obtain a LIMS sequence number by generating an empty LIMS sequence; specify the analysis and instrument, number associated with the samples to be analyzed.

Enter sample sequence in the instrument software. Include the laboratory sample number (work order-sample number) in the “Sample” field and dilution level, if any in the “Multiplier” field. Use the LIMS sequence number to name instrument QC as outlined in Appendix D.

Enter the BNA method name in the "Method" field; analyze the DFTPP sample with this method.

Enter the daily instrument SIM method name in the "Method" field; analyze all standards and samples with this method.

Name the data files according to the data file naming convention outlined in Appendix E.

Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:

1. DFTPP
2. CCV
3. QLS
4. Samples, sample dilutions, and or QC samples as needed
5. Instrument Blanks, as needed

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and the characteristic ions of the peak must match those of the standard.

If a compound cannot be verified using these criteria but in the technical judgment of the analyst is present, report the analyte and include supporting evidence in the raw data package.

Cross out all reported hits that do not meet qualitative criteria and document the reason on the quantitation report.

Review the chromatogram for possible false negatives and edit results as needed.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out ChemStation detailed quantitation reports and chromatograms. Use the average relative response factor from the initial calibration for quantitation.

Analyte concentrations in the sample extracts as shown on the ChemStation quantitation report are calculated as follow:

LIMS calculates final analyte concentrations in samples. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

$$\text{Conc. } (\mu g/L) = Ax * AMTIS * DF * 1000) / (AIS * RRF_{avg} * V)$$

Where:

Ax = area of the characteristic ion of the compound
AMTIS = amount of internal standard in µg/L
DF = dilution factor
AIS = area of the characteristic ion of the associated internal standard
RRF_{avg} = analyte average relative response factor from the initial calibration
V = Volume extracted in mL

For soil samples, calculate results for target analytes

$$\text{Conc. ug / Kg (dry weight basis)} = \frac{A_x \times C_{is} \times V_t \times V_i \times DF \times GPC}{A_{is} \times \overline{RRF} \times W \times D}$$

Where:

A_X = area of the quantitation ion of the compound
C_{IS} = concentration of Internal Standard in µg/L (500 µg/L)
D = dry weight factor (Percent solids/100)
W = weight of sample in grams
A_{IS} = area of the characteristic ion of the associated internal standard
RRF = analyte mean relative response factor from the initial calibration
Vt = volume of concentrated extract in µL
DF = dilution factor
GPC = GPC factor, normally 1.0 if not used, 2.0 if used
Vi = volume of extract injected in µL

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 Data and QC Review

- Process and review the results for the CCV and CRL instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV results are within QC limits. Use Chemstation, Excel or LIMS to verify that the CRL is within QC limits. See Section9.2 for instrument QC requirements and Appendix C for acceptance criteria.

- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for Batch QC requirements.

- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.

- Review all sample results to determine if any samples need to be re-analyzed at a dilution.

- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

- Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.3.5 Data Export and LIMS Entry

- Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

- Populate the empty LIMS sequence file by editing the sequence using Data Tool to import the sequence information.

- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table.

- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems for GC and MS operations. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 GC Maintenance

Symptoms of common problems:

- Carryover
  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.2 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio

- DFTPP ion 275 ratio is outside acceptance range
- Failing tune checks

Resolution: Clean the source.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

9.2.1 Mass calibration

Review the FC43 spectrum for compliance with the criteria list in Appendix C.

If the FC43 spectrum does not meet the criteria, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate FC43 spectra, further maintenance such as cleaning the ion source may be required.

9.2.2 GC/MS Tune

Review the DFTPP spectrum for compliance with the criteria list in Appendix C.

Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE. Calculate the breakdown of DDT using peak areas of each quantitation ion (Qion) in the following equation:

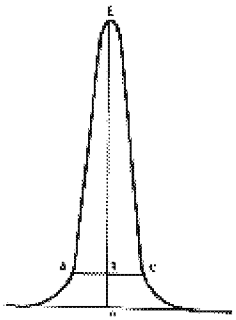
$$\%\ 4,4'\text{-DDT Breakdown} = \frac{\text{Total Qion Area (DDE + DDD)}}{\text{Total Qion Area (DDE + DDD + DDT)}} \times 100$$

where:

Qions of DDE: 246 Dalton, DDD: 235 Dalton, DDT: 235 Dalton

Benzidine and pentachlorophenol should be present at their normal responses. The tailing factor is calculated by the following equation:

$$TailingFactor = \frac{BC}{AB}$$



Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and DB is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

If the ion abundances, degradation, or tailing fail to meet the criteria, the DFTPP chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.). If the problem is related to poor chromatography, take the necessary corrective action and re-analyze the DFTPP. If the DFTPP continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the analytical time period has elapsed it must be re-analyzed.

9.2.3 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned pairs are benz(a)anthracene/chrysene and benzo(b)/benzo(k)fluoranthene.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound using the following equation:

$$RRF = (Ax)(Cis) / (Ais)(Cx)$$

Where

Ax	=	Area of quantitation ion of compound x. The recommended quantitation ions and internal standard assignments are listed in Appendix B.
Ais	=	Area of quantitation ion for associated internal standard
Cx	=	Concentration of compound x
Cis	=	Concentration of the associated internal standard

The data system calculates the average RRF (RRF_{avg}) for all analytes.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/ RRF_{avg})*100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{ave})^2}{n-1}}$$

As an exception, pentachlorophenol is calibrated using a quadratic curve. When this curve type is employed it is possible to report false positives on very low area counts. To prevent this error, analyze a standard at half of the quantitation limit along with the initial calibration. Note the area count for pentachlorophenol in this standard and do not report any results with less than this area count.

The %RSD, R^2, and SCV recovery requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. If failure persists, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.4 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

If the area for any internal standard does not meet the criteria, the CCV may be re-analyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine the retention times of internal standards in the calibration verification standard. If the retention time for any internal standard does not meet the criteria, inspect the chromatographic system for malfunctions and take corrective action as needed and prepare a new calibration curve.

The data system calculates the percent difference (%D) of the RRF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\ 100$$

Where:

RRF_c = Relative Response Factor of compound c.
RRF_{avg} = Average Relative Response Factor.

If the continuing calibration does not meet %D criterion listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.2.5 Quantitation Limit Standard

QLS must be analyzed at the beginning of the analytical run, typically just after the CCV. The QLS concentrations match the QL concentration (at the instrument). The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in the ug/L.

Check that the recoveries meet the criteria specified in Appendix C.

If the QLS recovery does not meet criteria provided in Appendix C, rerun the QLS once to verify. If still unacceptable determine the cause, take corrective action.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.3 Batch QC

9.3.1 Method Blank

- Extract and analyze a method blank (MB) with each extraction batch to demonstrate that the entire analytical system, from extraction through GC/MS analysis, is free of contamination.

- If the surrogate recovery exceeds acceptance criteria (high bias) and is ND, narrate the error and continue. If the surrogate recovery fails acceptance criteria low, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, evaluate sample surrogate recoveries to determine acceptability. If samples have acceptable recovery and are ND, report. Otherwise, re-extract any sample that is ND and fails surrogate low or any sample that has a hit. Note that if any samples in the batch are reported, the MB must also be reported and a note placed in the LIMS work order memo field.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action - If the MB result exceeds QC limits, check the associated samples as follow:

  1. If the sample result is less than five times the MB result, re-analyze the MB. If the MB result still exceeds QC limits, the batch may have to be re-extracted. Consult with the Technical Director or designee.

2. If the sample result is greater than five times the MB result or is not detected, report the sample result.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. The LCS is an MB spiked with matrix spiking solution.

- Calculate the percent recovery (%R) using the following equation:

$$\% R = [MR/SA] \times 100$$

Where,
MR = Measured result
SA = Spike added

- The %R must be within the QC limits in Appendix C. If acceptable recoveries cannot be achieved, re-analyze the LCS. If the LCS result still exceeds QC limits, re-extract the LCS and all associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed for each batch of twenty or fewer samples extracted as a group.

- Calculate the recovery of each analyte.

$$\% R = [(SSR - SR)/SA] \times 100$$

Where,
SSR = Spiked sample result
SR = Unspiked sample result
SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

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

Where,
MSC = Measured concentration of analyte in MS
MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

  The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS – = FAIL								
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Extraction batch acceptable.
Case 2: Extraction batch acceptable; matrix effect confirmed.
Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.
Cases 5, 6, 7, & 8: Extraction batch rejected. If additional sample volume is available, the batch should be re-extracted.

9.4 Sample QC

9.4.1 Surrogate Recovery

Note: in some instances, samples extracted under EPA Region 9 Lab SOP 275 *Extraction of Water Samples by Continuous Liquid-Liquid Extraction* may be analyzed by this procedure. In this event, the surrogate concentrations will exceed the calibration range and will not be reported.

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

  $$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- Take the following steps if surrogate recovery is not within the limits listed in Appendix C:

    1. Ensure that there are no calculation errors, and check the system performance.
    2. Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

- Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted.

- Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

- If the surrogate recoveries of the re-analysis are within limits, then the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. The problem must be documented in the LIMS MMO field.

- If the re-analysis does not solve the problem and additional sample volume is available, the failing samples should be re-extracted unless the sample is ND with failing high recovery.

- If sample re-extraction is unfeasible, or surrogate recoveries of the re-extraction are also outside the QC limits, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis. The problem must be documented in the LIMS MMO field.

9.4.2 Internal Standard Area:

- Evaluate the internal standard areas in all field and QC samples immediately after analysis.

- The internal standard areas must be within QC limits outlined in Appendix C.

- Take the following steps if the internal standard areas are not within the limits:

    1. Check the system performance.

2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

- Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

- Do not re-analyze the MS/MSD samples, even if internal standard areas are outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

- If the internal standard areas of the re-analysis are within limits, then, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS MMO field.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance in the EPA Region 9 Laboratory from January 1, 2012 to December 31, 2013 for water samples. Insufficient data are available to calculate statistics for other matrices during this time period.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Addition of internal standard: The amount and concentration of internal standard added is critical. The nominal concentration is used in calculating target analyte concentration.
2. Samples must be stored as outlined in the SOP to minimize analyte degradation and solvent evaporation.
3. Sample temperature: Sample extracts must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
4. Poor column condition may results in inadequate analyte separation and inaccurate integration.

10 DOCUMENTATION

10.1 Standards

Record all standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be available for printing in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the Element database or in the instrument Run Log, date of analysis, QC solution IDs, analyst initials, lab sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventative or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.6 SOP Distribution and Acknowledgement

After approval, make available an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA

Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent 6890 Gas Chromatograph Users Manual

Agilent 7890 Gas Chromatograph Users Manual

Agilent 5973 MSD Hardware Manual

Agilent 5975 MSD Hardware Manual

Agilent Environmental Analysis User's Guide

Agilent EnviroQuant ChemStation User's Guide

USEPA Method 525.3, Determination of Semivolatile Organic Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography / Mass Spectrometry, Revision 1.0, February2012.

USEPA Method 3500C, Organic Extraction and Sample Preparation, Revision 3, February 2007.

USEPA Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

USEPA Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2007.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. SW-846 method 3500C referenced by method 8270D specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 100 mg/L.

2. Mass spectra used for target analytes are from the NIST library and are included in the reports to demonstrate that appropriate masses have been selected for quantitation and monitoring. However, the selected ion scans will not resemble the NIST spectra – comparison with the NIST spectra is not used for identification.

3. Relative Retention Time (RRT) of chromatographic peak is not evaluated in this SOP as documented in the reference method. ChemStation calculates a retention time window and does not calculate RRT window. The retention time window of ± 0.2 min in this procedure is more stringent than the ± 0.06 RRT units in the reference method.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following is the target compounds list for semivolatile organics that have been detected using this SOP, as well as the internal standards and surrogates. Include are the CAS number, primary and secondary ion quantitation ions, associated internal standard and surrogate, and quantitation limits. The parameters below are recommended starting points and may be modified to meet method and project requirements. All parameters are documented in the ChemStation method.

Low Level PAH (polynuclear aromatic hydrocarbons):

Compound	CAS Number	Primary Quant Ion	Secondary Ion(s)	Int. Std	Surrogate	Water ng/L	Soil ug/kg	On Col. pg
Naphthalene	91-20-3	128	102	1	1	50	2.5	50
2-Methylnaphthalene	91-57-6	142	141	1	1	50	2.5	50
1-Methylnaphthalene	90-12-0	142	141	1	1	50	2.5	50
Acenaphthylene	208-96-8	152	151, 153	2	1	50	2.5	50
Acenaphthene	83-32-9	153	152, 154	2	1	50	2.5	50
Fluorene	86-73-7	166	165	2	1	50	2.5	50
Phenanthrene	85-01-8	178	179, 152	3	2	50	2.5	50
Anthracene	120-12-7	178	179, 152	3	2	50	2.5	50
Fluoranthene	206-44-0	202	101	3	2	50	2.5	50
Pyrene	129-00-0	202	101, 100	4	2	50	2.5	50
Benz(a)anthracene	56-55-3	228	229,114	4	2	50	2.5	50
Chrysene	218-01-9	228	114, 229	4	2	50	2.5	50
Benzo(b)fluoranthene	205-99-2	252	253, 126	5	2	50	2.5	50
Benzo(k)fluoranthene	207-08-9	252	253, 126	5	2	50	2.5	50
Benzo(a)pyrene	50-32-8	252	253, 126	5	2	50	2.5	50
Indeno(1,2,3-cd)pyrene	193-39-5	276	138	5	2	50	2.5	50
Dibenzo(a,h)anthracene	53-70-3	278	139, 279	5	2	50	2.5	50
Benzo(g,h,i)perylene	191-24-2	276	138, 277	5	2	50	2.5	50
Surrogates (as utilized)								
2-Fluorobiphenyl	321-60-8	172	171	2	1			
Terphenyl-d14	1718-51-0	244	122	4	2			

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Compound	CAS Number	Primary Quant Ion	Secondary Ion(s)	Int. Std	Surrogate	Water ng/L	Soil ug/kg	On Col. pg
Internal Standards								
Naphthalene-d8	1146-65-2	136	108	1				
Acenaphthene-d10	15067-26-2	164	162, 160	2				
Phenanthrene-d10	1517-22-2	188	160	3				
Chrysene-d12	1719-03-5	240	120, 236	4				
Perylene-d12	1520-96-3	264	132, 265	5				

Low Level Phenols

Compound	CAS Number	Primary Quant Ion	Secondary Ion(s)	Int. Std	Surrogate	Water ug/L	Soil ug/kg	On Col. pg	Report
2-Chlorophenol	95-57-8	128	64,130	1	1	1	33	1000	X
3&4-Methylphenol	108-39-4/ 106-44-5	107	108,77	1	1	1	33	1000	X
2,4-Dichlorophenol	120-83-2	162	63,164	2	1	1	33	1000	X
3&4-Chlorophenol	108-43-0/ 106-48-9	128	65,130	2	1	1	33	1000	X
2,4,6-Trichlorophenol	88-06-2	196	198,97,132	3	2	1	33	1000	X
2,4,5-Trichlorophenol	95-95-4	196	198,97,132	3	2	1	33	1000	X
3,5-Dichlorophenol	591-35-5	162	164, 99,63	3	1	1	33	1000	X
3,4-Dichlorophenol	95-77-2	162	164, 99,63	3	1	1	33	1000	X
2,3,4,6-Tetrachlorophenol	58-90-2	232	230.131,133	3	2	1	33	1000	X
3,4,5-Trichlorophenol	609-19-8	196	198, 133,62	3	2	1	33	1000	X
Pentachlorophenol	87-86-5	265.9	264, 268	4	2	1	33	1000	X
Surrogates (as utilized)									
2-Chlorophenol-d4	93951-73-6	132	68,134	1	1				
2,4,6-Tribromophenol	118-79-6	330	332, 141,62	3	2				
Internal Standards									
1,4-Dichlorobenzene-d4	3855-82-1	150	152,115	1					
Naphthalene-d8	1146-65-2	136	108,54,68	2					
Acenaphthene-d10	15067-26-2	162	164, 160,80	3					
Phenanthrene-d10	1517-22-2	188	80, 94	4					

APPENDIX C.
QUALITY CONTROL PARAMETERS AND CRITERIA

ANALYSIS	SUMMARY	FREQUENCY
MS Tune (FC 43)	Mass / Target % of Mass 69 50 / 0.3-5 69 / 100 131 / 20-120 219 / 20-120 414 / 0.3-10 502 / 0.3-10	With every ICAL
GC/MS System Performance Check (DFTPP analysis)	The ion abundance ratios must meet the following criteria. Mass (m/z) / Relative Ion Abundance Criteria 51 / 10-80% of Base Peak 68 / < 2% of mass 69 70 / < 2% of mass 69 127 / 10-80% of Base Peak 197 / < 2% of mass 198 198 / Base peak, or > 50% of Mass 442 199 / 5-9% of mass 198 275 / 10-60% of Base Peak 365 / > 1% of mass 198 441 / present but < 24% of mass 442 442 / Base Peak, or > 50% of mass 198 443 / 15-24% of mass 442 Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and the peak-tailing factor should be less than 2. Breakdown criteria for DDT is less than 20%.	At the start of 12-hour analytical sequence
Initial Calibration	90% of reported analytes should meet the maximum %RSD of 20. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met: The %RSD of the reported analytes that exceed the limit is ≤ 30 The mean of the %RSD values for all reported analytes is less than or equal to 20%. Pentachlorophenol uses a quadratic curve fit. The coefficient of determination, R^2 must be ≥ 0.99	As needed

ED_006532_00005075-00220

ANALYSIS	SUMMARY	FREQUENCY
Second Source Calibration Verification	Recovery for 90% of reported analytes must be within 70-130%. Data must be flagged as failing initial calibration criteria for analytes not within the acceptance limits.	Once with every ICAL
Continuing Instrument Calibration Verification	All reported analytes should meet a maximum %D of 20 and minimum RRF of 0.010. If one or more reported analytes exceed maximum %D limit, the calibration verification may still be acceptable if the following conditions are met: 90% of reported analytes meet a maximum %D of 20 The %D of the reported analytes that exceed the limit is $\leq$ 30 The mean of the %D values for all reported analytes is less than or equal to 20. Internal standard retention time should be within 30 seconds from that in the mid-point standard level of the most recent initial calibration. EICP area for any of the internal standards should be within (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence.	Once every 12-hours
Quantitation Limit Verification	The percent recovery for 90% of the reported analytes should be between 60 to 140 percent of the actual concentration.	Once every 12-hours
Method Blank (MB)/Instrument Blank	The MB is acceptable if it contains less than one-half the quantitation limit (QL) of all target compounds.	One per extraction batch
Target Analytes	All ions present in the standard or reference mass spectrum at a relative intensity of 20 % of the most abundant ion should be present in the sample spectrum if that ion is being monitored. The relative intensities of the ions in the sample mass spectrum should agree within 30% of the relative intensities of those ions that are monitored in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum.	
Internal Standards (covering reported analytes)	Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. The retention time for any internal standard should be within 0.5 minute and the total area of internal standard should be recovered within -50% to +100% from the mid-point standard of the most recent	

ED_006532_00005075-00221

ANALYSIS	SUMMARY	FREQUENCY
	initial calibration. Compare the IS retention times and areas in the field and QC samples analyzed within the 12-hour analytical period to the associated 12-hour CCV standard. The retention time for any internal standard should be within 0.5 minute and the total area of internal standard should be recovered within -50% to +100% from the associated 12-hour CCV standard.	
Laboratory control sample (LCS)	90% of reported analytes should meet the acceptance criteria or the batch may require re-extraction. Refer to the tables below for control limits.	One per batch or every 20 samples, whichever is more frequent.
Matrix Spike/ Matrix Spike Duplicate MS/MSD	Refer to the tables below for control limits. Flag outliers.	One per batch or every 20 samples, whichever is more frequent

ED_006532_00005075-00222

LCS and MS/MSD QC Criteria:

LCS and MS/MSD criteria are based on results obtained from January 1, 2012 to December 31, 2013 for water samples. A default value of 20% will be used for the RPD for waters and 30% for other matrices. These limits will be applied to all matrices until sufficient data are available to calculate statistical limits.

Low level Polynuclear Aromatic Hydrocarbons

	LCS		Matrix Spike		
Analyte	**Lower**	**Upper**	**Lower**	**Upper**	**RPD**
1-Methylnaphthalene	20	110	37	110	20/30
2-Methylnaphthalene	20	110	40	110	20/30
Acenaphthene	25	110	45	111	20/30
Acenaphthylene	35	110	56	110	20/30
Anthracene	56	110	64	110	20/30
Benz(a)anthracene	70	125	42	136	20/30
Benzo(a)pyrene	62	110	32	115	20/30
Benzo(b)fluoranthene	63	111	28	117	20/30
Benzo(g,h,i)perylene	59	110	27	110	20/30
Benzo(k)fluoranthene	63	116	31	117	20/30
Chrysene	64	110	37	115	20/30
Dibenz(a,h)anthracene	60	121	32	117	20/30
Fluoranthene	65	110	43	123	20/30
Fluorene	36	110	51	112	20/30
Indeno(1,2,3-cd)pyrene	60	116	29	116	20/30
Naphthalene	20	110	25	116	20/30
Phenanthrene	49	110	55	110	20/30
Pyrene	57	114	34	134	20/30

Surrogate Recovery

Surrogate criteria are based on sample results obtained from January 1, 2012 to December 31, 2013 for water samples.

Surrogate	**Lower Percent**	**Upper Percent**
2-Fluorobiphenyl	32	110
Terphenyl-d14	39	136

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Low level Phenols

	LCS		Matrix Spike		
Analyte	**Lower**	**Upper**	**Lower**	**Upper**	**RPD**
2,3,4,6-Tetrachlorophenol	49	110	52	132	20/30
2,4,5-Trichlorophenol	52	110	49	142	20/30
2,4,6-Trichlorophenol	51	110	33	134	20/30
2,4-Dichlorophenol	61	110	40	132	20/30
2-Chlorophenol	60	110	53	110	20/30
3&4-Chlorophenol	57	110	39	135	20/30
3&4-Methylphenol	63	110	20	148	20/30
3,4,5-Trichlorophenol	55	110	67	150	20/30
3,4-Dichlorophenol	55	110	55	136	20/30
3,5-Dichlorophenol	55	110	58	133	20/30
Pentachlorophenol	29	110	55	150	20/30

*Insufficient historical data to establish limit. Default values appear in the table.

Surrogate Recovery

Surrogate criteria are based on sample results obtained from January 1, 2012 to December 31, 2013 for water samples.

Surrogate	**Lower Percent**	**Upper Percent**
2,4,6-Tribromophenol	20	150
2-Chlorophenol-d4	26	125

ED_006532_00005075-00224

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

A. DFTPP Method

INSTRUMENT CONTROL PARAMETERS

6890 GC METHOD

OVEN
- Initial temp: 40 'C (On)
- Initial time: 2.00 min
- Maximum temp: 350 'C
- Equilibration time: 0.50 min
- Ramps:

#	Rate	Final temp	Final time
1	15.00	330	6.00
2	0.0(Off)		

- Post temp: 0 'C
- Post time: 0.00 min
- Run time: 27.33 min

FRONT INLET (SPLIT/SPLITLESS)
- Mode: Pulsed Splitless
- Initial temp: 280 'C (On)
- Pressure: 6.03 psi (On)
- Pulse pressure: 30.0 psi
- Pulse time: 0.50 min
- Purge flow: 20.0 mL/min
- Purge time: 0.40 min
- Total flow: 23.5 mL/min
- Gas saver: On
- Saver flow: 20.0 mL/min
- Saver time: 2.00 min
- Gas type: Helium

BACK INLET (UNKNOWN)

COLUMN 1
- Capillary Column
- Model Number: Agilent 122-5536
- DB-5ms, 0.25mm * 30m * 0.5um
- Max temperature: 350 'C
- Nominal length: 30.0 m
- Nominal diameter: 250.00 um
- Nominal film thickness: 0.50 um
- Mode: constant flow
- Initial flow: 0.9 mL/min
- Nominal init pressure: 6.04 psi
- Average velocity: 34 cm/sec
- Inlet: Front Inlet
- Outlet: MSD
- Outlet pressure: vacuum

COLUMN 2
- (not installed)

FRONT DETECTOR ()

BACK DETECTOR ()

```
SIGNAL 1
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

SIGNAL 2
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

COLUMN COMP 1
   (No Detectors Installed)

COLUMN COMP 2
   (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  30.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

POST RUN
   Post Time: 0.00 min

TIME TABLE
   Time       Specifier                    Parameter & Setpoint


                              7673 Injector


     Front Injector:
        Sample Washes                 0
        Sample Pumps                  3
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        Nanoliter Adapter           Off
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number :
 Column 2 Inventory Number :

                              MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File                 : 040214DFT.U
Acquistion Mode           : Scan
```

```
MS Information
-- -----------

Solvent Delay            : 3.00 min

EM Absolute              : True
Resulting EM Voltage     : 1200.0

[Scan Parameters]

Low Mass                 : 50.0
High Mass                : 550.0
Threshold                : 500
Sample #                 : 2       A/D Samples    4
Plot 1 low mass          : 50.0
Plot 1 high mass         : 550.0

[MSZones]

MS Quad                  : 200 C   maximum 200 C
MS Source                : 250 C   maximum 250 C


                    END OF MS ACQUISITION PARAMETERS


                         TUNE PARAMETERS
                   ----------------------------

 EMISSION     :      34.610
 ENERGY       :      69.922
 REPELLER     :      28.783
 IONFOCUS     :      90.157
 ENTRANCE_LE  :       0.000
 EMVOLTS      :    1141.176
 AMUGAIN      :    2150.000
 AMUOFFSET    :     126.000
 FILAMENT     :       1.000
 DCPOLARITY   :       0.000
 ENTLENSOFFS  :     20.078@ 50    13.553@ 69    14.055@131    12.549@219
10.290@414    10.039@502
MASSGAIN      :     241.000
MASSOFFSET    :     -15.000
```

B. PAH Method

INSTRUMENT CONTROL PARAMETERS

6890 GC METHOD

OVEN

Initial temp: 40 'C (On)
Initial time: 2.00 min
Maximum temp: 350 'C
Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	25.00	150	0.00
2	15.00	330	6.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 24.40 min

FRONT INLET (SPLIT/SPLITLESS)

Mode: Pulsed Splitless
Initial temp: 280 'C (On)
Pressure: 6.03 psi (On)
Pulse pressure: 30.0 psi
Pulse time: 0.50 min
Purge flow: 20.0 mL/min
Purge time: 0.40 min
Total flow: 23.5 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

BACK INLET (UNKNOWN)

COLUMN 1

Capillary Column
Model Number: Agilent 122-5536
DB-5ms, 0.25mm * 30m * 0.5um
Max temperature: 350 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.50 um
Mode: constant flow
Initial flow: 0.9 mL/min
Nominal init pressure: 6.04 psi
Average velocity: 34 cm/sec

COLUMN 2

(not installed)

```
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR ()                        BACK DETECTOR ()

SIGNAL 1                                 SIGNAL 2
   Data rate:  20 Hz                        Data rate:  20 Hz
   Type:  test plot                         Type:  test plot
   Save Data:  Off                          Save Data:  Off
   Zero:  0.0 (Off)                         Zero:  0.0 (Off)
   Range:  0                                Range:  0
   Fast Peaks:  Off                         Fast Peaks:  Off
   Attenuation:  0                          Attenuation:  0

COLUMN COMP 1                            COLUMN COMP 2
   (No Detectors Installed)                 (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  30.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

                                         POST RUN
                                            Post Time: 0.00 min

TIME TABLE
   Time       Specifier                     Parameter & Setpoint


                              7673 Injector


     Front Injector:
        Sample Washes                 0
        Sample Pumps                  3
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        Nanoliter Adapter           Off
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number :
 Column 2 Inventory Number :

                              MS ACQUISITION PARAMETERS
```

```
General Information
------- -----------

Tune File                 : 041714DFT.U
Acquistion Mode           : SIM


MS Information
-- -----------

Solvent Delay             : 3.60 min

EM Absolute               : True
Resulting EM Voltage      : 1247.1

[Sim Parameters]

GROUP 1
Group ID                  : 21
Resolution                : High
Plot 1 Ion                : 136.0
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                          ( 102.0,     25) ( 108.0,     25) ( 128.0,
25)
                          ( 136.0,     25) ( 141.0,     25) ( 142.0,
25)
                          ( 171.0,     25) ( 172.0,     25)

GROUP 2
Group ID                  : 43
Resolution                : High
Group Start Time          : 10.16
Plot 1 Ion                : 151.0
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                          ( 139.0,     25) ( 151.0,     25) ( 152.0,
25)
                          ( 153.0,     25) ( 154.0,     25) ( 160.0,
25)
                          ( 162.0,     25) ( 164.0,     25) ( 168.0,
25)

GROUP 3
Group ID                  : 52
Resolution                : High
Group Start Time          : 11.14
Plot 1 Ion                : 166.0
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                          ( 152.0,     25) ( 160.0,     25) ( 165.0,
25)
                          ( 166.0,     25) ( 167.0,     25) ( 178.0,
25)
```

```
                         ( 179.0,     25) ( 188.0,     25)

GROUP 4
Group ID                 : 66
Resolution               : High
Group Start Time         : 13.94
Plot 1 Ion               : 101.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 100.0,     25) ( 101.0,     25) ( 122.0,
25)
                         ( 202.0,     25) ( 244.0,     25)

GROUP 5
Group ID                 : 71
Resolution               : High
Group Start Time         : 16.58
Plot 1 Ion               : 240.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 114.0,     25) ( 120.0,     25) ( 228.0,
25)
                         ( 229.0,     25) ( 236.0,     25) ( 240.0,
25)

GROUP 6
Group ID                 : 77
Resolution               : High
Group Start Time         : 18.35
Plot 1 Ion               : 264.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 126.0,     25) ( 132.0,     25) ( 252.0,
25)
                         ( 253.0,     25) ( 264.0,     25) ( 265.0,
25)

GROUP 7
Group ID                 : 80
Resolution               : High
Group Start Time         : 20.61
Plot 1 Ion               : 278.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 138.0,     25) ( 139.0,     25) ( 276.0,
25)
                         ( 277.0,     25) ( 278.0,     25) ( 279.0,
25)

[MSZones]

MS Quad                  : 200 C   maximum 200 C
MS Source                : 250 C   maximum 250 C


                         END OF MS ACQUISITION PARAMETERS
```

```
                          TUNE PARAMETERS
                     ------------------------------

 EMISSION    :      34.610
 ENERGY      :      69.922
 REPELLER    :      28.783
 IONFOCUS    :      90.157
 ENTRANCE_LE :       0.000
 EMVOLTS     :    1141.176
 AMUGAIN     :    2150.000
 AMUOFFSET   :     126.000
 FILAMENT    :       1.000
 DCPOLARITY  :       0.000
 ENTLENSOFFS :     20.078@ 50    13.553@ 69    14.055@131    12.549@219
10.290@414    10.039@502
MASSGAIN     :     229.000
MASSOFFSET   :     -15.000


                        END OF TUNE PARAMETERS
                   -----------------------------------



                        END OF INSTRUMENT CONTROL PARAMETERS
                        ------------------------------------
```


ED_006532_00005075-00232

C. Phenol Method

```
                              INSTRUMENT CONTROL PARAMETERS:    AG5973L
                              ----------------------------------------

   C:\MSDCHEM\1\2014\METHOD\041814PCP_M&B.M
      Fri Apr 18 16:15:56 2014

Control Information
------- -----------

Sample Inlet      :  GC
Injection Source  :  GC ALS
Mass Spectrometer :  Enabled

==============================================================================
===
                                  6890 GC METHOD
==============================================================================
===


OVEN
   Initial temp:  40 'C (On)                Maximum temp:  350 'C
   Initial time:  0.00 min                  Equilibration time:  0.00 min
   Ramps:
      #  Rate  Final temp  Final time
      1 15.00      220        0.00
      2 25.00      330        6.00
      3   0.0(Off)
   Post temp:  50 'C
   Post time:  0.00 min
   Run time:  22.40 min


FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (UNKNOWN)
   Mode:  Pulsed Splitless
   Initial temp:  275 'C (On)
   Pressure:  7.06 psi (On)
   Pulse pressure:  30.0 psi
   Pulse time:  0.50 min
   Purge flow:  40.0 mL/min
   Purge time:  0.40 min
   Total flow:  43.8 mL/min
   Gas saver:  Off
   Gas type:  Helium


COLUMN 1                                COLUMN 2
   Capillary Column                        (not installed)
   Model Number:  Restek RTX-1
   30m X 0.25MM X 0.25df
   Max temperature:  350 'C
```

```
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow
   Initial flow:  1.0 mL/min
   Nominal init pressure:  7.07 psi
   Average velocity:  36 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum


FRONT DETECTOR (NO DET)                  BACK DETECTOR (NO DET)


SIGNAL 1                                 SIGNAL 2
   Data rate:  20 Hz                        Data rate:  20 Hz
   Type:  test plot                         Type:  test plot
   Save Data:  Off                          Save Data:  Off
   Zero:  0.0 (Off)                         Zero:  0.0 (Off)
   Range:  0                                Range:  0
   Fast Peaks:  Off                         Fast Peaks:  Off
   Attenuation:  0                          Attenuation:  0


COLUMN COMP 1                            COLUMN COMP 2
   (No Detectors Installed)                 (No Detectors Installed)


THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)


                                         POST RUN
                                            Post Time: 0.00 min


TIME TABLE
   Time       Specifier                     Parameter & Setpoint


                              GC Injector


     Front Injector:
        Sample Washes                0
        Sample Pumps                 3
        Injection Volume          1.00 microliters
        Syringe Size              10.0 microliters
```

```
        PreInj Solvent A Washes       1
        PreInj Solvent B Washes       1
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               0 seconds
        Plunger Speed              Slow
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes


     Back Injector:
No parameters specified

 Column 1 Inventory Number :
 Column 2 Inventory Number :

                                MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File                : 041814DFT.U
Acquistion Mode          : SIM


MS Information
-- -----------

Solvent Delay            : 4.30 min

EMV Mode                 : Absolute
Resulting EM Voltage     : 1200

[Sim Parameters]

GROUP 1
Group ID                 : 1
Resolution               : High
Plot 1 Ion               : 64.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 64.00,     25) ( 68.00,     25) ( 77.00,
25)
                         (107.00,     25) (108.00,     25) (115.00,
25)
                         (128.00,     25) (130.00,     25) (132.00,
25)
                         (134.00,     25) (150.00,     25) (152.00,
25)

GROUP 2
Group ID                 : 2
Resolution               : High
Group Start Time         : 7.36
Plot 1 Ion               : 54.00
```

```
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 54.00,     25) ( 63.00,     25) ( 65.00,
25)
                         ( 68.00,     25) ( 98.00,     25) (108.00,
25)
                         (128.00,     25) (130.00,     25) (136.00,
25)
                         (162.00,     25) (164.00,     25)

GROUP 3
Group ID                 : 3
Resolution               : High
Group Start Time         : 9.32
Plot 1 Ion               : 63.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 63.00,     25) ( 80.00,     25) ( 97.00,
25)
                         ( 99.00,     25) (132.00,     25) (160.00,
25)
                         (162.00,     25) (164.00,     25) (196.00,
25)
                         (198.00,     25)

GROUP 4
Group ID                 : 4
Resolution               : High
Group Start Time         : 11.63
Plot 1 Ion               : 332.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 62.00,     25) (131.00,     25) (133.00,
25)
                         (141.00,     25) (196.00,     25) (198.00,
25)
                         (230.00,     25) (232.00,     25) (330.00,
25)
                         (332.00,     25)

GROUP 5
Group ID                 : 5
Resolution               : High
Group Start Time         : 13.13
Plot 1 Ion               : 80.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,
Dwell)
                         ( 80.00,     25) ( 94.00,     25) (188.20,
25)
                         (264.00,     25) (265.90,    100) (268.00,
25)

[MSZones]

MS Source                : 230 C   maximum 250 C
MS Quad                  : 150 C   maximum 200 C
```

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS for SN: US21863784

Trace Ion Detection is OFF.

```
EMISSION    :      34.610
ENERGY      :      69.922
REPELLER    :      25.767
IONFOCUS    :      78.769
ENTRANCE_LE :       0.000
EMVOLTS     :    1200.000
                              Actual EMV  :    1200
                              GAIN FACTOR :       2.39
AMUGAIN     :    1944.000
AMUOFFSET   :     122.000
FILAMENT    :       1.000
DCPOLARITY  :       0.000
ENTLENSOFFS :     13.804@  3    13.804@ 50    12.298@ 69    11.796@131
13.804@219    15.812@414    15.059@502    15.059@799
MASSGAIN    :    -153.000
MASSOFFSET  :      -8.000
```

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA

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BFB	BFB
DFTPP	DFT

C: Channel (use when applicable):

Front	A
Back	B
Both	AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)

Water	W
Solid	S
Air	A
Oil	O
Other	X

YY: Year i.e. 12 for 2012

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Split vent trap	Annually	Replace.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	With each ICAL	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.

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MS Maintenance

Maintenance schedule

Task	Every week	Every 6 months	Every year	As needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check the calibration vial(s)		✓		
Replace the foreline pump oil[1]		✓		
Clean the ion source				✓
Check the carrier gas trap(s) on the GC				✓
Replace the worn out parts				✓
Lubricate sideplate or vent valve O-rings[2]				✓

1 Every 3 months for CI MSDs using ammonia reagent gas.

2 Vacuum seals other than the side plate O-ring and vent valve O-ring do not need to be lubricated. Lubricating other seals can interfere with their correct function.

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APPENDIX G.
METHOD PERFORMANCE

Low level Polynuclear Aromatic Hydrocarbons

Analyte	Number of Points	Mean	StdDev	Lower Performance	Upper Performance
1-Methylnaphthalene	20	49.1	10.9	27.2	70.9
2-Methylnaphthalene	35	48.5	11.4	25.7	71.3
Acenaphthene	35	57.8	10.9	36.1	79.5
Acenaphthylene	20	65.6	10.2	45.2	86.0
Anthracene	20	78.8	7.6	63.5	94.0
Benzo(a)anthracene	35	97.7	9.1	79.4	116.0
Benzo(a)pyrene	36	85.8	8.0	69.7	102.0
Benzo(b)fluoranthene	35	87.1	7.9	71.2	103.0
Benzo(g,h,i)perylene	35	84.4	8.6	67.3	102.0
Benzo(k)fluoranthene	35	89.8	8.8	72.2	107.0
Chrysene	35	85.7	7.2	71.3	100.0
Dibenz(a,h)anthracene	35	90.6	10.2	70.1	111.0
Fluoranthene	35	85.7	7.0	71.6	99.7
Fluorene	35	66.3	10.0	46.2	86.3
Indeno(1,2,3-cd)pyrene	35	88.2	9.4	69.4	107.0
Naphthalene	35	51.9	10.6	30.7	73.2
Phenanthrene	35	72.8	8.0	56.8	88.7
Pyrene	35	85.5	9.6	66.3	105.0

Low level Phenols

Analyte	Number of Points	Mean	StdDev	Lower Performance	Upper Performance
2,3,4,6-Tetrachlorophenol	18	73.3	8.1	57.1	89.5
2,4,5-Trichlorophenol	23	77.7	8.5	60.8	94.6
2,4,6-Trichlorophenol	23	76.7	8.5	59.6	93.7
2,4-Dichlorophenol	23	81.0	6.7	67.5	94.5
2-Chlorophenol	23	79.8	6.5	66.8	92.9
3&4-Chlorophenol	23	79.0	7.3	64.3	93.6
3&4-Methylphenol	23	85.4	7.5	70.4	100.0
3,4,5-Trichlorophenol	23	82.4	9.0	64.4	100.0
3,4-Dichlorophenol	23	78.7	8.0	62.8	94.7
3,5-Dichlorophenol	23	78.3	7.7	62.9	93.7
Pentachlorophenol	24	66.0	12.2	41.5	90.5

NOTE: The above data are from analysis of LCS in water for January 1, 2012 to December 31, 2013.

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APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 375
Revision: 5, Effective: 05/09/14

Low Level Semivolatile Organics Analysis

Revision	Effective Date	Description
3	04/13/09	Complete update of procedure to reflect multiple changes in the method. Included phenols, added method performance data, updated procedures for analytical methods.
4	02/01/12	1. Replaced Method Performance and QC Limits with recent data. 2. Updated tune criteria to Method 8270D recommendations. 3. Miscellaneous edits throughout for consistency with EPA Region 9 Laboratory practices (internal COC, waste labeling, etc.).
5	05/09/14	1. Updated Method Performance and QC limits and instrument parameters. 2. Changed DFTPP injection amount to prevent overloading. 3. Miscellaneous edits throughout for consistency with EPA Region 9 Laboratory practices (SOP 850, internal COC, waste labeling, etc.). 4. Phenol, 2-methylphenol, and 2,4-dimethylphenol were removed from the low level phenol method.

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USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 380
PURGEABLE HYDROCARBONS BY GC FID

Revision 8
Effective Date: January 15, 2014

Reviewed by: _____ 1/9/14
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: _____ 1-9-2014
Lucrina Jones, Laboratory QA Officer — Date

Approved by: _____ 1/9/14
Brenda Bettencourt, Laboratory Director — Date

Periodic Review:

Signature	Title	Date
	ESAT QA Officer	2/23/16

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105015-16584.

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD
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APPENDIX C. QUALITY CONTROL MEASURES AND CRITERIA
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APPENDIX F. PREVENTIVE MAINTENANCE REQUIREMENTS
APPENDIX G. REVISION HISTORY

1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used to determine total petroleum hydrocarbons in the gasoline range (TPH-GRO) by gas chromatography (GC) in water and solid matrices. This SOP is based on procedures from EPA SW 846 Method 5030C Revision 3, May 2003; Method 5035A Draft Revision 1, July 2002; and Method 8015C Revision 3, February 2007. Deviations from reference methods are described in Appendix A.

Analytes and quantitation limits are provided by matrix in Appendix B.

2 METHOD SUMMARY

An inert gas is bubbled through a portion of an aqueous sample (or methanol extract from solid samples). Volatile organic compounds are vaporized and swept through a sorbent column where they are adsorbed. The sorbent column is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column. A temperature program is used in the gas chromatograph to separate the organic compounds followed by detection using a flame ionization detector (FID).

TPH-DRO is quantitated by determining the retention times of 2-methylpentane and 1,2,4-trimethylbenzene and using these markers to establish the retention time range of the gasoline. The area sum response of the sample over this retention time range is compared to the area sum response of gasoline standards analyzed under the same conditions. Probable identification of gasoline in samples is done by comparing the chromatographic pattern generated by analysis of the sample to the chromatographic pattern generated by analysis of gasoline standard analyzed under the same conditions. The identification of TPH as a specific fuel type may be complicated by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

Storage Blank (SB) – An aliquot of reagent water stored with samples in the sample storage refrigerator. The storage blank indicates whether contamination may have occurred during sample storage.

Gasoline Range Organics (GRO) Hydrocarbons that elute in the GC retention time range from 2-methylpentane and to 1,2,4-trimethylbenzene, as described in Section 8.2.1. This corresponds approximately to a carbon range of C_6-C_{10}.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including laboratory coats, safety glasses, and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager to determine if additional treatment is required. Refer to the Material Safety Data Sheets located in the library and the LAN at I:\MSDS IMAGES for additional information.

4.1.1 Methanol

Methanol is the primary solvent used for the preparation of standards and for soil sample extraction in these procedures. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing, shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness, and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly.

Use methanol in a laboratory fume hood with appropriate personal protective equipment (laboratory coat, nitrile gloves, and safety glasses). Store methanol in a flammable storage cabinet away from oxidizers and sources of ignition.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Many parts of the GC and autosampler operate at temperatures high enough to cause serious burns. Allow heated zones to cool below 50°C before working on or around them.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever

possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedures*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Aqueous waste (wastewater)	Hazardous Waste	Toxic
Methanol waste	Hazardous Waste	Flammable, toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

5.1.1 Water Samples:

Water samples should be collected in pre-cleaned 40-mL screw cap vials equipped with Teflon-faced silicone septum. Volume collected should be sufficient to allow for replicate analysis yet minimize waste disposal. Three 40-mL vials should be sufficient to meet these objectives.

Water samples should be preserved with hydrochloric acid (HCl) to pH < 2 at the time of sampling. If an unpreserved water sample is received, inform the Chemistry Technical Director immediately so that the proper notifications can be made.

5.1.2 Soil Samples:

Soil samples should be collected using 5 g EnCore™ samplers when possible. Alternative collection methods are allowable if storage conditions and holding times conform to requirements. The following table summarizes the available techniques for soil samples:

Field Sampling, Storage, and Transport Options				
Collection Container	Field Preservation	Field/Transport Temperature	Holding Time Under Field Storage Temp.	Laboratory Options (see below)
Encore*	None	4 ± 2° C or < -7° C	48 hours	1
40-mL vial	None	4 ± 2° C or < -7° C	48 hours	1
40-mL vial	Methanol	4 ± 2° C or < -7° C	14 days	2
Laboratory Options If not analyzed within 48 hours of sampling.				
Option	Laboratory Preservation	Lab Storage Temperature	Holding Time (collection to analysis)	
1	Methanol	< -7° C and ≥ -20 C	14 days	
2	As received	< -7° C and ≥ -20 C	14 days	

* Samples received in Encore samplers are transferred to 40-mL vials prior to completing laboratory options or analysis within 48 hours of sampling.

Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. Three 5-g Encore containers or samples extruded into 40-mL VOA vials should be sufficient to meet these objectives.

Use of sediment jars, 25g EnCore samplers, or other methods of unconsolidated soil sample collection is unacceptable due to the substantial loss of volatile organics under these conditions. Request guidance from the supervisor or Technical Director if samples are received for analysis in these containers.

Note: A separate 10 gram aliquot of solid material should be collected for percent solids determination if results are required on a "dry weight" basis.

5.1.3 Waste samples:

Waste samples (non-aqueous liquids, solid matrices other than soils) should be collected in a pre-cleaned 40-mL screw cap vial equipped with a Teflon-faced silicone septum vial. The vial should be filled to minimize headspace and stored or analyzed as outlined above. Only one vial need be collected as the volume will be sufficient for repeated analysis.

In general, storage, preservation, and holding times for wastes are the same as for soil samples (see section 5.1.2). However, if high concentrations of target analytes are suspected, waste samples should be segregated from low concentration volatile samples to prevent cross contamination, additionally, waste samples must be reviewed on a case-by-case basis and diluted to prevent damage to instrumentation due to either matrix interferences (e.g. foaming or volatile acids) or high concentrations of target analytes that could contaminate instruments. Non-aqueous liquids are frequently highly contaminated and should be preserve or dilute such that the sample to solvent ratio is 100 mg to 1 g in 10 mLs of methanol instead of the usual 5 grams. The original sample should be frozen.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form. Notify the sample custodian of any discrepancies.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

Samples are delivered by the Sample Custodian to Room 201, logged into the Laboratory Information Management System (LIMS), and transferred to the sample refrigerator (or freezer, as applicable). The LIMS database is then updated to change the container disposition to "available in".

Check the following information to ensure that the information on the sample containers corresponds to the information on the tracking sheets and the chain-of custody record:

- EPA Work Order Number
- EPA sample number.
- Case number.
- Sample Delivery Group number

5.3 Preservation Verification

Verify that the samples are preserved as outlined in section 5.1.1 or 5.1.2.

5.4 Sample Storage

Water samples must be stored at >0 and < 6 ° C. See section 5.1.2 for soil and waste storage requirements.

Maintain additional aliquots under these storage conditions until the holding time has expired and analysis is completed.

Retain samples and extracts for 60 days after the final analytical report is sent to the data user. This allows for confirmation of labeling information should questions arise. Storage conditions do not need to be monitored or comply with the above criteria.

5.5 Holding Time

Acid preserved water samples must be analyzed within 14 days from the date of sample collection; unpreserved water samples must be analyzed within 7 days from the date of sample collection. See section 5.1.2 for soil and waste holding time requirements.

6 INTERFERENCES

Method interference may be caused by impurities in the purge gas, organic compounds out gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during storage and handling.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105° C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

Solvents and other compounds, which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Dichloromethane, acetone and other common laboratory chemicals are target analytes under this SOP and must be excluded from Room 201. Particular attention must be paid to the possibility of transport of solvent vapors on individuals. Analysts should never enter Rooms 201 or 209 after being in the extraction laboratories or glassware washing area.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Analytical balance - capable of measuring differences of 0.01 g.
- Gas chromatograph (Agilent AG6890 gas chromatograph, Agilent AG7890 gas chromatograph, or equivalent) equipped with a FID detector (or PID/FID in series) and a splitless injection port or an OI Low-Dead-Volume Injector, or equivalent.
- Data Acquisition and Processing System - able to control the GC and to acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Agilent Technologies EnviroQuant ChemStation software and data acquisition computers (or equivalent).
- Fused Silica Capillary Gas Chromatography Column - 75m x 0.53mm x 3µm RTX-624 wide bore capillary column (Restek part # 10974, or equivalent). Any capillary column that provides adequate resolution, capacity, accuracy, and precision may be used.
- Purge and trap concentrator OI Eclipse 4660, Tekmar 3000 purge and trap concentrator, or equivalent.
- Autosampler: OI Archon 4552, Varian Archon, or equivalent.
- VOCARB 3000 type K trap, EST Vocarb 300 cat # E70300-K03, or equivalent – alternate traps may be used provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision.

7.2 Reagents

All chemicals must be entered into the EMS inventory upon receipt. The analyst must enter all reagent receipt and preparation in the LIMS.

- Methanol (Purge & Trap grade).
- Hydrochloric acid (HCl), concentrated, reagent grade
- Hydrochloric acid, 6N HCl - Slowly add 250 mL of reagent grade concentrated HCl to250 mL of organic-free method blank water. Prepare as needed, not to exceed annually. Also known as 1:1 or 1+1 HCl.
- Organic-free method blank water (prepared using USEPA Region 9 Laboratory SOP 205).

7.3 Standards

All standards must be entered into the EMS inventory upon receipt. The analyst must enter all standards into the LIMS. Standards and samples must not be stored in the same refrigerator or freezer. Protect all standards from light.

Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials. Store ampulated stock standard solutions in the Room 201 refrigerator at >0° to < 6° C. Follow manufacturer's recommendations for solution expiration date.

Store all working standard solutions in glass bottles or vials with Teflon lined screw caps at <-10° C.

Fresh standards should be prepared every six months, or sooner if comparison with check-standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months or sooner if QC results indicate a problem.

Opened ampules of standards must be discarded six months after opening, at the manufacturer's expiration date, or earlier if evidence of degradation is observed. LIMS expiration dates must be revised when ampules are opened if the remaining time on the vendor expiration date exceeds six months. The vendor expiration date should be recorded in the comment portion of the standard record.

The following solution concentrations are recommended only; other concentrations and / or suppliers can be used.

CAUTION: Allow all standard solutions to equilibrate to room temperature before use.

- Gasoline Stock Standard: Restek #30205 (XHc Unleaded Gasoline Composite Standard at 50,000 µg/mL), or equivalent. This standard is also used as the MS/MSD and LCS source for soil/solid matrices.

- Gasoline Primary Dilution Standards (PDS): Prepare a solution by diluting the Gasoline Stock Standard to concentration 1,000 µg/mL in P&T methanol (200 uL to 10 mL), or equivalent.

- SCV Stock Standard: Supelco # 47516-U (Gasoline at 20,000 µg/mL), or equivalent.

- SCV Primary Dilution Standards (SCVPDS): Prepare a solution by diluting the SCV Stock Standard to concentration 1000 µg/mL in P&T methanol (500 uL to 10 mL)), or equivalent.

- Second Source Verification (SCV) - Equivalent to the mid-point initial calibration solution, 500 µg/L but prepared from a source different from the source of calibration standards (use SCV Primary Dilution Standards (SCVPDS) to make this standard).

- Window Defining Standard (WDS): AccuStandard Custom Mix S-10760-2.5X or equivalent. This solution contains 2-methylpentane and 1,2,4-trimethylbenzene at 5,000 µg/mL in methanol.

- Window Defining Standard Primary Dilution Standards (WDSPDS): Prepare by diluting the WDS standard to 1000 µg/mL in P&T methanol (1000 uL to 5 mL), or equivalent.

- Surrogate Spike Stock: Restek # 30083, solution of α,α,α-trifluorotoluene in methanol at 10,000 µg/mL, or equivalent.

- Surrogate Spike: Prepare a solution by diluting the Surrogate Spike Solution Stock Standard to concentration of 625 µg/mL in P&T methanol (625 uL to 10 mL), or equivalent.

- As needed, other hydrocarbon mixtures at 500 µg/L in water. These standards are used for identification purpose only.
    - Kerosene, 50 mg/mL; Restek 31256
    - Diesel, 50 mg/mL; Restek 31258
    - Stoddard, 20.0 mg/mL; AccuStandard HS-005S-40X

- Lacquer Thinner, 20.0 mg/mL; AccuStandard HS-001S-40X
- Mineral Spirits, 20.0 mg/mL; AccuStandard HS-002S-40X
- Naptha, 20.0 mg/mL; AccuStandard HS-003S-40X
- Turpentine, 20.0 mg/mL; AccuStandard HS-004S-40X
- Hydraulic Fluid, 20.0 mg/mL; AccuStandard FU-020-D-40X
- Turbine (Jet) fuel comp. 20.0 mg/mL; AccuStandard FU-006-40X

- Site specific hydrocarbon standards may also be supplied by the project manager for use in the laboratory.

7.3.1 Calibration Solutions

The following calibration solution concentrations are typical concentrations only; other concentrations may be used. Use of gastight syringes is required for sample and standard preparation.

Prepare all working calibration standards in organic-free method blank water.

- Prepare the calibration standards by adding the following solutions to 50 mL of water in a gastight syringe to make standards at recommended concentrations prior to mixing and transferring the resulting solution to a 40-mL VOA vial and loading the vial onto the autosampler.

QC Type	Solution	Conc. µg/mL	Volume Used, µL	Final Volume, mL	Final Conc., µg/L
WDS	WDSPDS	1000	25	50	500
ICAL 1 QLS	Gas PDS	1000	2.5	50	50
ICAL 2	Gas PDS	1000	5	50	100
ICAL 3 CCV/LCS	Gas PDS	1000	25	50	500
ICAL 4	Gas PDS	1000	50	50	1,000
ICAL 5	Gas PDS	1000	100	50	2,000
SCV	SCV PDS	1000	25	50	500

7.4 The autosampler introduces 1 uL of the Surrogate Spike Solution to each sample at 625 µg/mL in P&T methanol for a final concentration of 125 µg/L.

7.5 Supplies

- Disposable Pasteur pipettes.

- Fritted sparge vessels (10 mL and 25-mL).
- Gastight syringes (5-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 25-mL, and 50 mL). All syringes utilized must be rinsed with Purge and Trap grade methanol.
- pH paper (pH 0-14 range).
- Screw-cap vial, 40-mL VOC vials for standards with screw-hollow cap lined with 22 mm PTFE-faced silicone septa.
- Stainless steel spatulas
- Trap (VOCARB 3000 type K, or equivalent).
- Volumetric flasks, Class A - appropriate sizes with ground glass stoppers.
- EnCore extrusion tool.
- 10 mL Disposable syringes.
- 40-mL VOC vials for standards with screw-hollow cap lined with 22 mm PTFE faced silicone septa.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Note: If the instrument is equipped with a functioning PID, the detector should be calibrated for the surrogate. The information provided by the more selective detector can be used to verify that the presence of aromatic hydrocarbons even in the presence of significant amounts of other, i.e., straight chain hydrocarbons. However, the surrogate should always be reported from the FID; the PID calibration is not required for method control (i.e. do not stop analysis or rerun samples for PID failure).

Set up instruments using operating parameters provided in Appendix D. Adjust as needed to meet method and SOP requirements and chromatographic practice.

Enter data into ChemStation using file naming conventions provided in Appendix E.

Bake the trap and the GC oven for at least 14 minutes each day before samples are analyzed.

Prior to analyzing calibration, QC, or field samples, make a LIMS batch and sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

Ensure that all appropriate waste containers are properly connected and labeled.

8.2 Calibration and Standardization

The calibration standards preparation is detailed in Section 7.3.1. The same calibration is used for water and soil samples.

Set up the purge and trap concentrator for water analysis ensuring that the sparge needles reach to within 5 mm of the bottom of the sparge cells. The same calibration is used for the analysis of both water and soil methanol extracts.

8.2.1 Initial Calibration

The retention time range for GRO is defined during initial calibration. Two specific gasoline components are used to establish the range, 2-methylpentane and 1,2,4-trimethylbenzene. The retention time range is then calculated based on the lower limit of the RT window for 2-methylpentane and the upper limit of the RT window for 1,2,4-trimethylbenzene.

Perform an initial calibration using standards prepared in Section 7.3.1. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Check that compound type in ChemStation is set to H. This setting sums the area between the start and end of the analyte range.

An example of initial calibration sequence appears below:

	Sample Name		Sample Name
1	IB	6	ICAL 4
2	WDS standard	7	ICAL 5
3	ICAL 1 (QLS)	8	IB
4	ICAL 2	9	SCV
5	ICAL 3 (CCV)	10	Other fuels as needed

Spike the water with the appropriate amount of primary dilution standard for the specific calibration solution being analyzed. See Section 7.3.1 for details.

Quantitate each calibration standard and samples using this retention time range established using WDS standard.

1. In the ChemStation data analysis module, load the current initial calibration method as outlined in the "ChemStation File Naming Convention"
2. Perform an initial calibration using the recommended concentrations listed in Section 7.3.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time for the surrogate in the method using the newly acquired continuing calibration level.
5. Save the method as outlined in the "ChemStation File Naming Convention"

6. Generate "Response Factor Report."
7. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
8. Check the time and date to ensure that the correct update is used.
9. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report".
10. Verify that the method was updated correctly.
11. Print page 3 of the ChemStation ICAL for gasoline to show that the method was updated correctly.
12. Copy the method to the LAN as outlined in the "ChemStation File Naming Convention"
13. Manually calculate a result for the surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
14. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

If the initial calibration, the SCV, and the IB meet all criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples.

As needed, analyze other hydrocarbons with each ICAL.

8.2.2 Retention Time Windows

Based on experience and historical data, the EPA Region 9 Laboratory uses a default retention time window of +/- 0.03 minutes for single component analytes. This approach is based on the insignificant retention time drift observed historically and the option listed in SW846 Method 8000C section 11.6 to select an alternative approach to the usual analysis of standards for the calculation of retention time windows.

Establish the ChemStation retention time window as ± 0.06 minutes for the surrogate (peaks that drift more than 0.03 minutes will be flagged "f" by the data system as possible false positive).

All surrogates in the field and QC samples must fall within the established retention time windows.

All target analytes, surrogates, and/or n-alkanes in the calibration verification analyses must fall within previously established retention time windows. If the retention time of any analyte does not fall within the established window, then corrective action must be taken to restore the system or a new calibration curve must be prepared for that compound.

8.2.3 Continuing Calibration Verification (CCV)

Perform calibration using standard prepared in Section 7.3.1. Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

1. In the ChemStation data analysis module, load the current initial calibration method .
2. Acquire the continuing calibration using the current initial calibration method.
3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Manually calculate the result for the surrogate to insure that the correct RFs are being used. Record the result on the quantitation report.
6. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "QLast Update : Mon Jul 25 08:15:58 2011"), is recorded on each file header.
7. If QLast Update time stamp changes, state the reason, repeat steps 4-6, and include the reports generated in the package.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.4 Quantitation Limit Verification Standard (QLS)

Analyze a quantitation limit standard using standard prepared in Section 7.3.1. Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Refer to Appendix C for acceptance criteria and corrective action requirements.

8.3 Sample Analysis

Check that the LIMS ID and client sample ID on the vials coincide with the numbers on the LIMS Work Order to ensure that the correct sample is being analyzed.

If the sample has an unusual color, or other physical characteristic such as more than one phase, the presence of a precipitate, unusual viscosity, or physical signs of contamination. A screening analysis is required to protect the analytical system from damage or contamination and to determine the appropriate subsequent dilution. If an initial screening is necessary, analyze the sample at a 1:50 dilution, unless the group leader or Technical Director specifies otherwise. Document observed anomalies in the LIMS MMO field.

MS/MSD and LCS spiking is preformed at time of analysis. CCV and LCS requirements maybe satisfied in one analysis.

8.3.1 Water Sample Preparation

Note in the LIMS MMO field in the work order window if there is headspace present in the sealed sample vial. If the bubble exceeds 6 mm in diameter, data qualification may be required.

Water Spike Amounts

Sample	Surrogate Spike, µL*	Gas PDS, µL
Blanks	1.0	NA
Samples	1.0	NA
CCV/LCS	1.0	25.0
MS/MSD	1.0	20.0

Prepare LCS in 50-mL gas-tight and transfer to 40-mL vial.
NA = Not Applicable
* SS is added by autosampler.

- Allow the samples to reach ambient room temperature before analysis.
- Break the chain of custody seal on the vial with a scalpel or other appropriate implement, and note if the seal is missing or compromised in any way.
- To spike the MS and MSD, quickly remove the cap from each 40-mL sample vial and spike directly in the field sample vial and recap the vial.
- Load the samples in the autosampler. The autosampler will add surrogate.
- After analysis, check the pH of the sample using pH 0-14 range pH paper. Record the pH in the injection logbook. Note any samples that have a pH greater than 2 in the LIMS MMO field in the work order window.

8.3.2 Soil Sample Preparation

The typical sample weight is 5 g (nominal).

The percent moisture is determined from a separate aliquot as described in EPA Region 9 Laboratory SOP 460, *Percent Moisture Determination*.

To prevent the loss of certain volatile organics the sample must not be allowed to reach room temperature. The following steps must be taken as rapidly as

possible to prevent loss of volatile components. Have the LIMS benchsheet prepared and all vials, standards, etc. ready prior to beginning the next steps.

1. Remove the sample from the refrigerator or freezer immediately prior to extraction or analysis. Samples should be extracted as soon as possible after receipt even if analysis will not to be performed immediately.

2. Break the chain of custody seal on the container with a scalpel or other appropriate implement, again making note in the logbook if the seal is missing or compromised in any way. Observe the sample closely for evidence of contamination. If the sample appears to contain hydrocarbons (an oily appearance or sheen), the sample must be analyzed at a dilution to prevent damage to the analytical system.

3. If possible, all samples within a sample delivery group should be extracted at the same time along with the MB preparation.

4. To extract samples collected with the EnCore™ sampling device, transfer the contents of the EnCore™ sampler into a 40-mL tared vial.

5. To extract bulk samples, use a stainless steel spatula. Immediately transfer approximately 5 g into a 40-mL tared vial.

6. Record the weight of soil added to the container to the nearest 0.01 g in the Volatile Extraction Logbook. Weight information is also entered in LIMS bench sheet at time of analysis.

7. Quickly add 10.0 mL of purge and trap grade methanol to the vial.

8. Prepare a soil MB adding approximatly 10 mL of purge and trap grade methanol used to extract field samples to the vial.

9. Store extracted samples in the laboratory freezer. Use this extract for the analysis and any subsequent dilutions that may be necessary.

8.3.3 Analytical Sequence and Sample Analysis

Set up a ChemStation data acquisition sequence from the LIMS sequence using the GC operating parameters in Appendix D. Include the client sample ID and the laboratory sample ID in the sample description field. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials. Enter this sequence in the instrument run log, if used.

For water analysis:

1. The method defaults are 5 mL sample, 5 mL final volume, and dilution factor 1. These values produce correct reporting limits but are only a starting point for data entry.
2. Batch samples as usual and leave the initial and final values in the batch as 5 mL and 5 mL respectively.
3. In the bench sheet, the sample initial and final volumes default to 5 mL.
4. Edit the bench sheet initial volume for samples and QC to reflect the actual volumes used.
5. When setting up the ChemStation sample sequence, enter 1 as the dilution factor in the multiplier field.

For soil analysis:

Spike MS/MSD samples with 5 uL of the Gasoline Stock Standard containing 50,000 µg/mL of gasoline to the vial containing the sample and methanol. Cap the vial and vortex for 30 seconds. These steps must be done rapidly in order to prevent the loss of volatile organics from the sample.

Prepare the soil method blank by adding 1 mL of the methanol used in preserving the soil samples in section 8.3.2 to 49 mL of reagent water in a syringe. Mix and transfer the resulting solution to a 40-mL VOA vial and load the vial onto the autosampler.

Add 1 mL of the extract to 49 mL of reagent water in a syringe. Mix and transfer the resulting solution to a 40-mL VOA vial and loading the vial onto the autosampler.

1. The LIMS batch defaults are 5 g sample, 5 mL final volume, and dilution factor 100. These values produce correct reporting limits but are only a starting point for data entry.
2. Batch samples as usual and leave the initial and final values in the batch as 5 g and 5 mL, respectively. (Note that the 5 mL volume represents the volume of the aqueous solution analyzed, not the methanol extract volume.)
3. In the bench sheet, the sample weight defaults to 5 g. Edit the initial weight to the actual weight used as needed.
4. Edit the bench sheet final volumes for samples and QC from 5 mL to the actual volume of methanol used to extract the samples (which is usually 10 mL).
5. When setting up the ChemStation sample sequence, enter 50 as the dilution factor in the multiplier field. (Do not apply the multiplier field to sample or surrogate results in ChemStation; LIMS does this later). The dilution factor, D = syringe volume/methanol extract volume in the syringe. This is typically 50 mL/1 mL = 50. If a greater dilution is required, calculate the

dilution factor based on the volume of methanol used, e.g. for 100 uL, D is 50 mL/0.1 mL = 500.

See Section 9.3 for batch quality control (QC) frequency and corrective action requirements. It is highly recommended that the MB, LCS, and MS/MSD be analyzed as early as possible in the analysis of a batch to allow for time to check QCs.

Example Field Sample Analysis Sequence:

	Sample Name		Sample Name
1	Prep (as needed)	6	MSD (as needed)
2	CCV/LCS*	7-18	Field samples (as needed)
3	QLS	19	IB (as needed)
4	MB/IB	20	CCV
5	MS (as needed)		

* CCV and LCS requirements may be satisfied in one analysis.
** MB and IB requirements may be satisfied in one analysis.

Enter the first and last sample positions in the concentrator and, with the ChemStation software in data acquisition mode, press the start button on the concentrator to begin purging the first sample. The purge and trap concentrator parameters are found in Appendix D.

When possible or if there are indications that the sample may foam, observe the initial purging. If the sample does foam, it can be analyzed as long as the foam does not enter the sparge vessel neck and enter the transfer line leading to the trap.

If it appears that the sample will foam excessively, discontinue the purging by pressing the [2nd], [on], and [enter] keys. Drain the sparge cell; rinse it with methanol, then reagent water. Place the sample waste and rinsate in the aqueous waste container. Bake out the trap and the GC for 25 minutes before analyzing additional samples. Analyze reagent water blank to show that the sampler is free from contamination before analyzing sample.

Analyze the sample at a 1:10 dilution, or other appropriate dilution to prevent foaming even though the detection limits are elevated. Document any sample foaming in the run log and the LIMS MMO field.

8.3.4 Analyte Identification and Quantitation

Update the center of the retention time window for the surrogate by using the absolute retention times from the calibration verification standard at the beginning of the analytical shift.

All surrogates in the field and QC samples must fall within the ± 0.03 minute retention time window or the analyst must reject the analysis or review and accept the data with a written comment such as "retention time shift due to high concentration of interfering hydrocarbon".

If the retention time does not fall within the retention time window and no source of drift is identified, then take corrective action to restore the system. If repairs to the system are required then a new initial calibration must be performed.

Review the sample chromatograms for appropriate qualification. Several situations are routinely encountered:

- The chromatographic pattern resembles the standards; proceed with quantitation and reporting.
- The chromatogram differs markedly from the standard; visually compare the sample chromatogram to available hydrocarbons analyzed with the initial calibration. Software tools such as overlaying various standard chromatograms on the sample chromatogram should be employed when helpful or to support the qualification.
- All detected results should be flagged in LIMS to qualify the reported value. When possible, indicate the product or fuel type.
- The majority of the area is due to a single-component and not a hydrocarbon mixture; consult the group leader and/or technical director to determine if the peak should be excluded from the quantitation. Use the WO Memo field and appropriate qualifier flags to report the data.
- The client has requested qualitative review against various standards; refer to the TDF and project notes to determine the project specific analysis and reporting procedures. This may include calibrating with a source supplied by the client, review against numerous standard chromatograms, or other procedures. Always document this process in the WO Memo field and in the data package and report as necessary

Quantitate the sample data using the ChemStation software using the appropriate initial calibration mean CFs. If applicable, indicate degree of similarity of sample chromatogram to the gasoline standard. Print out quantitation reports and chromatograms for each field and QC sample.

LIMS calculates final analyte concentrations in samples. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

8.3.4.1 Water Calculations

Calculate target analyte concentrations in aqueous samples using Equation 1.

Equation 1:

$$\text{Concentration (ug / L)} = \frac{A_x \times DF}{RF}$$

Where:

A_x = area response for analyte x
DF = dilution factor
RF = mean response factor from the initial calibration (area/concentration)

8.3.4.2 Soil Calculations

Calculate target analyte concentrations in soil samples using Equation 2.

Equation 2:

$$\text{Concentration (mg / Kg dry weight basis)} = \frac{A_x \times V_t \times DF \times V_p \times 1{,}000}{RF \times W \times D \times V_i \times 1{,}000}$$

Where:

A_x = area response for analyte x
D = dry weight factor (Percent solids/100)
W = weight of sample in grams
RF = mean response factor from the initial calibration (area/concentration)
V_t = total volume of extract in mL (see note)
DF = dilution factor (volume of water divided by volume of extract (nominally 5 mL / 0.1 mL or 50)
V_i = volume of extract injected in µL
Vp = volume of extract purged in mL (i.e. 5 mL)
1,000 (in numerator) 1000 µL = 1 mL
1,000 (in denominator) 1000 mL = 1 L

Yields concentration units of µg/g = mg/Kg

Note: V_t is equal to the volume of methanol (see benchsheet) plus the volume of water from the solid calculated as (1 - % solid) * W. See EPA Region 9 Lab SOP 460 for percent solids determination.

8.3.5 Manual Integration

Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the sample components. If in the judgment of the analyst, it does not, then correct the integration using the ChemStation QEDIT software module. Document manual integrations, if any, following the procedure described in USEPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

8.3.6 Data and QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, review the following QC data for compliance with SOP requirements:

- Target analyte results must be within range of initial calibration.
- Process and review the results for the IB, CCV, and QLS instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and QLS QC sample results are within QC limits. See Section 9.3 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Check that surrogate compound retention times are within the window specified in Section 9.4.1 and Appendix C. Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution. If any of the target compounds in soil extract or water samples exceed the initial calibration range of the instrument, dilute by using a smaller aliquot of the water sample or soil extract combined with reagent water.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report. Initial and date the comment.

8.3.7 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using

DataTool. .Review final results in the LIMS. The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

1. Generate epatemp.txt files for field and QC samples by also printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

2. Copy data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and for archiving.

3. Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table.

4. Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using Data Tool.

5. After making an empty upload file containing the samples analyzed in the LIMS batch or sequence, import and merge the data files using the LIMS Data Tool module. Load the resulting merged data file into the LIMS Data Entry/Review table.

6. In order to take the dilution that occurs during soil sample preparation into account, the dilution factor for undiluted soil samples in the LIMS Data Entry/Review table must be 50. Any actual sample dilutions must be multiplied by 50 to obtain the effective sample dilution to be entered in LIMS. Edit dilutions in DataTool or LIMS entry table as needed.

7. Review results in the LIMS. The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL values over the calibration range as estimated (J). The analyst must manually add a qualifier flag (C1 or C2) indicating that the reported concentration is estimated because it is less than the quantitation limit or exceeds the calibration range. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Preventative maintenance procedures are listed in Appendix F.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 Purge and trap maintenance

Symptom:

- Carryover
  Possible causes: Cold spot in system, especially the transfer lines between the sparge unit and the concentrator or between the concentrator and the GC or analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.
  Possible cause: Degradation of trap.
  Corrective action: Replace trap.

- Loss of all purged analytes.
  Possible cause: Leak in system.
  Corrective action: Leak check purge and trap system. Inspect sparge ferrules and replace them when worn or distorted.

8.4.2 GC Maintenance

Symptom:

- Carryover
  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: as necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability (DOC)

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

Acceptance criteria for QC parameters are listed in Appendix C of this document.

9.2.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed

The GC system must be calibrated whenever corrective action that changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

- The data system calculates the calibration factor (CF) using Equation 3.

  Equation 3

  $CF = (A_x)/ (C_x)$

  Where
  Ax = Area of analyte x, or area sum response of gasoline
  Cx = Concentration of the standard injected (µg/L)

- The data system calculates the percent relative standard deviation (%RSD) of the CF values for each analyte using Equation 4.

  Equation 4

  $\%RSD = (SD/ CF_{avg}) \times 100$

  Where SD is the sample standard deviation and is calculated as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - CF_{avg})^2}{n-1}}$$

  Where:
  CF_{avg} = Mean calibration factor from the initial calibration.
  CF_i = Calibration factor for a calibration level.

- Print a ChemStation Response Factor Report. Verify that the %RSD of the target analytes and the surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.

- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

- Analyze an SCV sample immediately after each initial calibration. Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 3.

- Calculate the percent difference (%D) between the SCV CF and the initial calibration average CF for the target analytes and the surrogate using Equation 5.

  Equation 5:

$$\%D = \frac{CF_c - CF_{avg}}{CF_{avg}} x100$$

  Where:
  CF_c = SCV or CCV CF
  CF_{avg} = ICAL mean CF

- See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

9.2.2 SCV Analysis

Analyze an SCV sample immediately after each initial calibration. See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

Note: The SCV may not serve as the blank spike (BS/LCS).

9.2.3 Continuing Calibration Verification

- Analyze a CCV standard at the beginning of each analytical period and at the end of the analytical period. The analytical period begins with the injection of the CCV standard and ends with the injection of the last sample that can be injected within the period.

- Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 3.

- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target analytes and the surrogate using Equation 5.

- The %D must be within QC limits. See Appendix C for QC limits. If an analyte fails this criterion, a second calibration verification may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

  If repairs to the system are required, then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

- Acceptable sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.2.4 Quantitation Limit Standard

- Analyze a quantitation limit standard (QLS) each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

- Calculate the concentration of the target analytes using Equation 1.

- Calculate the percent of true value (TV) for the target analytes using Equation 6.

  Equation 6:

  $$\% \text{ True Value} = (Cd / Tv) \times 100$$

  Where:
  Cd = Concentration determined by analysis
  Tv = True value of standard

- If the % TV is not within the QC limits in Appendix C, analyze a second QLS sample. Repeated failure requires that the cause be determined and corrected before analysis of samples can begin. If repairs to the system are required, then a new initial calibration must be performed.

9.2.5 Instrument Blank

- At a minimum, one acceptable IB is required for each analysis period.

- Evaluate the IB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- If the IB results are not within QC limits, analyze a second IB. If the second IB also fails but the system is significantly cleaner, another IB may be analyzed; if not, take corrective action.

- Corrective action - If the IB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed.

- Surrogate recovery is not evaluated for IB QC samples.

- The IB may serve as the Method Blank for water analysis or Method Blank for soil or water analysis if it contains the methanol used for extracting soil samples.

9.3 Batch QC

9.3.1 Method Blank

- Extract and analyze a method blank (MB) to demonstrate that the entire analytical system – from extraction through GC analysis – is free of contamination.

- For aqueous samples, a MB is identical to an IB. For soil sample analysis, it is necessary to prepare an extracted MB.

- Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

- If the surrogate recovery does not meet acceptance criteria, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, the cause should be determined and corrected before analysis of samples can begin.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action – if the MB result exceeds QC limits and the sample result is less than five times the MB analyte result, re-analyze the MB. If the MB result still exceeds QC limits, then the MB and all associated samples must be re-prepared and re-analyzed. If the MB result exceeds QC limits and the

sample result is ≥ five times the MB result or is not detected, then report the sample result.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. Since the CCV and LCS are prepared from the same source and level, the Continuing Calibration Verification run also serves as the LCS for aqueous samples, but the LCS uses historical control limits.

- Calculate the percent recovery (%R) using Equation 7.

  Equation 7:

  $$\% \text{ Rec} = (\text{LCS}/\text{SA}) \times 100$$

  Where,
  LCS = LCS result
  SA = Spike added

- The %R must be within the QC limits in Appendix C.
- If the LCS recovery does not meet criteria provided in Appendix C, rerun the LCS once to verify. If still unacceptable determine the cause, take corrective action and document these actions.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed for each batch extracted as a group. Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the matrix spike sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. Do not choose any obvious field blanks or trip blanks as the QC sample.

- Calculate the recovery of each analyte using Equation 8.

  Equation 8:

  $$\% \text{ Rec} = ((\text{SSR} - \text{SR})/\text{SA}) \times 100$$

  Where

  SSR = Spiked sample result

SR = Unspiked sample result
SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using Equation 9.

  Equation 9:

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

  Where,
  MSC = Measured concentration of analyte in MS
  MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

  The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS – = FAIL

CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Extraction batch acceptable.
Case 2: Extraction batch acceptable; matrix effect confirmed.
Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.

Cases 5, 6, 7, & 8: Extraction batch rejected. If additional sample volume is available, the batch should be re-extracted.

9.3.4 Storage Blank

- Every Monday morning, or the first workday of the week, fill three 40-mL screw-cap volatile vials with PTFE-faced silicone septum with reagent water, acidify to pH ≤ 2, and store them with the samples in the sample storage refrigerator.

- Analyze storage blank (SB) once every week while samples are being stored waiting for analysis. The storage blank indicates whether contamination may have occurred during sample storage.

- If samples have been stored in the refrigerator during the previous week, analyze the storage blank the following Monday, or on the first work day of that week. If samples have not been stored in the refrigerator during the previous week, discard the blanks and place new storage blanks in the refrigerator.

- Evaluate the SB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- If the SB does not meet QC criteria, all affected data must be qualified.

9.4 Sample QC

9.4.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis, using the following formula:

Equation 10:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.

- Take the following steps if surrogate recovery is not within the limits:

1. If the system is equipped with a functioning PID, the second detector can be used to provide further information. If sample matrix is the source of the error, as demonstrated by acceptable surrogate recovery on the PID, document the issue in the WO MMO field and on the chromatogram and continue. If not, proceed with troubleshooting.
2. Ensure that there are no calculation errors and check the system performance.
3. Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
4. If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case-by-case basis.

- Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

- Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the matrix interference is confirmed and the sample does not need re-analysis.

- If the surrogate recoveries of the re-analysis of the extract are within limits, then:

  1. If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Mark the first chromatogram as "Not Reported, see re-analysis."

  2. If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the LIMS WO MMO filed. Mark the first chromatogram as "Not Reported, see re-analysis."

  3. If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction, mark the first chromatogram as "Not Reported, see re-analysis."

4. If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses.

9.5 Method Performance

The following table summarizes method performance by matrix for the period 11/12/2012 to 11/13/2013.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery,%	STD, % (σ)	95% Confidence Interval (2σ)
TPH-GRO	Water	LCS	27	99.9	5.74	88.4 - 111
TPH-GRO	Solid	LCS	32	98.3	6.76	84.8 - 112

The following functional areas of the SOP may be significant sources of analytical error:

- Poor purge efficiency due to specific analyte characteristics or other problems.
- Standard degradation.
- Volatile compound losses in spike solutions and standards.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the Element database. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventative or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix G.

11 REFERENCES

Agilent Technologies EnviroQuant ChemStation User's Guide

Agilent AG6890 Gas Chromatograph Users Manual.

Agilent AG7890 Gas Chromatograph Users Manual.

Varian Archon Autosampler and HP 3000 Concentrator Operator's Manuals.

OI 4660 and 4552 Operator's Manuals.

U.S. Environmental Protection Agency, *Method 5030C*, *Purge-and-Trap for Aqueous Samples*, Revision 3, May 2003.

U.S. Environmental Protection Agency, *Method 5035A*, *Closed-system Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*, Draft Revision 1, July 2002.

U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations*, Revision 3, March 2003.

U.S. Environmental Protection Agency, *Method 8015C*, *Nonhalogenated Organics Using GC/FID*, Revision 3, February 2007.

U.S. EPA Region 9 Laboratory SOP 205, *Preparation of Organic Free Method Blank Water.*

U.S. Environmental Protection Agency Region 9 SOP 460, *Percent Solids Determination*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. The CF is area/concentration unit (µg/L) not area/mass (ng) as in the reference method. The formulas for determining sample analyte concentrations have been modified to reflect this change.\
2. This SOP, following the EPA Region 9 Laboratory Quality Assurance Plan, specifies preservation and storage temperatures for water samples of >0° to < 6°C, while the reference method specifies < 4°C.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Analyte	QL, 5g Solid, mg/kg	QL, 5 mL Water, µg/L
TPH-GRO	5.0	50

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

QC Measurement	Frequency	Criteria
Initial Calibration (ICAL) RSD	Instrument setup, after maintenance, and when CCV fails criteria	≤ 20
Second Source Verification (SCV) %D	After each ICAL	± 30
Calibration Verification (CCV) %D	Beginning of each daily sequence, every 12 hours, end of sequence	±20
Quantitation Limit Standard (QLS)	After first CCV of sequence, and after 40 samples.	± 40% of TV
Blanks :		< ½ QL
MB	One per Batch	
IB	After each CCV	
SB	Once per week	
Laboratory Control Sample (LCS) %R	One per Batch	Water: 81 - 119 Soil: 78 - 119
MS/MSD %R	One per SDG	Water:66 - 148 Soil: 73-127
MS/MSD RPD	One per SDG	Water:5 Soil: 10
Surrogate Recovery of QC and field samples (except IB) %R	Every sample	Water:87 - 110 Soil: 76 - 124
Retention Time Windows	Each CCV	±.03 minutes

*ChemStation window is ±6 SD of RT Study (SD is usually 0.01 min) and peaks are flagged at the more restrictive window.

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APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

AG 6890 OR AG7890 Gas Chromatograph

INSTRUMENT CONTROL PARAMETERS

==========
6890 GC METHOD
==========

OVEN
Initial temp: 35 'C (On) Maximum temp: 260 'C
Initial time: 3.00 min Equilibration time: 0.50 min
Ramps:
Rate Final temp Final time CRYO (N2)
1 10.00 240 2.00 Cryo: Off
2 0.0(Off) Cryo fault: Off
Post temp: 0 'C Cryo timeout: 120.00 min (Off)
Post time: 0.00 min Quick cryo cool: Off
Run time: 25.50 min Ambient temp: 25 'C

FRONT INLET (SPLIT/SPLITLESS) BACK INLET (UNKNOWN)
Mode: Split
Initial temp: 225 'C (On)
Pressure: 13.73 psi (On)
Split ratio: 2:1
Split flow: 20.0 mL/min
Total flow: 32.9 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)
Model Number: restek Rtx-624
75M, .53id, 3.0um
Max temperature: 240 'C
Nominal length: 75.0 m
Nominal diameter: 530.00 um
Nominal film thickness: 3.00 um
Mode: constant flow
Initial flow: 10.0 mL/min
Nominal init pressure: 13.73 psi
Average velocity: 53 cm/sec
Inlet: Front Inlet
Outlet: Front Detector

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Outlet pressure: ambient

FRONT DETECTOR () BACK DETECTOR ()
Temperature: 280 'C (On)
flow: 30.0 mL/min (On)
flow: 450.0 mL/min (On)
Mode: Constant column+makeup flow
Combined flow: 30.0 mL/min
Makeup flow: On
Makeup Gas Type: Nitrogen
Flame: On
Electrometer: On
Lit offset: 2.0

SIGNAL 1 SIGNAL 2
Data rate: 10 Hz Data rate: 10 Hz
Type: front detector Type: front detector
Save Data: On Save Data: Off
Start Save Time: 0.70 min Zero: 0.0 (Off)
Stop Save Time: 22.50 min Range: 0
Zero: 0.0 (Off) Fast Peaks: Off
Range: 0 Attenuation: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1 COLUMN COMP 2
Derive from front detector Derive from front detector

POST RUN
Post Time: 0.00 min

TIME TABLE
Time Specifier Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 0
Sample Pumps 6
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
Nanoliter Adapter Off
PostInj Solvent A Washes 0
PostInj Solvent B Washes 0
Viscosity Delay 0 seconds
Plunger Speed Fast

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Back Injector:
Sample Washes 0
Sample Pumps 6
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
Nanoliter Adapter Off
PostInj Solvent A Washes 0
PostInj Solvent B Washes 0
Viscosity Delay 0 seconds
Plunger Speed Fast

Column 1 Inventory Number : Rtx-624
Column 2 Inventory Number :

END OF INSTRUMENT CONTROL PARAMETERS

OI 4660 Concentrator

Recommended operating settings for the OI 4660 purge & trap concentrator that is interfaced with the HP 5890 Series II GC and the DPM-16 autosampler is as follows.

PARAMETER	SETTING
Purge temperature	20° C
Sample temperature	ambient
Purge Time	11 minutes
Dry purge	2.3 minutes
Purge Flow	35 - 40 mL/min
Desorb	2.00 minutes @ 240° C
Bake	14 minutes @ 240° C
Valve temperature	100° C
Mount temperature	40° C
Line temperature	100° C
DPM16 transfer line	100° C
DPM Valve temperature	100° C
Water Management	ON
Purge Temperature	100° C
Desorb Temperature	20° C
Bake Temperature	240° C

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Recommended Purge and Trap Concentrator operating parameters

Tekmar 3100 Concentrator

The recommended operating method for the Tekmar 3100 A purge & trap concentrator which is interfaced with the AG6890 GC and Varian Archon Autosampler is as follows.

PARAMETER	SETTING
Standby temperature	32° C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient for medium-level/20° C for low-level
Purge Time	11 min
Dry purge	0.6 min
Purge Flow	35 - 40 mL/min
Desorb preheat temperature	245° C
Desorb	2 min @ 250 ° C
Bake	10 min @ 260 ° C
Auto drain	On
Bake gas bypass	Off
Valve temperature	140 ° C
Mount temperature	100 ° C
MSS line temperature	40 ° C
Line temperature	140 ° C
Bottom of trap temperature	NA

Varian Archon/OI 4662 Autosampler

The recommended operating method for the Archon autosampler which is interfaced with the Tekmar 3000 and the HP5973 GC/MS is as follows.

PARAMETER	SETTING
Valve temperature	100 ° C
Line temperature	110 ° C

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APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO

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VOA	VOA
BFB	BFB
DFTPP	DFT

C: Channel (use when applicable):

Front	A
Back	B
Both	AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)

Water	W
Solid	S
Air	A
Oil	O
Other	X

YY: Year i.e. 12 for 2012

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APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	As Needed	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	As Needed	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	As Needed	Replace with liner or with signs of wear.
Inlet septum	As Needed	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet hardware	As Needed	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Column Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
FID Jets & collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting FID or keeping flame lit.
Purge/Sample lines	Annually or as needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.

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Item	Frequency	Actions/Comments
PID	As needed	Clean window

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APPENDIX G.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 380
Revision: 8, Effective: 1/15/2014

PURGEABLE AROMATICS AND HYDROCARBONS BY GC PID/FID

Revision	Effective Date	Description
6	06/26/09	1. Revised to remove reference to the analysis of BTEX and MTBE and to comply with current SOP format and recent changes to internal COC requirements. 2. Minor edits throughout.
7	03/01/10	1. Added the use of 2-methylpentane and 1,2,4-trimethylbenzene as the window defining standard for the integration of gasoline. Added the use of Tekmar/Archon autosampler. 2. Updated to reflect 8015C requirements.
8	1/15/2014	1. Changed surrogate spiking procedure to be consistent with EPA Region 9 Laboratory SOP 305. 2. Changed retention time window to default to be in line with other GC procedures. 3. Minor edits throughout.

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USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 385

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

Revision 5
Effective Date: March 21, 2014

Reviewed by: _____ 3/4/14
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: _____ 3/4/14
Lucrina Jones, Laboratory QA Officer — Date

Approved by: _____ 3/4/14
Brenda Bettencourt, Laboratory Director — Date

Periodic Review:

Signature	Title	Date
	ESAT QA Officer	3/31/16

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105016-16731.

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD
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1 PURPOSE AND APPLICABILITY

This procedure describes the determination of total petroleum hydrocarbons (TPH) as diesel range organics (DRO), assigned carbon rangeC_{10} - C_{24}, and oil range organics (ORO), assigned carbon range C_{24} – C_{40}, in extracts prepared from aqueous, solid and non-aqueous liquid samples. In instances where hydrocarbons in the sample more closely resemble other extractable petroleum hydrocarbon mixtures such as kerosene or hydraulic oil as determined by comparison to standards, a tentative hydrocarbon mixture identification is provided. This SOP is based on procedures contained in EPA SW-846 method 8015C, Revision 3, February 2007. Deviations from the reference method are described in Appendix A.

Water samples are prepared using EPA Region 9 Laboratory SOP 275 *Extraction of Water Samples by Continuous Liquid-Liquid Extraction*. Solid samples are prepared using EPA Region 9 Laboratory SOP 290 *Extraction of Soil Samples Using Pressurized Fluid Extraction.* Solid samples, including waste samples, may be prepared using EPA Region 9 Laboratory SOP 285 *Soxhlet Extraction of Solid Samples.* Waste samples and non-aqueous liquid samples may be prepared using EPA Region 9 Laboratory SOP 295 *Waste Dilution* if they are miscible with an appropriate solvent.

Modification of these procedures, such as quantitation based on hydrocarbon mixtures other than DRO and ORO or the use of silica gel cleanup to remove polar hydrocarbons must be arrange in advance through the Chemistry Technical Director.

Quantitation limits are provided in Appendix B by matrix and analyte.

2 METHOD SUMMARY

Sample extracts, which have been fortified with surrogate, are injected into a gas chromatograph (GC) with a flame ionization detector (FID). Sample components are separated in a fused-silica capillary GC column during temperature programming and detected by the FID.

Probable identification of fuels in samples is based on a comparison of the chromatographic pattern generated by analysis of the extract to the chromatographic pattern of known hydrocarbon fuel standards analyzed under the same conditions as the sample extract. The identification of specific fuel types may be complicated by substantial variation in fuel composition, and by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type. Data are qualified in a manner that reflects the qualitative uncertainty of the fuel identification.

The hydrocarbon concentration in the sample extract is determined by comparing the area sum response in the extract to the area sum response of hydrocarbon standards analyzed under the same conditions as the sample extract. The retention time range for the area response sum is determined from elution times of alkane hydrocarbons.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

DCM – Dichloromethane

MeOH - Methanol

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

4.1.1 Dichloromethane

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals. Emergency and first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Get emergency medical assistance. Ingestion: call local poison

control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.1.2 Acetone

Acetone liquid and vapors are highly flammable. Avoid heat, sparks, open flame, open containers, and poor ventilation. Effects of overexposure: Acetone is a mild eye and mucous membrane irritant, primary skin irritant, and central nervous system depressant. Acute exposure irritates the eyes and upper respiratory tract. Direct skin contact produces dermatitis, characterized by dryness and erythema through defatting of skin. High concentrations produce narcosis and hypoglycemia. Emergency first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer CPR. Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or their designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Sample Extracts	Hazardous Waste	See solvent, diesel fuel and motor oil MSDs

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Refer to EPA Region 9 Laboratory SOPs 275, 285, 290 or 295, as applicable (see Section 1).

5.2 Internal Chain-of-Custody

Sample extracts for GC analysis are received from the extraction laboratory personnel and custody transferred to the GC laboratory staff by signing the appropriate sections of the bench sheet.

The extracts are marked with the Region 9 Laboratory numbers and checked against the LIMS work order and chain-of-custody record to determine the client sample number, case number, and Sample Delivery Group (SDG) number.

5.3 Sample Extract Storage

Store sample extracts in the freezer in Room 406 maintained at ≤ -10 °C before and after analysis. Retain sample extracts under these conditions until the holding time has expired. Note that following analysis and reporting, the extracts must be stored an additional 60 days before segregating for disposal.

5.4 Extract Holding Time

Sample extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

6.1 Sample Matrix Interference

This method uses an FID – a relatively nonselective detector – so any combustible organic compounds present in the sample that are soluble in the extraction solvent may cause positive interferences. For example, polar hydrocarbons such as biogenic organics including lipids, plant oils, tannins, lignins, animal fats, proteins, humic acids, fatty acids, and resin acids may cause positive interference.

6.2 Extract contaminants

Chromatographic interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in chromatograms, or by carryover when low concentration extracts are analyzed after high concentration extracts. Specifically, phthalate esters are commonly used as plasticizers and are easily extracted from plastic materials. Avoid contacting samples, solvents, reagents, glassware, extracts, or other sample processing apparatus with plastic materials.

6.3 Carryover

Instrument contamination may occur when a sample extract containing low analyte concentrations is analyzed immediately after a sample extract containing relatively high analyte concentrations. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of an extract containing high analyte concentrations, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample.

Instrument contamination may occur when an extract containing oil range hydrocarbons, especially with carbon numbers exceeding C_{40}, is analyzed. After analysis of a sample extract containing oil range hydrocarbons, an instrument blank should be analyzed to ensure that accurate values are obtained for the next sample. The column may need to be heated to an elevated temperature, not exceeding the column limit, until the baseline returns to previous levels. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Gas chromatograph with FID detector and splitless injection port (Agilent 6890, 7890, or equivalent).
- Fused silica capillary gas chromatography column – Any capillary column with a phase ratio (β) of about 265 that provides adequate resolution and capacity may be used. The column used for method validation was 15M x 0.32 mm x 0.1 µm Rtx-1.
- Data acquisition and processing system -- software to control the GC and acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in sample extracts. Agilent Technologies EnviroQuant ChemStation software and data acquisition computers (or equivalent).

7.2 Reagents

All reagents must be entered into the LIMS.

- Acetone - capillary GC/GC-MS solvent grade.
  Caution: Acetone liquid and vapors are highly flammable. See Section 4.1.2 for precautions.

- Dichloromethane - recycled or capillary GC/GC-MS solvent grade.
  Caution: Dichloromethane is a suspected carcinogen. See Section 4.1.1 for precautions.

7.3 Standards

All standards must be entered into the LIMS.

7.3.1 Calibration Stock Standards:

The following standard composition and concentrations are recommended only; other mixtures and concentrations can be used as required by the project.

Description	Suggested Vendor and Catalog #	Compounds	Concentration
Diesel Fuel #2	Restek 31258	Diesel	50,000 µg/mL in DCM
Motor Oil	Restek 31464	Motor oil	50,000 µg/mL in DCM
Surrogate	INC Biomedical	N-Hexacosane ($n\text{-}C_{26}H_{54}$)	neat (1,000,000 µg/mL)
Second Source Diesel	Ultra Scientific RGO-616	Diesel Fuel	50,000 µg/mL in DCM
Second Source Oil	SPEX S-050W-20K	Motor oil, SAE50E	20,000 µg/mL in DCM
Florida TRPH n-alkane series	Restek 31266	C8-C40	500 µg/mL in hexane
Fuel Pattern Recognition	AccuStandard; FU-020D-40X	Hydraulic Fluid	20000 µg/mL in DCM
Fuel Pattern Recognition	AccuStandard HS-002S-40X	Mineral Spirits	20000 µg/mL in MeOH
Fuel Pattern Recognition	AccuStandard HS-003S-40X	Naphtha	20000 µg/mL in MeOH
Fuel Pattern Recognition	Restek 30205	Unleaded Gasoline	50000 µg/mL in MeOH
Fuel Pattern Recognition	Restek 31256	Kerosene Composite	50000 µg/mL in DCM
Fuel Pattern Recognition	AccuStandard FU-006-40X	Turbine (Jet) Fuel	20000 µg/mL in MeOH
Fuel Pattern Recognition	AccuStandard HS-004S-40X	Turpentine	20000 µg/mL in MeOH

Description	Suggested Vendor and Catalog #	Compounds	Concentration
Fuel Pattern Recognition	AccuStandard HS-001S-40X	Lacquer Thinner	20000 µg/mL in MeOH
Fuel Pattern Recognition	AccuStandard HS-005S-40X	Stoddard Solvent	20000 µg/mL in MeOH

Note: Check for project-specific quantitation requirements to determine if the instrument should be calibrated using an alternative mixture such as kerosene or a sample of the fuel or oil that is contaminating the site. The calibration standard should be selected prior to the start of the project in conjunction with the client.

7.3.2 Working Standards

- Surrogate Spiking Solution - Solution of n-hexacosane (n-$C_{26}H_{54}$) in dichloromethane:acetone 2:1 v/v at 2,500 µg/mL. Prepare from neat n-hexacosane by weighing 125 mg n-hexacosane into a 50 mL volumetric flask, dissolving it in 33 mL of dichloromethane (may require sonication or warming) and diluting to volume with acetone.

- Instrument Blank - Solution of n-hexacosane in dichloromethane at 50 µg/mL. Prepare from the surrogate spiking solution by diluting 1 mL to 50 mL in dichloromethane.

- TPH Matrix Spiking Solution - A solution of the fuel of interest at a concentration of 2,500 µg/mL in acetone. This solution is valid for six months from the date of preparation, or until ongoing QC indicates a problem exists, whichever is sooner.

- Calibration Verification Standard (CCV) - Equivalent to the mid-point initial calibration solution.

- Quantitation Limit Standard (QLS / CRL) - Equivalent to the lowest level calibration standard. The QLS is used to verify instrument response at the quantitation limit.

- Second Source Calibration Verification (SCV) – Approximately equivalent to the mid-point initial calibration solution but prepared from a source independent from the source of the calibration standards. The SCV is used to check the accuracy of the initial calibration solutions. See table above for suggested vendors for SCV standards.

7.3.3 Calibration Solutions

7.3.3.1 TPH solutions

The instructions provided below assume that the stock standards listed in section 7.3.1 are the source materials. If other stock standards are used, initial concentrations may vary – confirm dilution ratios prior to preparing the working standards.

Prepare TPH-DRO and TPH-ORO calibration solutions at five concentrations in dichloromethane from stock standard solutions. Recommended levels are shown in the tables below.

TPH-DRO Solution	Volume Used, µL	Final Volume, mL	Final Concentration, µg/mL
Stock Standard	10	10	50 (QLS)
Surrogate Spike	40	10	10
Stock Standard	30	10	150
Surrogate Spike	100	10	25
Stock Standard	100	10	500 (CCV)
Surrogate Spike	200	10	50
Stock Standard	250	10	1,250
Surrogate Spike	300	10	75
Stock Standard	800	10	4,000
Surrogate Spike	400	10	100

TPH-ORO Solution	Volume Used, µL	Final Volume, µL	Final Concentration, µg/mL
Stock Standard	40	10	200 (QLS)
Surrogate Spike	200	10	50
Stock Standard	80	10	400
Surrogate Spike	200	10	50
Stock Standard	200	10	1,000 (CCV)
Surrogate Spike	200	10	50
Stock Standard	800	10	4,000
Surrogate Spike	200	10	50
Stock Standard	2000	10	10,000
Surrogate Spike	200	10	50

7.3.3.2 Retention Time Standard (RT)

Prepare a standard containing the homologous n-alkane series covering the expected range at a concentration of 20 µg/mL. Prepare by diluting Florida TRPH standard in dichloromethane (e.g. dilute 40 µL of the 500 µg/mL stock to 1 mL).

7.3.3.3 Alternative Stock Standard Preparation

As an alternative to purchasing commercially available calibration solutions, standards may be prepared from neat fuels or oils as follows: Determine the density of the hydrocarbon fuel mixture by filling a tared 10 mL volumetric flask to volume with neat fuel at room temperature; record the weight in grams to the nearest 0.1 mg. Divide the net weight by 10 mL to obtain the density in g/mL. Use the experimentally determined density in the following calculations.

Prepare a 4,000 µg/mL (nominal) range standard by injecting 5 µL of neat standard per mL of dichloromethane. The actual concentration, in µg/mL, will be 5,000 times the density of the neat standard in g/mL. For example, injecting 250 µL of kerosene into about 49 mL of solvent in a 50 mL volumetric flask, then adding additional solvent to volume, would result in a 3,910 µg/mL standard assuming a density of 0.782 g/mL for kerosene.

If the neat standard, such as motor oil, is too viscous to measure with a microliter syringe, weigh out about 200 mg (0.2 g) using an analytical balance and dilute to 50 mL with dichloromethane.

Prepare the other calibration solutions by serially diluting the 4,000 µg/mL standard.

7.3.4 Storage of Standard Solutions

Store the unopened ampulated stock standard solutions at > 0°C to 6°C. Transfer opened stock standard solutions and all working standard solutions to glass bottles or vials with Teflon lined screw caps and store at ≤-10°C; protect all standards from light. Fresh standards should be prepared every six months, or sooner if comparison with check-standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months or sooner if comparison with SCV indicates a problem.

CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use. Hexacosane has poor solubility at low temperatures. Solutions containing hexacosane must be sonicated before use.

7.4 Supplies

- Volumetric flasks, type A, 100-mL, 50-mL, 25-mL, and 10-mL.
- Microliter syringes (10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1-mL).

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set up the instrument control parameters provided in Appendix D. Adjust as needed to meet method and SOP requirements. Instrument parameters must be the same between an initial calibration and all extracts quantitated using that calibration.

Prior to analyzing calibration or instrument QC make a LIMS sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

Ensure that all appropriate waste containers are properly connected and labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

The initial calibration is a minimum 5-level external standard calibration using the mean CF for calculating analyte concentrations. See Section 9.2.1 of this SOP for required frequency.

Prepare calibration solutions according to Section 7.3.3.

Analyze each of the initial calibration standards and an instrument blank as described in Section 8.3. The following table shows an example initial calibration sequence:

Sequence	Sample Name
1	IB
2	RT
3	Level 1 DRO (QLS)
4	Level 2 DRO
5	Level 3 DRO (CCV)
6	Level 4 DRO
7	Level 5 DRO
8	Level 1 ORO (QLS)
9	Level 2 ORO
10	Level 3 ORO (CCV)
11	Level 4 ORO
12	Level 5 ORO
13	DRO SCV
14	ORO SCV
15-24	Fuel Pattern Recognition STDs (as needed)

Analyze each of the initial calibration standards and an instrument blank using the same instrument conditions to be used analyzing field sample extracts. Using the chromatography software and the following steps, calculate the average calibration factors and %RSD.

- Review the instrument blank to confirm that the analytical system is free of contamination.

- Review the RT standard to determine the elution time for C10, C24, and C40. Enter the carbon marker retention times into the method and obtain area sums for each fuel mixture in the designated time ranges using the following ranges: DRO:C_{10}– C_{24} and ORO:C_{24} – C_{40}

- Review the chromatograms and draw a manual baseline if the baseline drawn by the data system integrator does not accurately reflect the total area response, including the unresolved area that lies below the individual peaks, of the fuel. For DRO, draw a manual baseline beginning at the elution time of C10 to the elution time of C24. For ORO, draw a baseline beginning at the elution time of C24 and going to the elution time of C40. Manual integrations must conform to U.S. EPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures.* See Appendix E for example chromatograms.

- The data system calculates the calibration factor (CF) for the target fuel or n-alkane mixture from its area sum response and for the surrogate for all five calibration standards using Equation 1.

  Equation 1

  $$CF = (A_x)/ (C_x)$$

  Where
  Ax = Area of compound x
  Cx = Concentration of the standard injected (µg/mL)

- The data system calculates the average CF for all analytes.

- Using the above information, the data system calculates the percent relative standard deviation (%RSD) of the CF values for each compound using Equation 2.

Equation 2

$$\%RSD = (SD/\ CF_{avg}) \times 100$$

Where SD is calculated as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - CF_{avg}\right)^2}{n-1}}$$

Verify that the %RSD of both the target fuel(s) and surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.

8.2.1.1 Retention Time Windows

Based on experience and historical data, the EPA Region 9 Laboratory uses a default retention time window of +/- 0.03 minutes for single component analytes. This approach is based on the insignificant retention time drift observed historically and the option listed in SW846 Method 8000C section 11.6 to select an alternative approach to the usual analysis of standards for the calculation of retention time windows.

To prevent false negatives, set the ChemStation window to ± 0.06 minutes so the software will identify peaks within the wider window and flag those which exceed the default retention time window with the "f" flag (the flag is added to peaks outside one half the ChemStation window) to prevent false negatives.

8.2.1.2 Second Source Calibration Verification (SCV)

Analyze a SCV standard immediately after each initial calibration. See Section 9.2.2 of this SOP for frequency and QC limits.

If the initial calibration, the SCV, and the IB meet all the criteria specified in Appendix C, the remainder of the analytical period may be used for the analysis of field and QC samples using the average CF from the initial calibration to quantitate the data.

8.2.2 Calibration Verification

Calibration verification is required at the beginning of each analytical period and at the end of the analytical period. The analytical period begins with the injection of the calibration verification standard and ends with the completion of

analysis of the last sample that can be injected within the period. Analysis of calibration verification standards after every ten samples is recommended to minimize the amount of re-runs necessary if a calibration verification should fail. The calibration verification standard is used to validate the initial calibration for the samples run during the associated period.

- Analyze an instrument blank and the calibration verification standard according to Section 8.3.
- Review the instrument blank to confirm that the analytical system is free of contamination.
- Calculate the calibration factor (CF) for the target fuel from its area sum response and for the surrogate compound using Equation 1.
- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target fuel and the surrogate using Equation 3.

Equation 3.

$$\%D = \frac{\mathrm{CF_c} \times \mathrm{CF_{avg}}}{\mathrm{CF_{avg}}} \times 100$$

Where:
$\mathrm{CF_c}$ = calibration verification CF
$\mathrm{CF_{avg}}$ = initial calibration average CF

The %D must be within QC limits. See Appendix C for QC criteria and section 9.2.3 for corrective action.

8.2.3 Quantitation Limit Standard

Analyze a standard of the fuel of interest at the concentration of the lowest initial calibration level according to Section 8.3 of this SOP and calculate the concentration of the target fuel.

Calculate the percent recovery for the target fuel using Equation 4.

Equation 4:

$$\%\,R = (\,Cd/Tv\,) \times 100$$

Where:
%R = Percent Recovery
Cd = Concentration determined by analysis
Tv = True value of standard

See Section 9.2.4 for QLS requirements and Appendix C for QC limits.

8.3 Sample Analysis

8.3.1 Sample Extract Preparation

Sample extracts can be analyzed only after the initial calibration or calibration verification, QLS, MB, and IB meet all of the appropriate criteria specified in Appendix C.

Generate a LIMS sequence as required prior to analyzing QC or field sample extracts to obtain LIMS assigned IDs for the calibration and QC samples.

8.3.2 Analytical Sequence and Analysis

Set up a data acquisition sequence from the LIMS sequence using the GC control parameters used in the analysis of the initial calibration. The sample description shall include the laboratory sample ID. Additional header information should include the dilution factor, instrument ID, and the analyst's initials.

Include all QC sample extracts. It is highly recommended that the MB, BS, and MS/MSD extracts be analyzed as early as possible in the analysis of a batch.

The following table is an example field sample analysis sequence:

Sequence	Sample Name	Sequence	Sample Name
1	Priming	8	MB
2	IB	9	MS Sample
3	DRO CCV	10	MS
4	DRO QLS	11	MSD
5	ORO CCV	12-21	Field Samples
6	ORO QLS	22	DRO CCV
7	LCS	23	ORO CCV

8.3.3 Analyte Identification and Quantitation

After completion of analysis, review the chromatogram to identify the fuel in the sample. Compare the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of fuels analyzed under the same conditions as the sample by visually comparing the printed chromatograms or by electronically overlaying the chromatograms, if needed.

Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the fuel in the sample. If in the judgment of the analyst, it does not, then draw a manual baseline from the elution time of C10 to the elution time of C24. See Appendix E for examples. Document any manual integration following the procedure described in U.S. EPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

Quantitate the chromatogram using the appropriate initial calibration mean CFs for the identified fuel. If applicable, indicate degree of similarity of sample chromatogram to the fuel to which it is being compared. Print out quantitation reports and chromatograms for each field and QC sample.

The fuel hydrocarbon mixtures, including diesel and oil, contain large numbers of chemical components which overlap. Use the following tables to report the diesel and oil ranges:

Report	Chromatogram indicates the presence of:			
	Diesel Fuel Only	Motor Oil Only	Both Diesel Fuel and Motor Oil	Other hydrocarbon mixtures
DRO: C_{10}-C_{24}	Quantitate against the TPH-diesel range standard and report. Apply the appropriate LIMS flag to describe the fuel or product type (examples below).	Quantitate the overlap area against the TPH-diesel range standard and report the value as "non-detect" U at that concentration (i.e. raise the sample QL).	Draw both integrations to the respective alkane markers and report both fuels Apply the appropriate LIMS flags for each to describe the fuel or product types (examples below).	Quantitate, the area in the DRO range. Apply the appropriate LIMS flag to describe the fuel or product type (examples below).
ORO: C_{24}-C_{40}	Quantitate the overlap area against the oil range standard and report the value as "non-detect" U at that concentration (i.e. raise the sample QL).	Quantitate against the oil range standard and report. Apply the appropriate LIMS flag to describe the fuel or product type (examples below).		Quantitate, area in the ORO range. Apply the appropriate LIMS flag to describe the fuel or product type (examples below).

LIMS Qualifier Flags

LIMS Flag	Description
F0	[CUSTOM]
F2	Fuel Type: Gasoline
F3	Fuel Type: Kerosene or Jet Fuel
F4	Fuel Type: Diesel
F5	Product Type: Motor Oil
F6	Product Type: Hydraulic Fluid
F7	Product Type: Lacquer Thinner
F8	Product Type: Mineral Spirits
F9	Product Type: Naphtha
F10	Product Type: Stoddard Solvent
F11	Product Type: Turpentine
F12	Single component, unidentified
F13	Fuel or Product Type: mixed or unknown

All detected results should be flagged in LIMS using the above designations to characterize the product or fuel type. If a mixture is present, multiple flags may be appropriate (diesel and motor oil, kerosene and hydraulic fluid). Use the F0 flag to briefly narrate further information when it is available (e.g. Single component, tetrachloroethene identified by GCMS).

In the event that the client provides a fuel/product for calibration, the Technical Director will enter a project specific LIMS analysis. Use the F0 flag to indicate if the reported concentration resembles the standard used for calibration. If the sample contains a known product or fuel, use the appropriate flag, but quantitated against the client standard unless otherwise instructed. Describe the standard and calibration procedure in the work order memo field.

- Water calculations

Calculate results for target analytes using Equation 5:

Equation 5:

$$\text{Conc. ug / L} = \frac{A_x \times V_t \times DF}{CF \times V_o}$$

Where:

A_x = area sum response of the sample
DF = dilution factor
CF = mean calibration factor from the initial calibration
V_o = volume of water extracted in Liters
V_t = volume of concentrated extract in mL

- Soil calculations

  Calculate results for target analytes using Equation 6:

  Equation 6:

$$\text{Conc. mg/kg (dry weight basis)} = \frac{A_x \times V_t \times DF}{CF \times W \times D}$$

  Where:

  A_x = area sum response of the sample
  D = dry weight factor (Percent solids/100)
  W = weight of sample in grams
  CF = mean calibration factor from the initial calibration
  V_t = volume of concentrated extract in mL
  DF = dilution factor

  Yields concentration units of µg/g = mg/kg

- Check surrogate recovery for each sample with criteria in Appendix C.

- Dilute and inject a new aliquot of the extract if the on-column concentration of the fuel of interest in any sample exceeds the initial calibration range. Use the following criteria in performing dilutions:

  1. Use the results of the original analysis to determine the approximate dilution factor required to get the fuel of interest within the initial calibration range.
  2. Do not dilute MS/MSD samples to get either the spiked or non- spiked target compounds within the initial calibration range. If the sample from which the spike aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the work order memo field.
  3. In the case of extremely contaminated samples several dilutions may be required.
  4. Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.
     Review the results for the sample analyzed immediately after a contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The sample should not contain

a concentration above the QL for the target compound that exceeded the limits in the contaminated sample.

5. The most common cause of carryover is due to hydrocarbons in the oil/asphalt range. Cleaning the injection port and baking out the column may be required.

8.3.4 Data and QC Review

Review results of instrument QC (CV, QLS) immediately after their analysis to verify that the results are within QC limits. If the instrument QC results are not within QC limits, stop the sequence and take corrective action before resuming the sequence. See Section 9.2; see Appendix C for QC limits.

Review results of batch QC (MB, BS, MS/MSD). See Section 9.3; see Appendix C for QC limits.

Review results of sample QC (surrogate recovery). See Section 9.4; see Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

LIMS will report all results to two significant figures and detected results to one-half the QL. LIMS flags values between one-half the QL and the QL as estimated (J); the analyst must manual add a "C1" flag to these results.

8.3.6 Instrument Maintenance

The following are suggested remedial actions that may improve method performance; re-calibration may be necessary after most of these actions:

- Check and adjust GC operating conditions and temperature programming parameters.
- Clean or replace the splitless injector liner with a new, silanized liner.
- Cut off a short portion of the GC column from the end near the injector, or replace the column. Cutting off a portion of the column will somewhat shorten the analyte retention times.
- Prepare fresh calibration solutions and repeat the initial calibration.
- Replace any components in the GC that permit analytes to come in contact with hot metal surfaces.

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Preventative maintenance procedures are listed in Appendix F.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix F for routine preventative maintenance procedures and schedule.

Symptom

- Carryover
  Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory

solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of the QC Criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in U.S. EPA Region 9 Laboratory SOP 880. *Demonstration of Capability*

9.2 Instrument QC

9.2.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed. The calibration is an external standard calibration method.

The GC system must be calibrated whenever corrective action changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

- Review the alkane standard to confirm that the correct elution times for C10, C24, and C40 are entered into the method to obtain area sums for each fuel mixture in the designated time ranges.

- Verify that the %RSD of the target fuel(s) and surrogate are within QC limits. See Appendix C for QC limits.

- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

9.2.2 SCV Analysis

An SCV sample is analyzed immediately after each initial calibration. See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards. Seek technical guidance from the group leader should the SCV fail repeatedly.

9.2.3 Calibration Verification

See Appendix C for QC for frequency and %D requirements. The %D must be within QC limits. If an analyte fails this criterion a second calibration verification may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

If significant repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

Reported sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.2.4 Quantitation Limit Standard (QLS)

See Appendix C for QC for frequency and %R requirements. The %R must be within QC limits. If an analyte fails this criterion a second QLS may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

9.2.5 Instrument Blank (IB)

Analyze an instrument blank at the beginning of each analytical sequence, or after any high level sample. The instrument blank chromatogram and quantitation report must be checked to insure it is within QC limits in Appendix C. It is also important to monitor the chromatographic baseline to insure there are no humps or disruptions which could be integrated as peak area when sample constituents elute on top of them. Surrogate recovery is not evaluated for IB samples. If the instrument blank meets these requirements sample analysis may proceed.

9.3 Batch QC

Equations for calculating percent recovery (%R) and relative percent difference (RPD) are found in section 27.2.2 of the LQAP.

9.3.1 Method Blank

- A method blank (MB) is extracted and analyzed with each extraction batch to demonstrate that the entire analytical system - from extraction through GC analysis - is free of contamination.

- Analyze the MB according to Section 8.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action - If the MB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the batch may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case by case basis.

- If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery fails high and the analytes in the blank are ≤ ½ the QL, report and narrate. If the surrogate fails low, all samples in the batch that are not ND may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case by case basis.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. A LCS is extracted and analyzed once per extraction batch. The LCS is a MB spiked with laboratory fortified matrix solution.

- Analyze a LCS containing the target fuel according to Section 8 of this SOP.

- Calculate the percent recovery (%R) and compare to the QC limits in Appendix C. If acceptable accuracy cannot be achieved, the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Laboratory fortified matrix (MS) and duplicate (MSD) samples are extracted and analyzed for the same matrix in an SDG. Additionally, all client-specified matrix QC samples must be prepared and analyzed. If there are no client-specified matrix QC samples, the extraction analyst will choose one representative sample for QC analysis. The extraction analyst shall not designate any obvious field blanks as the QC sample.

- If there is insufficient volume of sample to perform a matrix QC, it must be documented in the LIMS work order memo field and work order case narrative of the final report to notify clients.

- Analyze the MS/MSD extracts according to Section 8 of this SOP as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.

- Calculate the percent recovery (%R) and relative percent differences (RPD) in the MS and MSD. See Appendix C for QC limits.

  The MS/MSD recovery limits are advisory only. If the limits are not met, no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected values.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX+ = PASS ! = FAIL								
CASE	1	2	3	4	5	6	7	8
BS - %R	+	+	+	+	!	!	!	!
MS/MSD -%R	+	!	+	!	+	!	+	!
MS/MSD - RPD	+	+	!	!	+	+	!	!

Case 1: Extraction batch acceptable.

Case 2: Extraction batch acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in work order memo field.

Case 5: Extraction batch rejected. Batch may have to be re-extracted unless LCS problem is determined and documented.

Cases 6, 7 & 8: Extraction batch rejected. Re-extract batch.

9.4 Sample QC

9.4.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

Equation 7:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.

- Take the following steps if surrogate recovery is not within the limits:

  1. Ensure that there are no calculation errors, and check the system performance.
  2. Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
  3. If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case by case basis.

- Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

- Do not re-analyze the MS or MSD samples, even if surrogate recoveries are outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogate recoveries in the sample and spike analyses must be discussed in the work order memo field.

- If the surrogate recoveries of the re-analysis of the extract are within limits, then:

  1. If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. The LIMS distinguishes between the analysis and re-

analysis by adding an "RE" suffix to the client sample ID on the re-analysis. The problem must be documented in the work order memo field.

2. If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the work order memo field. The problem must be documented in the work order memo field.
3. If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the work order memo field.

- If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the work order memo field.

9.5 Method Performance

The following table summarizes method performance by matrix for the period 11/13/12 to 11/13/13.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Diesel	Water	LCS	35	84.1	67.5 – 101
Diesel	Solid	LCS	42	86	67.7 - 104

The primary sources of analytical error are:

- Poor extraction efficiency due to specific analyte characteristics or other problems.
- Standard degradation
- Chromatographic separation and peak integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the LIMS. A

copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

Document the analytical sequence in the LIMS.

Record the instrument ID and the LIMS calibration ID for each sequence. Record the Laboratory number, analysis, position, and LIMS standard ID, as applicable for each field and QC sample in the Element analysis sequence.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix G.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies 6890 Gas Chromatograph Users Manual

Agilent Technologies 7890 Gas Chromatograph Users Manual

Agilent Technologies EnviroQuant ChemStation User's Guide

U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations*, *Revision 3, March, 2003*.

U.S. Environmental Protection Agency, *Method 8015C*, *Nonhalogenated Organics Using GC/FID*, *Revision 3, Feb. 2007.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. In the SOP, the retention time range for Diesel Range Organics is C_{10} to C_{24} based on the analysis of an n-alkanes standard, not the retention time of C_{10} to C_{28} alkanes specified in the reference method. In addition, the SOP extends the chromatographic range of the method to include Oil Range Organics C_{24} to C_{40}.

2. The CF is area/concentration unit (µg/mL) not area/mass (ng) as in the reference method. The formulas for determining sample analyte concentrations have been modified to reflect this change.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Hydrocarbon Fuel	On column, µg/mL	Solid, mg/kg (30g sample)	Water, µg/L (1 L sample)
TPH – Diesel Range Organics	50	5	150
TPH – Oil Range Organics	200	20	600

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APPENDIX C.
CONTROL MEASURES AND CRITERIA

QC Measure		Criteria	Frequency
ICAL RSD		≤ 20%	After failure of CCV, with each ICAL
CCV %D		≤ 20%	Opening and closing per 12 hour sequence
SCV %D		≤ 30%	With each ICAL
LCS[1] %R	Water Solid	59 – 109% 59 – 113%	1/extraction batch or 20 samples
MB		<½ QL	1/extraction batch or 20 samples
QLS %R		60-140%	Beginning of sequence and every 40 samples
MS and MSD[1], %R	Water Solid	50 – 126% 21 – 112%	1/SDG or 20 samples[2]
MS/MSD[1], RPD	Water Solid	≤ 37% ≤ 50%	1/SDG or 20 samples[2]
Sample Retention Time Drift		±0.03 minutes	Method setup
IB		<½ QL	As necessary
Surrogate %R	Water Solid	47- 130% 20 - 111%	With each sample

[1] Spiked with diesel.
[2] Whichever is more frequent

Note: limits are based on data from November 13, 2012 to November 13 2013.

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APPENDIX D.
RECOMMENDED INSTRUMENT CONTROL PARAMETERS

AG6890-4 GC METHOD

OVEN
Initial temp: 50 'C (On) Maximum temp: 350 'C
Initial time: 2.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	25.00	330	10.00
2	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 23.20 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Pulsed Splitless
Initial temp: 320 'C (On)
Pressure: 5.33 psi (On)
Pulse pressure: 10.0 psi
Pulse time: 0.40 min
Purge flow: 40.0 mL/min
Purge time: 0.30 min
Total flow: 44.9 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)
Mode: Pulsed Splitless
Initial temp: 320 'C (On)
Pressure: 2.33 psi (On)
Pulse pressure: 10.0 psi
Pulse time: 0.40 min
Purge flow: 48.2 mL/min
Purge time: 0.30 min
Total flow: 52.2 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Restek RTX-1
15M x 0.32mm x 0.1um df
Max temperature: 350 'C
Nominal length: 15.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 0.10 um
Mode: constant flow
Initial flow: 2.0 mL/min
Nominal init pressure: 5.33 psi
Average velocity: 38 cm/sec
Inlet: Front Inlet
Outlet: Front Detector
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Restek RTX-1
Max temperature: 350 'C
Nominal length: 15.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 10.00 um
Mode: ramped pressure
Initial pressure: 2.33 psi
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

Post pressure: 0.00 psi
Nominal initial flow: 0.6 mL/min
Average velocity: 15 cm/sec
Inlet: Back Inlet
Outlet: Back Detector
Outlet pressure: ambient

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FRONT DETECTOR (FID)
Temperature: 350 'C (On)
Hydrogen flow: 40.0 mL/min (On)
Air flow: 440.0 mL/min (On)
Mode: Constant makeup flow
Makeup flow: 49.0 mL/min (On)
Makeup Gas Type: Nitrogen
Flame: On
Electrometer: On
Lit offset: 2.0

BACK DETECTOR (FID)
Temperature: 350 'C (On)
Hydrogen flow: 40.0 mL/min (On)
Air flow: 440.0 mL/min (On)
Mode: Constant makeup flow
Makeup flow: 49.0 mL/min (On)
Makeup Gas Type: Nitrogen
Flame: On
Electrometer: On
Lit offset: 2.0

SIGNAL 1
Data rate: 10 Hz
Type: front detector
Save Data: On
Start Save Time: 1.30 min
Stop Save Time: 20.00 min
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 10 Hz
Type: back detector
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
Derive from front detector

COLUMN COMP 2
Derive from back detector

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:

Sample Washes	2
Sample Pumps	3
Injection Volume	2.0 microliters
Syringe Size	10.0 microliters
PostInj Solvent A Washes	3
PostInj Solvent B Washes	3
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

Back Injector:
No parameters specified

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Column 1 Inventory Number : RTX-1 15M
Column 2 Inventory Number : RTX-1B

AG7890-2 METHOD

C:\MSDCHEM\1\2012\METHOD\012712DROA.M
Fri Dec 28 14:14:51 2012

Control Information
Sample Inlet : GC
Injection Source : Manual

Oven
Equilibration Time 0.5 min
Max Temperature 330 degrees C
Slow Fan Disabled
Oven Program On
50 °C for 2 min
then 95 °C/min to 115 °C for 0 min
then 65 °C/min to 175 °C for 0 min
then 45 °C/min to 330 °C for 6 min
Run Time 13.052 min

Front Injector
Syringe Size 10 µL
Injection Volume 2 µL
Solvent A Washes (PreInj) 3
Solvent A Washes (PostInj) 3
Solvent A Volume 8 µL
Solvent B Washes (PreInj) 3
Solvent B Washes (PostInj) 3
Solvent B Volume 8 µL
Sample Washes 2
Sample Wash Volume 8 µL
Sample Pumps 3
Dwell Time (PreInj) 0 min
Dwell Time (PostInj) 0 min
Solvent Wash Draw Speed 300 µL/min
Solvent Wash Dispense Speed 6000 µL/min
Sample Wash Draw Speed 300 µL/min
Sample Wash Dispense Speed 6000 µL/min
Injection Dispense Speed 6000 µL/min
Viscosity Delay 0 sec
Sample Depth Disabled
Injection Type Standard

L1 Airgap	0.2 µL

Back Injector

Syringe Size	10 µL
Injection Volume	1 µL
Solvent A Washes (PreInj)	3
Solvent A Washes (PostInj)	3
Solvent A Volume	8 µL
Solvent B Washes (PreInj)	3
Solvent B Washes (PostInj)	3
Solvent B Volume	8 µL
Sample Washes	0
Sample Wash Volume	8 µL
Sample Pumps	3
Dwell Time (PreInj)	0 min
Dwell Time (PostInj)	0 min
Solvent Wash Draw Speed	300 µL/min
Solvent Wash Dispense Speed	6000 µL/min
Sample Wash Draw Speed	300 µL/min
Sample Wash Dispense Speed	6000 µL/min
Injection Dispense Speed	6000 µL/min
Viscosity Delay	0 sec
Sample Depth	Disabled
Injection Type	Standard
L1 Airgap	0.2 µL

Sample Overlap
Sample overlap is not enabled

Front SS Inlet He

Mode	Pulsed Splitless
Heater	On 320 °C
Pressure	On 5.3292 psi
Total Flow	On 45 mL/min
Septum Purge Flow	On 3 mL/min
Gas Saver	On 20 mL/min After 1.5 min
Injection Pulse Pressure	10 psi Until 0.4 min
Purge Flow to Split Vent	40 mL/min at 0.3 min

Back SS Inlet He

Mode	Pulsed Splitless
Heater	On 320 °C
Pressure	On 5.339 psi
Total Flow	On 45.004 mL/min
Septum Purge Flow	On 3 mL/min
Gas Saver	On 20 mL/min After 1.5 min
Injection Pulse Pressure	10 psi Until 0.4 min
Purge Flow to Split Vent	40 mL/min at 0.03 min

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Column #1
Restek 10106: 1730.60105
Rtx-1
330 °C: 15 m x 320 µm x 0.1 µm
In: Front SS Inlet He
Out: Front Detector FID

(Initial)	50 °C
Pressure	5.3292 psi
Flow	2 mL/min
Average Velocity	37.778 cm/sec
Holdup Time	0.66176 min
Flow Program	Off
2 mL/min for 0 min	
Run Time	13.052 min

Column #2
Restek 10106: 1730.60105
Rtx-1
330 °C: 15 m x 320 µm x 0.1 µm
In: Back SS Inlet He
Out: Back Detector FID

(Initial)	50 °C
Pressure	5.339 psi
Flow	2.0043 mL/min
Average Velocity	37.847 cm/sec
Holdup Time	0.66056 min
Flow Program	Off
2.0043 mL/min for 0 min	
Run Time	13.052 min

Front Detector FID

Heater	On 350 °C
H2 Flow	On 40 mL/min
Air Flow	On 440 mL/min
Makeup Flow	On 47.8 mL/min
Const Col + Makeup	On 49.8 mL/min
Flame	On
Electrometer	On

Back Detector FID

Heater	Off
H2 Flow	Off
Air Flow	Off
Makeup Flow	Off

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Const Col + Makeup Off
Flame Off
Electrometer On

Signals
Signal #1: Front Signal Save On
10 Hz
Signal #2: Back Signal Save Off
50 Hz
Signal #3: Test Plot Save Off
50 Hz
Signal #4: Test Plot Save Off
50 Hz

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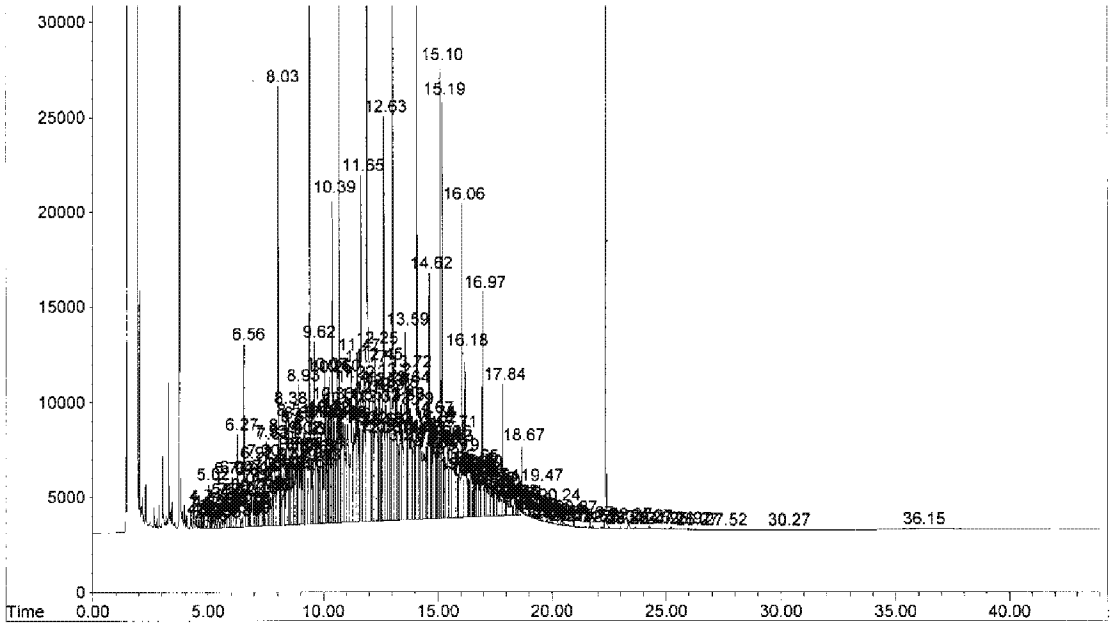
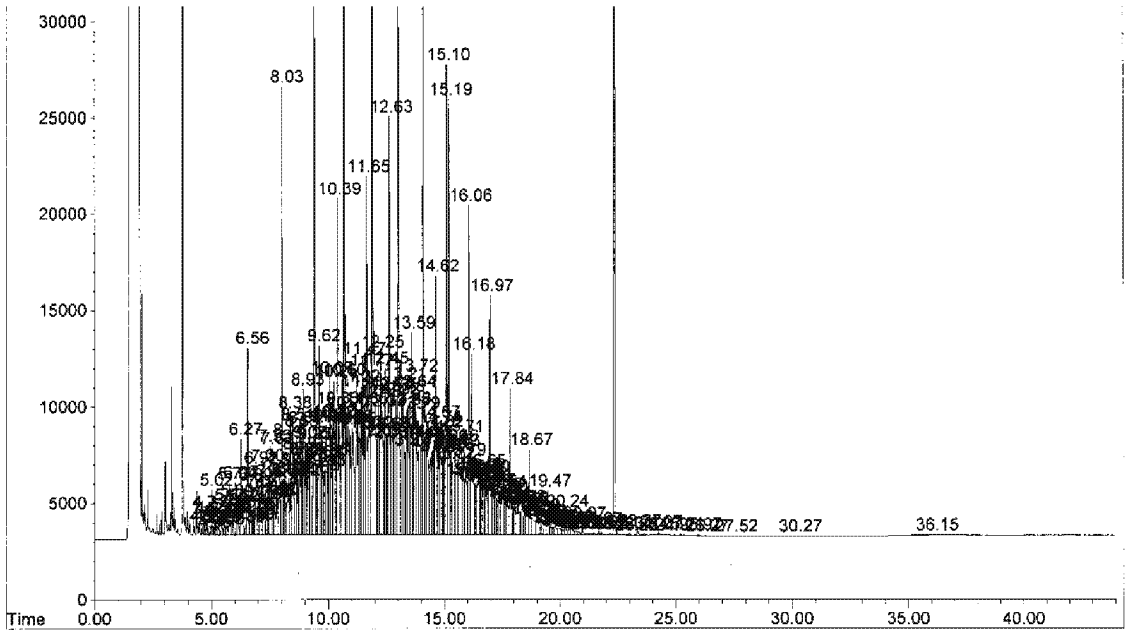
APPENDIX E.
INTEGRATION EXAMPLES



INCORRECT BASELINE INTEGRATION



CORRECT BASELINE INTEGRATION

APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Flowmeter calibration	2 years	Manual flowmeters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	As Needed	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
FID Jets & Collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting FID or keeping flame lit.
Purge/Sample Lines	As needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.

ED_006532_00005075-00334

APPENDIX G.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 385
Revision: 5, Effective: 3/21/14

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

Revision	Effective Date	Description
4	08/15/10	1. Changed reference method to EPA 8015C. 2. Revised quantitation and reporting procedures.
5	3/21/2014	1. Update historical control limits and method performance. 2. Include new instrumentation. 3. Updated reporting limit for water for consistency with QLS and solids. 4. Revise to current SOP 850 and laboratory practices and completed general edits throughout.

ED_006532_00005075-00335

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 505
DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-AES

Revision 9
Effective Date: July 15, 2015

Reviewed by: _____ 7/6/15
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: _____ 7/1/2015
Lucrina Jones, Laboratory QA Officer — Date

Approved by: _____ 7/6/15
Duane James, Acting Laboratory Director — Date

Periodic Review:

Signature	Title	Date

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-13-029). ESAT Document Control Number: 10105041-18070

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1 SCOPE AND APPLICABILITY

This SOP provides procedures for the determination of dissolved and total recoverable elements by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) in environmental samples for use in the USEPA Region 9 Laboratory, Richmond, CA. These procedures are applicable to water samples only. This SOP is based on EPA Method 200.7, Rev. 4.4, *Determination of Trace Elements in Waters and Wastes by ICP-AES*, May 1994. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

Water samples with turbidity > 1 NTU or where silver and/or total recoverable analytes are requested must be digested following Region 9 Laboratory SOP 403 *Aqueous Sample Preparation for ICP-AES and ICP-MS* prior to analysis. Other water samples may be analyzed directly after proper filtration and/or acid-preservation.

2 METHOD SUMMARY

An aqueous sample is nebulized and the resulting aerosol is introduced to the inductively coupled plasma torch of the ICP-AES instrument where element-specific emission spectra are produced. These spectra are dispersed by a grating and their intensities are monitored at specific wavelengths by a photomultiplier tube. The resulting intensities are proportional to the concentration of the trace elements and are processed by a computer system.

Water samples for total recoverable analytes, silver analysis, or having turbidity > 1 NTU are acid digested prior to analysis. However, dissolved elements are analyzed by "direct analysis" after filtration and acid preservation of aqueous samples. Drinking water samples are also analyzed by "direct analysis" without acid digestion if the samples have been properly acid-preserved and have turbidity of < 1 NTU.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

<u>CRL - This is a LIMS acronym for contract reporting limit. It is a LIMS QC sample type and is equivalent to the QLS.</u>

<u>Optical Alignment Solution</u> – A solution of manganese used to align the optical paths of the ICP-AES instrument.

<u>Spectral Interference Check (SIC) Solution</u> – A solution of selected method analytes of

higher concentration which is used to evaluate the procedural routine for correcting known inter-element spectral interferences with respect to a defined set of method criteria.

Total Recoverable Analyte Concentration – The concentration of an analyte in an unfiltered aqueous sample after preparation by acid digestion.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for

pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure.* Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable

Waste Stream Description	Waste Label	Hazard Properties
ICP-AES instrument liquid waste (nitric acid, hydrochloric acid, trace metals)	Hazardous Waste	Corrosive, Toxic

NOTE: Arsenic (50,000 mg/kg), beryllium (7500 mg/kg), cadmium (10,000 mg/kg), lead (1300mg/kg dry), selenium (10,000 mg/kg), and thallium (70,000 mg/kg) are listed as extremely hazardous wastes at concentrations greater than or equal to those indicated. As such, any sample, sample digestate, or sample extract/leachate with a concentration exceeding these levels must be handled as an extremely hazardous waste. Should one or more of these concentrations be determined, notify the LaSHEM (or designee).

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 500-mL sample volume should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form. If discrepancies are noted, inform the sample custodian.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

Sample digestates for metals analysis are received from the digestion lab personnel and custody is transferred to the metals analyst. The metals analyst acknowledges the receipt of the sample digestates by signing the appropriate section of the completed LIMS bench sheet.

5.3 Preservation Verification

5.3.1 Drinking Water Samples – Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is

sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH < 2 just prior to withdrawing an aliquot for turbidity measurement.

5.3.2 Dissolved Analyte Samples – The samples must be filtered through a 0.45-µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid contamination. The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with dilute (1:1) nitric acid immediately following filtration to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient).

5.3.3 Aqueous Total Recoverable Analyte Samples – Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH < 2 just prior to withdrawing an aliquot for digestion. If the pH of the sample is > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

5.4 Sample Storage

Samples must be stored at > 0 and ≤ 6° C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within six months from collection.

5.6 Sample Extracts/Leachates and Digestates

Retain sample extracts/leachates and digestates for 60 days after the final analytical report is sent to the data user.

6 INTERFERENCES

6.1 Spectral Interferences

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or the unresolved overlap of molecular band spectra.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. The location(s) used for the routine measurements must be free of off-line spectral interferences (inter-element or molecular) or adequately corrected to reflect the same change in background intensity that occurs at the wavelength peak.

Spectral overlaps can be compensated for by equations that correct for the inter-element contributions, which involve measuring the interfering elements. When present and uncorrected, these interferences will produce false-positive or false negative results and be reported as analyte concentrations.

When inter-element corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions. Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Inter-element corrections will also vary depending upon the choice of background correction points. Selecting a point where an interfering emission line may appear should be avoided when practical. Inter-element corrections that constitute a major portion of an emission signal may not yield accurate data. It should not be forgotten that some samples contain uncommon elements that could contribute spectral interferences.

The interference effects must be evaluated for each individual instrument. Intensities will vary not only with the optical resolution but also with the operating conditions (such as power, viewing height, and argon flow). The EPA Region 9 Laboratory has determined and documented for each wavelength the effect from the known interferences given in Table 1 of Appendix D, and utilizes a computer routine for their automatic correction on all analysis. To determine the appropriate location for the off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line inter-element spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference

effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 50 mg/L to 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit.

When inter-element corrections are **not** used, the ongoing SIC solutions (Section 7.3.7) must be analyzed to verify the absence of inter-element spectral interference. When the interference accounts for 10% or more of the analyte concentration, another approved test procedure must be used to complete the analysis. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference might not be available for all matrices. In these circumstances, the analyte must be determined using another approved test procedure.

6.2 Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as high solids nebulizer, diluting the sample, and using a peristaltic pump. Another problem that can occur is salt buildup at the tip of the nebulizer, which affects the aerosol rate and causes instrument drift. This problem can be controlled by a high solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample.

6.3 Chemical Interferences

Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), buffering the sample, matrix matching, and standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

6.4 Memory Interferences

Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the uptake tubing to the nebulizer, and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These

memory effects are dependent upon both the analyte being measured and sample matrix and are minimized through the use of extended rinse times.

6.5 Chemical Contamination

When determining boron in aqueous samples, only plastic, PTFE, or quartz labware should be used from time of collection to completion of analysis. When possible, borosilicate glass should be avoided to prevent contamination of boron.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Refer to EPA Region 9 Laboratory SOP 130 *Glassware Cleaning Procedures* for specific instructions.

7.1 Instruments and Equipment

- Perkin Elmer Optima 5300 DV Inductively Coupled Plasma – Optical Emission Spectrometer
- Perkin Elmer AS-93plus Auto-sampler

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Record all chemical and reagent preparations in the LIMS.

- Reagent Water – All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825 *Deionized Water Monitoring*.

- Hydrochloric Acid (HCl), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed).

- Nitric Acid (HNO_3), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed).
- Argon gas supply, high-purity grade, 99.99%.

7.2.1 Hydrochloric Acid, dilute (1:1) – Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Nitric Acid, dilute (1:1) – Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1L.

7.3 Standards

Record all standards and standard preparations in the LIMS.

7.3.1 Stock Standards

Stock standard solutions are available from a commercial suppliers such as Spex CertiPrep, Ultra Scientific, or Inorganic Ventures. Individual (1,000 mg/L or 10,000 mg/L) and multi-element solutions containing elements listed in Appendix B are typically used.

7.3.2 Initial Calibration Standards

Prepare initial calibration standard solutions to contain final concentrations listed in Table 2 of Appendix D. Prepare each calibration solution using an appropriate amount of the calibration stock standard (Section 7.3.1) and dilute to 200 mL with 2% nitric acid / 2% hydrochloric acid solution.

7.3.3 ICV/CCV/SCV Standard

The ICV and CCV standards are identical and only differentiated by their place within the analytical sequence. The ICV standard also serves as the SCV. This standard is obtained from an outside source different from the initial calibration stock standards. This standard is available from Spex and consists of solution LPC Standard 1, P/N LPC-1-500 (containing Al, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Sb, Se, SiO_2, Sn, Ag, Na, Sr, Tl, V, and Zn). Titanium and cerium are added from separate 1,000 mg/L individual stock standards. Prepare the ICV/CCV/SCV standard by adding 50 mL of the LPC Standard 1 and 1 mL each of the Ti and Ce 1,000 mg/L stock standards, dilute to 500 mL with 2% nitric acid / 2% hydrochloric acid solution.

The ICV/CCV/SCV concentrations are listed in Table 3 of Appendix D. Similar mixes from other vendors can be substituted as needed.

NOTE: ICV standard for lithium is prepared from a separate individual standard and run in a separate method.

7.3.4 CB

Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% nitric acid / 2% hydrochloric acid solution.

7.3.5 MB

Prepare the MB using reagent water plus all of the reagents used in processing the samples. The MB is taken through the entire preparation and analytical sequence.

7.3.6 LCS and MS/MSD

Use commercially available spiking solutions (e.g. Inorganic Ventures Laboratory Fortifying Stock Solutions WW-LFS-1 containing Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Se, Ag, Na, Sr, Tl, V, and Zn;and WW-LFS-2 containing Sb, Mo, SiO_2, Sn, and Ti). Prepare the LCS by spiking 0.5 mL each of the two spiking solutions into 50 mL reagent water and adding the appropriate acids. Prepare the MS and MSD by spiking 0.5 mL each of the two spiking solutions into 50 mL of the designated MS and MSD samples and adding the appropriate acids. The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

7.3.7 Spectral Interference Check (SIC) Solutions

When inter-element corrections are applied, spectral interference check (SIC) solutions containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors are needed. The SIC solutions used are 300 mg/L Ca, 200 mg/L Mg, 200 mg/L Al, 300 mg/L Fe, 50 mg/L Ba, 50 mg/L Cd, 50 mg/L Be, 50 mg/L Ce, 50 mg/L Co, 50 mg/L Cr, 50 mg/L Cu, 50 mg/L Mn, 50 mg/L Mo, 50 mg/L Ni, 50 mg/L Ti, and 50 mg/L V. Higher level SIC solutions or other SIC solutions may be used if high or unusual sample matrix are encountered. Prepare SIC solutions by diluting single element stock solutions in 2% nitric acid / 2% hydrochloric acid solution.

7.3.8 QLS (CRL in LIMS)

Prepare the QLS as needed from multi-element stock solutions (Section 7.3.1) in 2% nitric acid / 2% hydrochloric acid solution. The QLs are listed in Appendix B.

7.3.9 Optical Alignment Solution

A solution of 1 mg/L manganese is needed to align the optical paths of the instrument. The solution is made by diluting 1.0 mL of 1,000 µg/mL manganese stock standard to 1,000 mL with 2% nitric acid / 2% hydrochloric acid solution.

7.3.10 Rinse Blank

Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% nitric acid / 2% hydrochloric acid solution.

7.4 Supplies

- Automatic pipettes capable of delivering volumes of 10 to 1,000 µL.
- Class A volumetric flasks, graduated cylinders, and funnels (glass and/or metal-free plastic).
- Class A volumetric pipettes.
- Metal-free disposable tips.
- Narrow-mouth storage bottles with screw closure, 125-mL to 1-L capacities.
- Syringe with 0.45-µm disk filters.
- Wash bottle with screw closure, 1,000-mL capacity.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the ICP-AES following operating instructions provided by the manufacturer and discussed below. Use operating parameters provided in Appendix E as a starting point.

Ensure that all appropriate waste containers are properly connected and labeled and that the containers will not overflow.

Check the condition of the pump tubing for wear. Replace as needed. Tighten the pump tubing on the pump. Check torch for salt build up. Ignite the plasma and allow to stabilize for at least 30 minutes. During instrument warm up, observe the nebulizer and spray chamber for proper nebulization.

8.1.1 Method File Setup

Select the appropriate master method file and save it to correspond to the current date (e.g., 2007_150730 or yymmdd). Enter the results data set file

name to also correspond to the current date (e.g., 11507301, indicating ICP instrument number (1), present date (yymmdd), and analytical run number (1)) in the automated analysis control window. Save all changes.

Set up the sample information editor table with the desired sample run. The most recent sample information editor files may be written over and resaved. Print the run list from the automated analysis control window. Place the standards and samples in the racks as indicated by the run list.

8.1.2 Alignment of the Optical Paths

Alignment is performed when the sample introduction apparatus is adjusted, such as a new torch, injector tip, or after manipulation of the spray chamber. Align the axial and radial optical paths of the instrument using the 1 mg/L manganese solution. Aspirate the alignment solution and run the alignment routine as per the manufacturer's procedure.

8.2 Calibration

8.2.1 Initial Calibration

A calibration blank (Section 7.3.4) and a calibration standard (Section 7.3.2) are used for calibration. The calibration standards are given in Table 2 of Appendix D. The calibration is automatically saved in the result data set file as they are run.

Perform an initial calibration for every analytical batch. Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV/SCV, CB, QLS, and SIC (verification) according to Section 8.3.2 immediately after analyzing the initial calibration standards. If QC criteria are not met, take corrective action as described in Sections 9.2.3 and 9.2.4 and Appendix C.

8.2.2 Continuing Calibration

Prepare the CCV and CB as described in Sections 7.3.3 and 7.3.4. Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Digest samples with turbidity > 1 NTU and/or where silver is requested following EPA Region 9 Laboratory SOP 403 prior to analysis.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices, and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason, samples are digested prior to the determination of silver. The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, a smaller volume of a well-mixed sample aliquot must be digested until the analysis solution contains < 0.1 mg/L silver.

8.3.1.1 Aqueous Samples, Total Recoverable Analytes

For the determination of total recoverable analytes in water, digest samples following EPA Region 9 Laboratory SOP 403 prior to analysis.

The digestion procedures used in EPA Region 9 Laboratory SOP 403 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1mg/L silver.

8.3.1.2 Aqueous Samples, Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, add a 30-mL aliquot of the filtered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

The LCS and MS/MSD are prepared by spiking 0.3 mL each of the two spiking solutions (Section 7.3.6) into 30 mL of the designated LCS, MS, and MSD samples. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.3 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis

Drinking water samples with turbidity < 1 NTU must be acidified and analyzed directly without digestion. Add a 30-mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

The LCS and MS/MSD are prepared by spiking 0.3 mL each of the two spiking solutions (Section 7.3.6) into 30 mL of the designated LCS, MS and MSD samples. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log or the LIMS sequence page, if available.

After calibration, the auto-sampler continues with the samples and QC. Load SIC solutions according to the requested analyte list. An example of a typical loading list for an analytical run sequence is listed in the table below.

Seq.	Description	Seq.	Description	Seq.	Description	Seq.	Description
1	ICV/SCV	15	Mo SIC	29	S5	43	S17
2	CB	16	Ni SIC	30	S6	44	S18

Seq.	Description	Seq.	Description	Seq.	Description	Seq.	Description
3	QLS (CRL in LIMS)	17	Ti SIC	31	S7	45	S19
4	Ca SIC	18	V SIC	32	S8	46	S20
5	Mg SIC	19	MB	33	S9	47	MB
6	Ba SIC	20	LCS	34	S10	48	LCS
7	Al SIC	21	S1	35	S11	49	CCV
8	Cr SIC	22	S1-MS	36	S12	50	CB
9	Co SIC	23	S1-MSD	37	CCV	51	QLS (CRL in LIMS)
10	Cu SIC	24	S2	38	CB	52	S1
11	Fe SIC	25	CCV	39	S13	53	S2
12	Mn SIC	26	CB	40	S14	54	S3
13	CCV	27	S3	41	S15	55	CCV
14	CB	28	S4	42	S16	56	CB

NOTE: Be, Ce, and Cd SIC solution should be analyzed if samples contain these elements at a significant enough concentration to interfere on the analyte of interest (i.e. 1 mg/L).

Review results for QC compliance and off-scale results. Identify samples that must be re-analyzed. Samples having analytes at concentrations higher than 90% of the LDR must be diluted into range and reanalyzed. Refer to Appendix G for guidance on what elements may be reported from this analysis.

8.3.3 Analyte Identification and Quantitation

After set-up and calibration, the software reports results for the analyzed solution in the units of mg/L without inter-elemental correction. The data are then reprocessed to include inter-elemental correction when necessary.

8.3.4 Procedure to Acquire and Reprocess Data

1. Open the result data set in the Inter-Element Correction Model Builder (IEC Model Builder) set-up page. Assign the analyte limits of correction in the set limits page, generally ½ each of the corresponding QL.

2. Select the SIC samples and the interfering element.

3. Save the IEC Model Builder as 200.7IECmonth/day/year.

4. Update the daily method from the summarize factors page of the IEC Model Builder and save as the same method name with R at the end of name to indicate that it is a reprocessed method file.

5. Print the method and summarize factor table and include with the data package.

6. Open the data reprocessing window and reprocess the result data set. Print and save in a reprocessed result data set file with the same file name as the original data set with an R at the end to indicate that it is a reprocessed data.

7. The reprocessed data includes the calibrations and IEC corrected data for all samples analyzed.

8. An IEC table from a previous run may be used to reprocess data if the appropriate SIC solutions are run to verify the IEC factors according to Section 9.2.

8.3.4.1 Aqueous Samples – Data for aqueous samples should be reported in units of µg/L using the following calculation:

$$C = M \times \frac{1000ug}{mg} \times D$$

Where

C = final reported concentration, in µg/L;
M = measured concentration reported by instrument, in mg/L;
D = Sample analysis dilution factor, to account for any dilution performed after sample preparation. For samples analyzed by direct analysis, include the factor introduced by the addition of 1:1 nitric acid.

8.3.4.2 Hardness by Calculation

Hardness is determined by calculation if samples are known to contain high concentrations of heavy metals and cannot be analyzed by titration or when requested by a client. The calculation is based on calcium and magnesium results by EPA Method 200.7.

NOTE: Calcium and magnesium must be reported from one run – if one is over calibration, both should be reported from the dilution.

Hardness is calculated using the following equation based on Standard Method 2340B:

Hardness, mg/L $CaCO_3$ = Ca, mg/L (2.497) + Mg, mg/L (4.118)

8.3.5 Data and QC Review

Review the results of instrument QC (ICV/SCV, CB, QLS, and SIC) immediately after analysis to verify that the results are within QC limits. Refer to Section 9.2 for corrective action requirements and Appendix C for QC limits.

Review the results of batch QC (MB, LCS, MS/MSD) immediately after analysis to verify that the results are within QC limits. Refer to Section 9.3 for corrective action requirements and Appendix C for QC limits.

8.3.6 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using Data Tool. Review final results in the LIMS.

The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

Archive data files to the appropriate instrument data subdirectory on the EPA Region 9 LAN.

8.4 Maintenance

Perform the following maintenance:

- Inspect pump tubing for wear daily, replace if necessary.
- Inspect spray chamber for good nebulization.
- Inspect torch and tip if starting is difficult or if unusual carry over is observed during analysis. Remove and clean as necessary.
- Clean and lubricate auto-sampler as needed.

Refer to Appendix F for preventative maintenance procedures and schedules.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 Linear Dynamic Range

The upper limit of the LDR must be established for each element used in quantifying results. Analyze a series of standards with concentrations spanning the range from the QL to the LDR standard concentration. The upper concentration factor can be adjusted by the analyst to account for detector characteristics or dissolved solids limitations/restrictions. From the analysis determine the maximum concentration for which the measured and true concentration agree within 10%. This concentration is typically defined as the upper limit of the LDR. Samples with analyte concentrations that are greater than 90% of the upper LDR limit must be diluted and reanalyzed. The LDR should be verified annually or whenever the analytical conditions are changed.

9.2.2 Method Detection Limit

A method detection limit must be confirmed annually and must be <½ the QL.

9.2.3 Spectral Interference Measurement and Check

The laboratory must establish and initially verify an inter-elemental spectral interference correction routine to be used during sample analysis. Criteria for determining an inter-element spectral interference is the apparent positive or negative concentration on the analyte that is outside the limits of the calibration blank for the analyte. Once established, the interferences are measured daily as needed. The test criteria and the solutions are as follows:

- For interferences from aluminum and iron, only those correction factors (positive or negative) when multiplied by 100 that exceed ±½ the QL are tested daily.

- For all other interfering elements, only those correction factors (positive or negative) when multiplied by 10 that exceed ±½ the QL are tested daily.

- If the correction routine is operating properly, the determined apparent analyte concentration from analysis of each interfering solution should fall within a specific concentration range. The range shall be the greater of either ±½ the QL or a calculated concentration range (multiply the concentration of the interfering element by the value of the correction factor being tested and dividing by 10). If the apparent analyte concentration is outside the greater of the two ranges, the correction factor should be re-determined and samples re-analyze.

- If the samples analyzed do not contain concentrations of the interfering elements at a significant concentration, daily verification is not required. A significant concentration is the concentration of interfering elements the causes a false concentration of analyte greater than ½ the QL concentration.

9.2.4 Initial Calibration

An initial calibration is performed for every analytical batch using a blank and a calibration standard for each analyte.

If an ICAL fails because of one standard mix, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration standard mix), the system must be checked so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV and CB. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary. The analysis may also continue but samples cannot be analyzed for the out-of-control analytes.

9.2.5 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standards. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one

per 10 analytical samples and at the end of the analytical run. The recovery of analytes in the ICV and CCV are calculated as follows:

$$\%R = \frac{ICV / CCV}{s} \times 100$$

Where

$\%R$ = percent recovery
ICV/CCV = measured concentration of analyte in the ICV/CCV, mg/L
S = expected analyte concentration in the ICV/CCV, mg/L

The ICV recovery and RSD criteria are listed in Appendix C. If the %R or RSD for any analyte in the ICV falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analytes or analyze another second source solution containing the out-of-control analytes. If it passes, continue with analysis. Samples cannot be analyzed for the out-of-control analytes until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for any analyte in the CCV falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analytes or analyze another second source solution containing the out-of-control analytes. If it passes, continue with analysis. All samples not bracketed by acceptable CCV results must be reanalyzed.

9.2.6 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. The instrument must be recalibrated at least for the out-of-control analyte and all samples not bracketed by acceptable CB results must be reanalyzed.

9.2.7 Second Source Calibration Verification

Analyze an SCV daily to verify the calibration standards and acceptable instrument performance. The ICV serves as the SCV for this SOP.

9.2.8 Quantitation Limit Standard (CRL in LIMS)

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after 40 analytical samples.

If using an auto-diluter to analyze samples, use the diluter also to analyze the QLS.

The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
$\%R$ = percent recovery
M = measured concentration of analyte, mg/L
T = true concentration of the analyte in the QL, mg/L

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and reanalyze the QLS.

9.2.9 Spectral Interference Check

Analyze SIC solutions daily to measure and test inter-elemental spectral correction factors. If the SIC solutions do not meet the test criteria given in Section 9.2.3 and Appendix C, the factor must be updated before samples are analyzed for an affected analyte. If the affected samples do not contain concentrations of the interfering elements at a significant level, daily verification is not required. If the affected samples contain concentrations of analyte at less than ½ the QL, daily verification is not required. If the corrected concentration of the analyte due to spectral interference is less than 10% of the total analyte concentration, daily verification is not required.

9.3 Batch QC

9.3.1 Method Blank

Analyze one MB with each batch of 20 or fewer field samples of the same matrix. MB values ≥ ½ the QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared, reanalyzed, and flagged as estimated:

- If the MB analyte value is ≥ ½ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and reanalyzed. If agreed to by the Chemistry Team Leader, the associated sample results can also be reported but will be qualified as estimated "J" and flagged "B" and a note placed in the Work Order memo field in LIMS.

- If the MB analyte value is ≥ ½ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer samples of the same matrix. Recovery of analytes in the LCS is calculated as:

$$\%R = \frac{LCS}{s} \times 100$$

Where
$\%R$ = percent recovery
LCS = measured concentration of analyte in the LCS, mg/L
s = analyte concentration in the LCS, mg/L

If the recovery of the LCS does not meet the recovery criteria in Appendix C, reanalyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out- of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be re-prepared and reanalyzed. In some cases, the associated sample results can also be reported with prior approval from the Laboratory QA Officer or Technical Director. The results will be qualified as estimated "J".

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 20 or fewer field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analytes of interest prior to any sample preparation. The spiking level must be the same as that used for the LCS.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where
$\%R$ = percent recovery

C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions
C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions
s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where
RPD = relative percent difference
C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions
C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions

If the value of C is less than four times the value of s, apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s, $\%R$ is not meaningful. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Method Performance

The following table summarizes method performance for the period June 1, 2014 to June 19, 2015.

Method Performance

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation	95% Confidence Interval (2σ) Lower	Upper
Aluminum	70	103	4.58	93.8	112
Antimony	52	109	4.28	100	118
Arsenic	52	109	4.25	100	117
Barium	54	106	4.42	97	115
Beryllium	52	104	4.49	94.5	112
Boron	69	102	6.38	88.7	114
Cadmium	52	104	3.59	96.9	111

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation	95% Confidence Interval (2σ) Lower	Upper
Calcium	90	108	7.2	94	123
Chromium	54	104	3.79	96.2	111
Cobalt	55	103	3.45	95.7	109
Copper	66	99.9	3.28	93.4	106
Iron	94	103	5.3	92.5	114
Lead	52	104	3.81	96.4	112
Lithium	11	107	4.06	99.3	116
Magnesium	82	103	4.64	94.1	113
Manganese	55	103	4.77	93.2	112
Molybdenum	72	103	3.17	96.5	109
Nickel	67	105	3.81	97.4	113
Potassium	67	107	3.61	99.9	114
Selenium	53	111	4.94	101	120
Silica (SiO2)	52	110	4.75	101	120
Silver	52	104	4	96	112
Sodium	82	109	6.36	96.2	122
Strontium	55	107	4.52	98	116
Thallium	52	102	4.27	93.2	110
Tin	55	101	6.33	88.7	114
Titanium	73	103	3.8	95.2	110
Vanadium	73	104	2.96	97.9	110
Zinc	67	109	4.25	101	118

The primary sources of analytical error are:

- Analytical balance
- Digestion equipment contamination
- Instrument calibration
- Interferences (See Section 6)
- Pipette calibration

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV/SCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the standard pdf (printed upon request).

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Sequence Log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, dilution factors, and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained on the local area network or on the Lab QA SharePoint site in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on the local area network, LIMS, or the Lab QA SharePoint site for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

U.S. Environmental Protection Agency. Method 200.7, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 4.4, EMMC Version, May 1994.

Standard Methods for the Examination of Water and Wastewater, Method 2340B, Hardness by Calculation, 20th Edition, 1998.

Perkin Elmer, Optima 5000 Series Hardware Guide.

Perkin Elmer, *AS93plus User's Guide.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP does not include mercury as an analyte. Mercury is listed as an analyte in the reference method.

2. Aqueous samples with less than 1% undissolved solids are brought to a final volume of 50 mL. This procedure does not include the sample concentration step specified in the reference method.

3. The Region 9 Laboratory does not subtract the MB results from the LCS results for LCS recovery calculation. The reference method allows MB subtraction.

4. This SOP specifies that the MB acceptance criterion is less than one-half the QL. The reference method specifies no greater than 2.2 times MDL.

5. SIC acceptance criterion of ½ the QL is being followed in this procedure.

6. The SIC solutions of thallium, silica, and tin listed in the reference method are not necessary for this instrument and are not analyzed.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstract Services Registry Number (CASRN)	Quantitation Limit, µg/L
Aluminum (Al)	7429-90-5	100
Antimony (Sb)	7440-36-0	20
Arsenic (As)	7440-38-2	20
Barium (Ba)	7440-39-3	10
Beryllium (Be)	7440-41-7	0.5
Boron (B)	7440-42-8	100
Cadmium (Cd)	7440-43-9	5
Calcium (Ca)	7440-70-2	100
Chromium (Cr)	7440-47-3	10
Cobalt (Co)	7440-48-4	5
Copper (Cu)	7440-50-8	10
Iron (Fe)	7439-89-6	100
Lead (Pb)	7439-92-1	20
Lithium (Li)	7439-93-2	2
Magnesium (Mg)	7439-95-4	500
Manganese (Mn)	7439-96-5	5
Molybdenum (Mo)	7439-98-7	20
Nickel (Ni)	7440-02-0	10
Potassium (K)	7440-09-7	2000
Selenium (Se)	7782-49-2	20
Silica (SiO_2)	7637-86-9	500
Silver (Ag)	7440-22-4	5
Sodium (Na)	7440-23-5	500
Strontium (Sr)	7440-28-6	2
Thallium (Tl)	7440-28-0	20
Tin (Sn)	7440-31-5	100
Titanium (Ti)	7440-32-6	10
Vanadium (V)	7440-62-2	4
Zinc (Zn)	7440-66-6	10

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
ICV/SCV	After ICAL	95 - 105%
ICV	After ICAL	< 3% RSD
CCV	Every 10 samples and end of run	90 - 110%
CB	After each ICV/CCV	< ½ QL
QLS	After ICAL and after every 40 samples	60 - 140%
MB	Each batch of 20 or fewer samples	< ½ QL
LCS	Each batch of 20 or fewer samples	85 - 115%
MS/MSD, Accuracy	Every 20 or fewer samples in an SDG	70 - 130%
MS/MSD, Precision	Every 20 or fewer samples in an SDG	≤ 20 RPD
SIC	After ICAL, as needed per analyte	±½ QL or calculated acceptance window, whichever is greater

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APPENDIX D.
STANDARD TABLES

Table 1. Method Analytes and Potential Interfering Elements

Analyte	Wavelength, nm	Plasma View	Potential Interfering Elements***
Al	308.215	Radial	Co, Mo, Ti, V
Sb	206.836	Axial	Ce, Cr, Fe, Mo, Ti, V
As	188.979*	Axial	Ce, Cr, Co, Mo, Ti
As	193.696****	Axial	Co, Mn, Mo, Ti, V
Ba	233.527*	Radial	Mo, V
Be	313.107*	Radial	Ce, Cr, Ti, V
B	249.677	Radial	Co, Fe, Mo, V
Cd	226.502	Axial	Fe, Ni, Ti
Ca	315.887	Radial	Cr
Ce	413.764	Radial	None
Cr	205.560	Axial	Ce, Be, Fe, Mo, Ni
Co	228.616	Axial	Ba, Cd, Cr,Ni, Ti
Cu	324.752	Radial	Fe, Mo
Fe	273.955*	Radial	Ti
Pb	220.353	Axial	Al, Ce, Co, Cu, Fe, Mo, Ni, Ti
Li	670.784	Axial**	None
Mg	279.077	Radial	Mn
Mn	260.568*	Radial	Co, Fe
Mo	202.031*	Axial	None
Ni	231.604	Axial	Co, Mo
K	766.490	Radial	None
Se	196.026	Axial	Ce, Al, Co, Fe, Mn, Mo, Ti, V
SiO_2	251.611	Radial	Mo
Ag	328.068	Axial	Ce, Cu, Fe, Mn, Ti, V
Na	589.592*	Radial	None
Sr	421.552	Radial	None
Tl	190.801*	Axial	Ce, Cr, Co, Fe,Mn, Ti, V
Sn	189.927*	Axial	Mg
Ti	334.940	Radial	Ca, Cr
V	292.402	Axial	Ce, Cr, Fe, Mn, Mo, Ti
Zn	213.857	Radial	Ca, Cu, Fe, Ni

Note: *Wavelengths other than those recommended by Method 200.7
**Axial view with high resolution

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***All potential interfering elements based on ½ QL interference level. Underlined potential interfering element often requires daily testing per Section 9.2.3.

****Additional arsenic line added to monitor possible calcium background interference.

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Table 2. Calibration Standard Concentrations*

Analyte	Solution	Concentration mg/L	Analyte	Solution	Concentration mg/L
As	Cal 5	10.0	Co	Cal 4	2.0
Ca	Cal 5	10.0	V	Cal 4	2.0
Sb	Cal 5	5.0	Al	Cal 3	10.0
Ba	Cal 5	1.0	Cr	Cal 3	5.0
B	Cal 5	2.0	SiO_2	Cal 3	10.0
Cd	Cal 5	2.0	Sn	Cal 3	4.0
Cu	Cal 5	2.0	Ti	Cal 3	10.0
Mn	Cal 5	2.0	Zn	Cal 3	5.0
Se	Cal 5	5.0	Be	Cal 2	1.0
Ag	Cal 5	0.5	Fe	Cal 2	10.0
K	Cal 6	20.0	Mg	Cal 2	10.0
Mo	Cal 6	10.0	Ni	Cal 2	2.0
Na	Cal 6	10.0	Pb	Cal 2	10.0
Sr	Cal 6	1.0	Tl	Cal 2	5.0
Ce	Cal 4	2.0	Li**	Cal 2	2.0

Note: *Mixes are prepared as needed from individual stock standards. Prepared mixed standards may also be purchased. All calibration sources are different than the source of the ICV/CCV/SCV.
**Lithium standard is from an individual stock and is used for Li method only.
***Cal 1 is the calibration blank.

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Table 3. ICV/CCV/SCV, LCS/MS/MSD Concentrations

Analyte	ICV/SCV/CCV mg/L	LCS/MS/MSD mg/L
Al	2.0	2.0
Sb	2.0	0.80
As	2.0	0.80
Ba	2.0	0.20
Be	2.0	0.20
B	2.0	0.30
Cd	2.0	0.20
Ca	2.0	1.0
Ce	2.0	2.0
Cr	2.0	0.40
Co	2.0	0.20
Cu	2.0	0.30
Fe	2.0	3.0
Pb	2.0	1.0
Li	0.5	0.20
Mg	2.0	2.0
Mn	2.0	0.20
Mo	2.0	0.40
Ni	2.0	0.50
K	10.0	10.0
Se	2.0	2.0
SiO_2	10.0	2.0
Ag	0.5	0.075
Na	2.0	3.0
Sr	2.0	0.20
Tl	2.0	2.0
Sn	2.0	0.70
Ti	2.0	0.20
V	2.0	0.30
Zn	2.0	0.20

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APPENDIX E.
TYPICAL INSTRUMENT PARAMETERS

Nebulizer Gas Flow setting:	0.40 - 0.60 L/min
Auxiliary Gas Flow setting:	0.2 L/min
Plasma gas Flow setting:	15 L/min
ICP RF Power setting:	1500 W
Argon Line Pressure:	>100 psi
Resolution Setting:	Normal
Resolution Setting, Li Method:	High
Replicates:	4
Read Parameters:	minimum 2 – 5 sec., maximum 10 – 20 sec.
Rinse Time:	120 – 240 sec., typical
Flush Time:	50 - 70 sec.

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the PE Optima 5300 DV

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	As needed	Fill with 2% $HN0_3$ / 2% HCl
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
Drain Tubing	Daily	Check for good drainage, adjust as needed
Nebulizer Spray	Daily	Check, unclog by back flushing if needed
Torch Tip	Daily	Check for sample residues. Replace with clean glassware if needed.
Argon Dewar	Daily	Check for sufficient amount and pressure. Order as needed.
Auto-sampler and Peristaltic Pump	Daily	Wipe spills or residues.
Glassware	Weekly or needed	If excessive carryover, inspect and clean if needed.
Radial and axial windows	Monthly or as needed	If sensitivities fall or cloudiness noted replace with clean windows.
Air filters	Monthly	Clean as needed.

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APPENDIX G.
DECISION TREE FOR REPORTING METALS

Aluminum (Al)	X		XXX
Antimony (Sb)	X		XXX
Arsenic (As)	X		XXX
Barium (Ba)	X		XXX
Beryllium (Be)	X	XX	
Boron (B)		XX	
Cadmium (Cd)	X		XXX
Calcium (Ca)		XX	
Chromium (Cr)	X		XXX
Cobalt (Co)	X		XXX
Copper (Cu)	X		XXX
Iron (Fe)		XX	
Lead (Pb)	X		XXX
Magnesium (Mg)		XX	
Lithium (Li)		XX	
Manganese (Mn)	X		XXX
Molybdenum (Mo)	X		XXX
Nickel (Ni)	X		XXX
Potassium (K)		XX	
Selenium (Se)	X		XXX
Silica (SiO_2)		XX	
Silver (Ag)	X		XXX
Sodium (Na)		XX	
Strontium (Sr)		XX	
Thallium (Tl)	X		XXX
Thorium (Th)	X		
Tin (Sn)		XX	
Titanium (Ti)		XX	
Uranium (U)	X		
Vanadium (V)	X		XXX
Zinc (Zn)	X		XXX

Where:

X = reported by ICP-MS

XX = reported by ICP-AES

XXX = if all 200.7 QC passes and the concentration is above the 200.7 QL, an element may be reported from the 200.7 analysis.

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APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 505
Revision: 9, Effective: 07/15/2015

DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-AES

Revision	Effective Date	Description
7	09/17/09	1. Minor revision to integrate LIMS into procedure and revise format to current SOP 850 requirements. 2. Section 7.3.8, added Be and removed Sn as an SIC solution. 3. Section 8.3.2, updated analytical sequence and added a note on when to analyze Be, Ce, and Cd SIC solutions. 4. Section 8.3.3 step 1, changed limit correction from 1/5 to 1/2 the QL. 5. Appendix A, replaced Be with Sn as a not analyzed SIC solution. 6. Appendix B, changed Li QL to 5 *u*g/L from 10. 7. Appendix D, Table 1: (1) Updated potential interfering elements to current instrument conditions, (2) Updated Be to radial view; Cd and Sn to axial view. 8. Appendix D, Table 2, changed Ce concentration to 2 mg/L and to Standard III. 9. Appendix G, updated decision tree. 10. Appendix D updated 3/1/2011 to change plasma view on Cr, Co, Mo, Ni and V to axial for improved sensitivity.
8	06/01/12	1. Section 3, update CB definition. 2. Section 7.3.8, update SIC solutions used. 3. Sections 9.2.3 and 9.2.9, clarify SIC check. 4. Appendix B, lowered QL limits for Be, Co, Li, Ag, Sr, and V. 5. Appendix D, update interfering elements table. 6. Miscellaneous edits throughout.
9	07/15/15	1. Updated MS/MSD frequency to be consistent with the rest of the laboratory. 2. Additional arsenic line (193.696 nm) added to monitor possible calcium background interference. 3. Added note about elements exceeding extremely hazardous waste concentrations to Section 4.4. 4. Miscellaneous edits throughout.

ED_006532_00005075-00374

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 507
DETERMINATION OF TRACE ELEMENTS BY ICP-MS

Revision 7
Effective Date: February 1, 2012

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This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-06-041). ESAT Document Control Number: 01104008-14411

ED_006532_00005075-00375

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1 SCOPE AND APPLICABILITY

This SOP provides procedures for the determination of dissolved and total recoverable elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) in environmental samples for use in the USEPA Region 9 Laboratory, Richmond, CA. It is applicable to ground, surface, drinking, and storm runoff water samples; industrial and domestic waste waters. Additionally, this SOP has been extended to the analysis of fish tissue. The procedures are based on EPA Method 200.8, *Determination of Trace Elements in Waters and Wastes by ICP – MS*, Rev. 5.4, May 1994. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

Water samples with turbidity >1 NTU or where silver and/or total recoverable analytes are requested must be digested following EPA Region 9 Laboratory SOP 403 prior to analysis. Other water samples (primarily drinking water, but may also be a project specific request) may be analyzed directly after proper filtration and/or acid-preservation. Fish tissue is prepared by microwave digestion following EPA Region 9 Laboratory SOP 420 prior to analysis.

2 METHOD SUMMARY

This SOP describes the determination of trace elements in aqueous samples by ICP-MS by direct analysis or after digestion with nitric and hydrochloric acids. Sample solutions are introduced by pneumatic nebulization into a plasma, in which desolvation, atomization, and ionization occurs. Ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadruple mass spectrometer. The ions transmitted through the quadruple are detected by an electron multiplier. Ion intensities at each mass are recorded and compared to those obtained from external calibration standards to generate concentration values for the samples. Results are corrected for instrument drift and matrix effects using internal standards. Additional corrections are applied as necessary to correct for isobaric and polyatomic elemental interferences.

The dynamic reaction cell (DRC) simultaneously employs two techniques for the elimination of interferences, chemical resolution, and dynamic bandpass tuning (DBT). Chemical resolution involves the use of a gas within the DRC cell, which reacts with the interference to eliminate it. The DBT is applied at the same time using a bandpass mass filter which provides a high mass cut off and a low mass cut off to define a precise bandpass window, thus preventing the formation of new species that may interfere with the analysis.

3 DEFINITIONS

Analytical Sample – Any sample introduced into the ICP-MS instrument, excluding calibration standards, blanks, or QC reference samples.

Calibration Blank (CB) – A blank that is the same matrix as the calibration standards, but without the analytes. The calibration blank is also a zero standard used to calibrate the ICP-MS instrument. The CB is also known as the initial calibration blank (ICB) and the continuing calibration blank (CCB).

Continuing Instrument Calibration Verification (CCV) – The CCV standard is the same solution as the ICV standard and is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at end of the analytical run). The CCV is also known as the continuing instrument performance check (IPC) standard.

Dissolved Analyte – The concentration of analyte in an aqueous sample that is filtered through a 0.45-µm membrane filter assembly prior to sample acidification.

Initial Calibration Standard (ICAL) – Standards used to calibrate the instrument response with respect to analyte concentration.

Initial Instrument Calibration Verification (ICV) – A standard containing the analytes of interest that is used to verify the accuracy of the analysis. It is analyzed immediately after calibration. The ICV is also known as the initial instrument performance check (IPC) standard.

Internal Standard – An element added to all sample, extract, and standard solutions in the same known amount. Its response is measured throughout an analytical run and is used to correct for instrument drift and sample transport interferences. The internal standard should not be a sample constituent. Recommended internal standard elements are listed in Appendix D, Table 1.

Laboratory Control Sample (LCS) – An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

Laboratory Information Management System (LIMS) – The Element Database.

Linear Dynamic Range (LDR) – The concentration range over which the instrument response to an analyte is linear. The LDR study is used to define the concentration of the highest calibration standard.

Matrix Spike (MS) – An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be

determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as a laboratory fortified matrix (LFM) sample.

Matrix Spike Duplicate (MSD) – A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MSD is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MSD corrected for background concentrations. The MSD is also known a laboratory fortified matrix duplicate (LFMD) sample.

Method Blank (MB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as a laboratory reagent blank (LRB).

Method Detection Limit (MDL) – The minimum concentration of an analyte in an environmental sample that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Quantitation Limit (QL) – The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) – A standard used to check the accuracy of the analysis at the quantitation limit.

Sample Delivery Group (SDG) – A group of samples, usually twenty or fewer, from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) – A solution of method analytes of known concentration that is prepared from a source different from the source of the calibration standards. (A different lot from the same source may be used for multiple component analytes if a suitable second source is not available). It is used to check the accuracy of the initial calibration solutions. The SCV is also known as a quality control standard (QCS).

Stock Standard Solution (SSS) – A concentrated standard containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Total Recoverable Analyte Concentration – The concentration of an analyte in an unfiltered aqueous sample after preparation by acid digestion.

Tuning Solution – A solution containing selected elements over the entire mass range of the method. It is used to tune the mass calibration and resolution of the mass spectrometer, and to assess instrument performance prior to calibration and sample analysis.

Water Sample – For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

The ICP-MS emits radio frequency and intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The instrument is shielded to minimize exposure to these hazards and the shields should always be in place during operation.

Always wear safety glasses for eye protection (and a full face shield if large quantities of concentrated acids are being transferred), protective clothing, and observe proper mixing when working with these reagents.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
ICP/MS instrument liquid waste (nitric acid, hydrochloric acid, trace metals)	Hazardous Waste	Corrosive, Toxic
Pump Oil	Hazardous Waste	Other

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 500 mL sample volume should be sufficient to meet these objectives.

Whole fish samples are usually received wrapped in aluminum foil. Other tissue samples should be collected in pre-cleaned glass or plastic (if only inorganic analyses are requested) jars. There should be sufficient sample to ensure a representative sample, allow for replicate analysis and minimize waste disposal. A 10 g sample should be sufficient to meet project requirements if the analytical scope is limited to metals.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

1. Dissolved Analyte Samples

   The samples must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid contamination. The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with dilute (1:1) nitric acid immediately following filtration to pH <2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient).

2. Drinking Water Samples

   Samples are preserved by acidifying with dilute nitric acid to pH <2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH <2 just prior to withdrawing an aliquot for turbidity measurement. If the sample turbidity is <1 NTU, the sample can be analyzed directly without digestion (i.e. low level analysis). If turbidity is >1 NTU, perform the acid digestion for total recoverable analysis.

3. Aqueous Total Recoverable Analyte Samples

   Samples are preserved by acidifying with dilute nitric acid to pH <2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH <2 just prior to withdrawing an aliquot for digestion or 'direct analysis'. If the pH of the sample is >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2.

5.4 Sample Storage

Aqueous samples must be stored at > 0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

Fish tissue sample must be received and stored at ≤ -20 °C. Any deviations from the ≤ -20 °C temperature requirements must be noted in the report narrative. Any samples received unfrozen must be frozen upon receipt.

5.5 Holding Time

Aqueous samples must be analyzed within six months from collection.

Recommended tissue sample holding times are analysis dependent and vary by agency. The table below reflects the guidelines in *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume 1 Fish Sampling and Analysis,"* Office of Water, Washington, DC, Third Edition, November 2000. The analyst must review the project specific requirements with regard to holding times.

Analyte	Holding time
Metals (excluding Hg)	6 months

6 INTERFERENCES

1. Isobaric Elemental Interferences

Isobaric elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and cannot be resolved with the instrument's spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the interfering element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

All analytes listed in Appendix B have at least one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only antimony-123 (tellurium), molybdenum-98 (ruthenium), and selenium-82 (krypton) have isobaric elemental interferences. (Refer to Appendix D, Table 3). If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. Such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

2. Abundance Sensitivity Interference

Abundance sensitivity interference refers to the degree of peak overlap that can occur between adjacent peaks. The interference can occur when the shoulder of a large peak

significantly overlaps the peak of a neighboring minor peak, thereby contributing to its intensity. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

3. Isobaric Polyatomic Ion Interferences

Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and cannot be resolved by the instrument's spectrometer. Examples include $ArCl^+$ (mass 75), which interferes with As, and ClO^+ (mass 51) which interferes with V, which must be corrected by measuring ClO^+ at mass 53. This in turn must be adjusted for contribution from Cr at mass 53. These interferences are highly dependent on the matrix of the samples and day-to-day plasma conditions, so correction factors may be determined on the day of analysis. When possible, one should choose an interference-free isotope to measure.

The Region 9 Laboratory does not routinely calculate these correction factors and uses the recommended elemental equations for data calculations that are listed in Appendix D, Table 2. Alternatively, the Dynamic Reaction Cell (DRC) uses chemical resolution to remove polyatomic interferences using reaction gasses. The reaction gas is chosen such that it reacts with the interfering species to form a new, non-interfering species of a different mass. The new species is then mass separated prior to entry into the analyzer and the interference is effectively removed. The DRC can also use a reaction gas to react with the analyte of interest to form a new molecular species that is then analyzed at a mass that is free of the interference. An example is arsenic in the presence of oxygen in the DRC mode to form arsenic oxide, which is analyze at mass 92, thus eliminating the $ArCl^+$ interference present at arsenic mass 75.

4. Physical Interferences

Physical interferences result from the physical processes associated with the transport of sample to the plasma, sample behavior within the plasma, and transmission through the interface region between the plasma and the mass spectrometer. Viscosity and surface tension differences can affect results, as can deposits on the sample and skimmer cones caused by large quantities of dissolved solids in the samples. The interferences can be compensated for by the use of internal standards that approximate the analytical behavior of the elements being determined. Additionally, it is recommended that dissolved solids in samples be kept below 0.2% (w/v).

5. Memory Interferences

Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are

dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

The rinse times necessary for a particular analyte should be estimated prior to analysis. This can be achieved by aspirating a standard containing the analyte at a concentration ten times the highest calibration standard for the normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce the analyte signal to less than ten times the method detection limit should be noted. The minimum rinse time between samples should be set to this time. Memory interferences may also be assessed within an analytical run by using three or more replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should check for the possibility of a memory effect. If the analyte concentration in the previous sample is high enough to suspect analyte carryover, the sample should be re-analyzed after a long rinse period.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Refer to EPA Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures*, for specific instructions.

7.1 Instruments and Equipment

- Perkin Elmer Elan DRC Plus Inductively Coupled Plasma Mass Spectrometer
  - Cetac Autosampler
  - Cetac Autodilutor
  - Gilson Minipuls3 Peristaltic Pump
  - Polyscience 6105 – Refrigerated Circulator

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use. Record all reagent preparations in the LIMS.

- Reagent Water – All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825.

- Hydrochloric Acid (HCl), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Hydrochloric Acid, dilute (1:1) – Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.
- Nitric Acid (HNO_3), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Nitric Acid, dilute (1:1) – Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1L.
- Argon gas supply, high-purity grade, 99.99%
- DRC Reaction gas – Ammonia, electronic grade, 99.99%
- DRC Reaction gas – Oxygen, research grade

7.3 Standards

Record all standards and standard preparations in the LIMS.

7.3.1 Stock Standards

Stock standard solutions are available from commercial suppliers such as Spex or Inorganic Ventures. Multi-element solutions containing elements listed in Appendix B are typically used.

7.3.2 Initial Calibration Standards

Prepare initial calibration standards at a minimum of three levels. Use multi-element stock solutions (Section 7.3.1) as the source and dilute to the appropriate volume with 1% (v/v) nitric acid.

For routine analysis, prepare standards to contain 10 µg/L and 20 µg/L for all elements; 100 µg/L for As, Se, Be, Al, V, Cr, Mn, Co, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th, and U; and 200 µg/L for Ni, Cu, and Zn.

For low level, direct analysis, prepare standards to contain element concentrations at 10 µg/L, 20 µg/L, and 50 µg/L for each element.

NOTE: High level standards may also be used for undiluted samples containing levels of analytes greater than 50 µg/L. Higher level standards may

also be used as an additional calibration point to expand the linear range if warranted by high level concentrations inherent in samples.

Prepare fresh calibration standards every two weeks or as needed.

7.3.3 ICV/CCV Standard

The ICV standard and CCV standard are identical and only differentiated by their place within the analytical sequence. For routine analysis, a 50 µg/L ICV/CCV is typically analyzed. For low level, direct analysis, a 20 µg/L is typically used. Prepare each solution as needed from multi-element stock solutions (Section 7.3.1) in 1% (v/v) nitric acid.

7.3.4 CB

Dilute concentrated nitric acid with reagent water to obtain a 1% (v/v) nitric acid solution.

7.3.5 MB

Prepare the MB using reagent water plus all of the reagents used in processing the samples. The MB is taken through the entire preparation and analytical sequence.

7.3.6 LCS and MS/MSD

Prepare the LCS by fortifying an aliquot of reagent water from multi-element stock solutions (Section 7.3.1). Process the LCS and MS/MSD through the entire preparation and analytical sequence.

For routine analysis, prepare the LCS by fortifying an aliquot of reagent water to contain 40 µg/L of each analyte except aluminum which should be fortified at 80 µg/L. Prepare the MS/MSD by fortifying an aliquot of the QC sample with the stock standards to contain 40 µg/L of each analyte except aluminum which should be fortified at 80 µg/L

For low level, direct analysis, prepare the LCS and MS/MSD concentrations to contain 25 µg/L of each analyte.

7.3.7 SCV

Prepare SCV standards in 1% (v/v) nitric acid from multi-element stock standards from a source different from the calibration standards.

For routine analysis, prepare a standard to contain 50 µg/L of each analyte.

For low level, direct analysis, prepare a standard to contain 20 µg/L of each analyte.

7.3.8 QLS

Prepare the QLS as needed from multi-element stock solutions (Section 7.3.1) in 1% (v/v) nitric acid as shown in the following table:

QLS Concentrations

Element	Routine Analysis, µg/L	Low-level, Direct Analysis, µg/L
Co Ag U	0.25 µg/L	0.125 µg/L
Cd	0.4 µg/L	0.2 µg/L
As Be Mo Sb	0.5 µg/L	0.25 µg/L
Ba Cr Pb Ni Se Tl Th	1 µg/L	0.5 µg/L
Cu Mn	2 µg/L	1 µg/L
V	4 µg/L	2 µg/L
Zn	5 µg/L	2.5 µg/L
Al	20 µg/L	10 µg/L

7.3.9 Rinse Blank

Dilute concentrated nitric acid with reagent water to obtain a 2% (v/v) nitric acid solution.

7.3.10 Internal Standard Solution

Prepare internal standards from single-element stock standards (Section 7.3.1) to contain 200 µg/L lithium6 and 100 µg/L each of gallium, holmium, indium, rhodium, scandium, terbium, and yttrium in 1% (v/v) nitric acid.

7.3.11 Tuning Solution

Prepare an intermediate standard to contain 1,000 µg/L of barium, beryllium, cerium, cobalt, indium, lead, magnesium, thorium, and uranium from single-element stock standards (Section 7.3.1). Prepare a working solution from the intermediate standard at 1.0 µg/L in 1% (v/v) nitric acid.

7.3.12 Dual Detector Cross Calibration Solution

The dual detector cross calibration solution is used to correlate the pulse and analog modes of the detector for extended linear ranges.

Prepare a solution of all available elements across the entire mass range using the multi-element standards (Section 7.3.1) in 1% (v/v) nitric acid at concentrations of 100 µg/L to 500 µg/L.

7.4 Supplies

- Auto-sampler tubes
- Automatic pipettes capable of delivering volumes of 10 to 1,000 µL
- Class A volumetric flasks, graduated cylinders, and funnels (glass and/or metal-free plastic)
- Class A volumetric pipettes
- Metal-free disposable tips
- Narrow-mouth storage bottles with screw closure, 125-mL to 1-L capacities
- Syringe with 0.45 µm disk filters
- Wash Bottle with screw closure, 500-mL to 1,000-mL capacity

8 ANALYTICAL PROCEDURES

It is recommended that samples with unknown or unusual history be screened by ICP for elements at high concentration. Alternatively, samples may be screened using a semi-quantitative ICP/MS analysis at a 500-fold dilution.

8.1 Instrument Operation

Set-up the ICP-MS following operating instructions provided by the manufacturer and discussed below. Use operating parameters provided in Appendix E as a starting point.

Ensure that all appropriate waste containers are properly connected and labeled.

Ignite the plasma and stabilize for at least 30 minutes. During this stabilization period, run the tuning solution (described in Section 7.3.11) using indium signal to align the torch.

Open a method that contains all necessary masses for the analytes of interest or open a master method and edit so that all masses which are necessary to perform elemental calculations (for interference corrections) and which can provide information concerning data quality are monitored during the analytical run. Refer to Appendix D,

Table 2 for required masses. Enter the daily data set file name (report file name) in the report tab and save the method. Create a new data set file and save workspace.

At a minimum, masses for the elements of interest prescribed in Appendix D, Table 3 must be monitored in the same scan used for the collection of the data. For elements run in DRC mode, interference corrections calculations are not necessary. Create a new data set file and save workspace.

Initialize the autosampler and create a sample table. If the autodiluter is to be used, initialize the autodiluter and edit the autosampler table as appropriate.

Ensure that all appropriate waste containers are properly connected and labeled.

8.1.1 Tuning and Mass Calibration

After the plasma system (i.e., torch box, plasma, and spray chamber) has stabilized, verify and adjust the mass calibration and resolution.

Check the spectrometer resolution with beryllium, magnesium, cobalt, indium, and lead. Also monitor argon dimmer, cerium, and thorium.

The resolution should produce a peak width of approximately 0.75 atomic mass unit (amu) at 5% peak height. For the PE Elan, the resolution of 0.625 to 0.675 at 10% peak height corresponds to approximately 0.70 to 0.75 amu peak width at 5% peak height.

Adjust the mass calibration to ensure 0.1 amu accuracy from unit mass.

8.1.2 Sensitivity and Stability Check

Analyze the tuning solution (Section 7.3.11) a minimum of five times for daily performance check. The RSD for each element must be less than 5% before the instrument can be calibrated and samples analyzed.

Instrument sensitivity should be, at a minimum, as listed below:
Mg – 6,000 counts per second (CPS)
In – 30,000 CPS
U – 20,000 CPS

To avoid interferences, it is preferable that oxide (Ce) and ++ (Ba) levels not exceed 3%. If they do, depending on the specific analysis to be performed, maintenance or instrument adjustments may be required before proceeding with the analysis.

8.2 Calibration and Standardization

8.2.1 Internal Standardization

Internal standards are used to correct for instrument drift and physical transport interferences. Internal standards are automatically added to all samples, standards, and blanks by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. For full mass range scans, a minimum of three internal standards must be monitored and used for calculation.

NOTE: The concentration of the internal standard should be sufficiently high that good measurement precision is obtained while minimizing the bias introduced if the internal standard is naturally present in the sample (i.e., the signal intensity contributed from naturally occurring internal standard element in the sample is insignificant).

The typical concentration of the internal standard solution contains 200 µg /L lithium6 and 100 µg/L of gallium, holmium, indium, rhodium, scandium, terbium, and yttrium.

The typical final concentration of the internal standard solution after mixing with the sample is approximately one-fifth the initial concentration of the internal standard solution.

8.2.2 Initial Calibration

Perform an initial calibration daily or for every analytical batch, whichever is more frequent. For routine analysis and higher level direct analysis, analyze a minimum of three routine standards (Section 7.3.2) and a CB (Section 7.3.4) according to Section 8.3.2. For low-level, direct analysis, analyze a minimum of three low-level standards and a CB. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV, CB, and SCV according to Section 8.3.2 immediately after analyzing the initial calibration standards. Use the appropriate levels for routine or low-level analysis. If QC criteria are not met, take corrective action as described in Section 9.2 and Appendix C.

8.2.3 Continuing Calibration

Prepare the CCV (appropriate for routine or low-level analysis) and CB as described in Sections 7.3.3 and 7.3.4 and analyze according to Section 8.3.2. Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Digest samples with turbidity >1 NTU and/or where silver is requested following EPA Region 9 Laboratory SOP 403 prior to analysis. For fish tissue, digest tissue samples following EPA Region 9 Laboratory SOP 420.

8.3.1.1 Aqueous Samples, Total Recoverable Analytes

For the determination of total recoverable analytes in water, digest samples following Region 9 Laboratory SOP 403 prior to analysis.

The digestion procedures used in SOP 403 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains <0.1mg/L silver.

8.3.1.2 Aqueous Samples, Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, add a 30 mL aliquot of the filtered, acid preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

For LCS and MS/MSD analyses, spike the samples at 25 µg/L for all analytes.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.3 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis

Drinking water samples with turbidity <1 NTU must be acidified and analyzed directly without digestion. Add a 30 mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

For LCS and MS/MSD analyses, spike the samples at 25 µg/L for all analytes.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined by direct analysis. For this reason, samples for silver analysis should be digested.

8.3.1.4 Fish Tissue Samples

Dilute the fish tissue digestate times four prior to analysis with DI water. The sample is now ready for analysis.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the sequence log or the LIMS sequence page, if available.

Make appropriate dilutions on the basis of screening data, sample history, or other information. Samples for routine analysis are diluted two times using the autodiluter or manual dilution. Samples for low-level analysis are run without dilution.

1. Enter autosampler loading list into the data system, to include initial calibration, all required QC, and samples. If autodiluter is to be used, set-up the QLS, MB, LCS, and samples and specify autodiluter locations. For initial routine analysis, set the autodiluter for two times dilution.

2. Load the samples to be analyzed in the autosampler according to their

designated positions in the loading list. The following table shows a typical analytical sequence:

Seq.	Description	Seq.	Description	Seq.	Description
1	CB	15	S2	29	S12
2	Cal Std 1	16	S3	30	CCV
3	Cal Std 2	17	S4	31	CB
4	Cal Std 3	18	CCV	32	S13
5	Cal Std 4	19	CB	33	S14
6	ICV	20	S5	34	S15
7	CB	21	S6	35	S16
8	SCV	22	S7	36	S17
9	QLS	23	S8	37	S18
10	MB	24	S9	38	S19
11	LCS	25	S10	39	S20
12	S1	26	S11	40	CCV
13	S1-MS	27	S11-MS	41	CB
14	S1-MSD	28	S11-MSD	42	QLS*

NOTE: *Analyze QLS if more than 40 analytical samples are to be analyzed.

3. Start the autosampler analytical sequence and collect results.

4. Review the results for QC compliance and off-scale results. Identify samples that must be re-analyzed in a different analytical run. Samples having analytes at concentrations higher than the highest calibration must be diluted into range and re-analyzed.

5. Compare all analyte results generated in DRC mode with the run in standard mode. If results from the two modes differ significantly, interference may be present. If interference is suspected, dilute and reanalyze in both modes.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should be given to both primary

and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes. Check additional monitored masses (i.e. krypton, bromine, palladium) as indicators of potential interferences (refer to Appendix D).

8.3.3.2 After set-up and calibration the instrument reports results for the analyzed solution in the units of µg/L. The instrument calculations include elemental correction calculations, internal standard correction calculations, and calibration factors.

8.3.3.3 Report results in µg/L using the following equation:

$$C = M \times \frac{V_f}{V_i} \times D$$

Where

C = final reported concentration, in µg/L
M = measured concentration reported by instrument, in µg/L
V_f = final volume of sample solution after sample preparation, in mL
V_i = initial volume of sample used in sample preparation, in mL
D = Sample analysis dilution factor, to account for any dilution performed after sample preparation. For samples analyzed by the direct analysis, include the factor introduced by the addition of 1:1 nitric acid.

8.3.4 Data and QC Review

- Review the results of instrument QC (ICV, CCV, CB, SCV, and QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

- Review the results of batch QC (MB, LCS, MS/MSD) immediately after their analysis to verify that the results are with QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

- Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

- The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

8.4 Maintenance

Perform maintenance if the tune standard does not pass. Observe for measured mass parameter at ±0.1 amu. Observe for resolution parameter of peak width at 0.65 ±0.025. Adjust DAC parameters, if necessary.

If daily performance is unacceptable, check sample introduction (pump tubing, torch, nebulizer, cones, etc.) for wear and cleanliness. Clean or replace as necessary. If daily performance is still unacceptable, perform Optimizations procedure as described in Elan Software Guide.

Refer to Appendix F for preventative maintenance operations and schedules.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

9.2.1 Initial Calibration

An initial calibration is performed daily or for each batch of analysis using a blank and a minimum of three calibration standards. A linear calibration forced through zero is used for calculation. Refer to Appendix C for

acceptance criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV, CB, and SCV. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including re-analysis or re-preparation and reanalysis of the initial calibration if necessary. The analysis may also continue but samples cannot be analyzed for the out-of-control analytes.

9.2.2 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standard. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one per 10 analytical samples and at the end of the analytical run. The recovery of analytes in the ICV and CCV are calculated as follows:

$$\%R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard
M = measured concentration of the analyte, µg/L
T = true concentration of the analyte in the ICV/CCV, µg/L

The ICV recovery criteria are listed in Appendix C. If the %R for any analyte in the ICV falls outside of the QC criteria, the instrument must be re-calibrated for at least the out-of-control analytes. Samples cannot be analyzed for the out-of-control analytes until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for any analyte in the CCV falls outside of the QC criteria, the instrument must be re-calibrated for at least the out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control CCV must be re-analyzed for the affected analytes.

9.2.3 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. The instrument must be re-calibrated at least for the out-of-control analyte and all samples not bracketed by acceptable CB results must be re-analyzed.

9.2.4 Second Source Calibration Verification

Analyze a SCV daily to verify the calibration standards and acceptable instrument performance. If the measured concentrations are not within ±10% of the true values, the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

The recovery of analytes in the SCV is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
%R = percent recovery of the standard
M = measured concentration of the analyte, µg/L
T = true concentration of the analyte in the SCV, µg/L

9.2.5 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after each 40 analytical samples. If using an autodiluter to analyze samples, use the diluter also to analyze the QLS. The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100xD$$

Where
%R = percent recovery of the standard
M = measured concentration of the analyte, µg/L
T = true concentration of the analyte in the QLS, µg/L
D = sample analysis dilution factor, to account for any dilution performed after sample preparation

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and re-analyze the QLS.

9.3 Batch QC

9.3.1 Method Blank

Analyze at least one MB with each batch of 20 or fewer field samples of the same matrix. MB values ≥½ the QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared, re-analyzed, and flagged as estimated:

- If the MB analyte value is ≥½ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and re-analyzed. The associated sample results can also be reported but will be qualified as estimated "J".

- If the MB analyte value is ≥½ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer samples of the same matrix. Recovery of analytes in the LCS is calculated as:

$$\%R = \frac{M}{T} \times 100xD$$

Where

%R = percent recovery of the standard
M = measured concentration of the analyte, µg/L
T = true concentration of the analyte in the LCS, µg/L
D = sample analysis dilution factor, to account for any dilution performed after sample preparation

If the recovery of the LCS does not meet the recovery criteria in Appendix C, re-analyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out- of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be re-prepared and re-analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 10 field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analytes of interest prior to any sample preparation. The spiking level must be the same as that used for the LCS.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$ = percent recovery

C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions

C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions

s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where

RPD = relative percent difference

C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions

C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the value of C is less than four times the value of s, apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s, $\%R$ is not calculated. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Sample QC

Internal Standard Response – Monitor the signal intensity for the internal standard masses throughout the analytical run. This information is useful in detecting instrument drift, sensitivity shift; dissolved solids content, and inherent internal standard (i.e., a natural constituent in a sample). The absolute intensity of any one internal standard must not deviate more than 60 - 125% from its original intensity in the calibration blank. If deviations greater than these are observed, examine the internal standard intensities with the following actions:

- If the intensities of the internal standards for the ICV, CCV, or CB are out-of-control, recalibrate and re-analyze the analytes affected by the out-of-control internal standards in the affected samples.

- If the intensities of the internal standards for the ICV, CCV, and CB are within control limits but sample internal standards are out-of-control, rerun the sample or rerun at an appropriate dilution for the analytes affected by the out-of-control internal standard.

- Report results from the original, undiluted, or least diluted sample where the internal standards are within the acceptance limits.

9.5 Method Performance

The following table summarizes method performance by matrix for the period October 2010 to December 2011.

Method Performance

Analyte	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Aluminum (Al)	LCS	21	104	91.6 - 116
Antimony (Sb)	LCS	36	102	98.2 - 106
Arsenic (As)	LCS	27	95	87 - 103
Barium (Ba)	LCS	24	102	94.3 - 109
Beryllium (Be)	LCS	19	98.9	85.5 - 112
Cadmium (Cd)	LCS	35	101	96.9 - 105
Chromium (Cr)	LCS	31	100	94.7 - 106
Cobalt (Co)	LCS	21	102	95.8 - 109
Copper (Cu)	LCS	35	103	96.2 - 109
Lead (Pb)	LCS	34	103	97.5 - 109

Analyte	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Manganese (Mn)	LCS	31	101	93.6 - 109
Molybdenum (Mo)	LCS	31	102	97.9 - 107
Nickel (Ni)	LCS	30	101	97 - 105
Selenium (Se)	LCS	37	101	94.7 - 107
Silver (Ag)	LCS	37	101	92.9 - 110
Thallium (Tl)	LCS	35	101	97.3 - 105
Thorium (Th)	LCS			
Uranium (U)	LCS	4	102	98.1 - 106
Vanadium (V)	LCS	24	99.7	93.4 - 106
Zinc (Zn)	LCS	36	102	95.2 - 109

The primary sources of analytical error are:

- Analytical balance
- Instrument calibration
- Pipette calibration
- Vial contamination

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used in this SOP in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the sequence log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides decision tree for reporting metals. Appendix H provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Laboratory QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Laboratory QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix I.

11 REFERENCES

USEPA Region 9 Laboratory. *Business Plan.*

USEPA Region 9 Laboratory. *Chemical Hygiene Plan.*

USEPA Region 9 Laboratory. *Environmental Management System.*

USEPA Region 9 Laboratory SOP 110, *Sample Receiving and Login.*

USEPA Region 9 Laboratory SOP 125, *Sample Disposal.*

USEPA Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures.*

USEPA Region 9 Laboratory SOP 403, *Aqueous Sample Preparation for ICP-AES and ICP-MS.*

USEPA Region 9 Laboratory SOP 420, *Microwave Digestion of Solid Samples.*

USEPA Region 9 Laboratory SOP 462, *Analysis of Total Suspended Solids By EPA Method 160.2.*

USEPA Region 9 Laboratory SOP 706, *Laboratory Waste Management Procedure.*

USEPA Region 9 Laboratory SOP 820, *Laboratory Discrepancy and Corrective Action Procedures.*

USEPA Region 9 Laboratory SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level.*

USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

USEPA Region 9 Laboratory SOP 880, *Demonstration of Capability.*

Perkin Elmer, *ELAN 6100 DRC Software Kit and Elan 6100 DRC Hardware Guide.*

U.S. Environmental Protection Agency Method 200.8, *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC Version, May 1994.*

U.S. Environmental Protection Agency SW846 Method 6020, *Inductively Coupled Plasma-Mass Spectrometry, Revision 1, January 1998.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP does not include mercury as an analyte. Mercury is listed as an analyte in the reference method.

2. The MS/MSD and LCS are spiked at 40 µg/L for selenium; the referenced method specifies 200 to 500 µg/L.

3. This SOP specifies analysis of a MSD for precision; the reference method specifies analysis of a laboratory duplicate.

4. A linear dynamic range (LDR) standard is specified in the reference method but not specified in this SOP. The EPA Region 9 Laboratory requires any sample with a concentration above the highest calibration standard be diluted and reanalyzed.

5. This SOP includes gallium for internal standard based on the manufacture's recommendation. Gallium is not listed as an internal standard in the reference method.

6. This SOP specifies that the MB acceptance criterion is less than one-half the QL. The reference method specifies no greater than 2.2 times MDL.

7. The antimony, indium, and molybdenum elemental equations used for calculations are taken from the instrument software and differ slightly from those specified in the reference method.

8. The SOP specifies that arsenic results be reported from arsenic oxide (AsO mass 91) using the Dynamic Reaction Cell (DRC) mode and not arsenic at mass 75 as the reference method specifies.

9. The SOP specifies that thallium results be reported from thallium 203 and not thallium 205 as the reference specifies.

10. The SOP specifies that cadmium results be reported from cadmium 114 and not cadmium 111.

11. This SOP extends the scope of analysis to include fish tissue.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analyte list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	QL, Routine Analysis, Water, µg/L	QL, Low-Level Analysis, Water, µg/L
Aluminum (Al)	7429-90-5	20	10
Antimony (Sb)	7440-36-0	0.5	0.25
Arsenic (As)	7440-38-2	0.5	0.25
Barium (Ba)	7440-39-3	1	0.5
Beryllium (Be)	7440-41-7	0.5	0.25
Cadmium (Cd111)*	7440-43-9	0.4	0.2
Cadmium (Cd114)	7440-43-9	0.4	0.2
Chromium (Cr)	7440-47-3	1	0.5
Cobalt (Co)	7440-48-4	0.25	0.125
Copper (Cu)	7440-50-8	2	1
Lead (Pb)	7439-92-1	1	0.5
Manganese (Mn)	7439-96-5	2	1
Molybdenum (Mo)	7439-98-7	0.5	0.25
Nickel (Ni)	7440-02-0	1	0.5
Selenium (Se78)**	7782-49-2	2	1
Selenium (Se82)	7782-49-2	1	0.5
Silver (Ag)	7440-22-4	0.25	0.125
Thallium (Tl)	7440-28-0	1	0.5
Thorium (Th)	7440-29-1	1	0.5
Uranium (U)	7440-61-1	0.25	0.125
Vanadium (V)	7440-62-2	4	2
Zinc (Zn)	7440-66-6	5	2.5

*Cd at mass 111 is only reported when interference or poor performance is detected in concentration that interferes with Cd at mass 114.

**Se at mass 78 is only reported when bromine is detected in concentration that interferes with Se at mass 82.

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The following table provides the target analyte list for Fish Tissue with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	QL, Fish Tissue, mg/Kg
Aluminum (Al)	7429-90-5	8
Arsenic (As)	7440-38-2	0.2
Cadmium (Cd)	7440-43-9	0.2
Chromium (Cr)	7440-47-3	0.5
Copper (Cu)	7440-50-8	0.5
Lead (Pb)	7439-92-1	0.2
Nickel (Ni)	7440-02-0	0.4
Selenium(Se)	7782-49-2	0.4
Zinc (Zn)	7440-66-6	5

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
Correlation Coefficient	Each ICAL	≥ 0.995
ICV	After ICAL	90 - 110%
CCV	Every 10 Samples	90 - 110%
CB	After each ICV/CCV	<½ QL
SCV	After ICAL	90 - 110%
QLS	After ICAL & after every 40 analytical samples	60 - 140%
MB	Each Batch	<½ QL
LCS	Each Batch	85 - 115%
MS/MSD, Accuracy	Every 10 samples	70 - 130%
MS/MSD, Precision	Every 10 samples	≤20 RPD
Internal Standard	Every analysis	60 - 125% of initial CB

Instrument Sensitivity and Stability Check:

- For daily performance check, the RSD for each element must be <5%.
- Sensitivity should be, at a minimum, Mg - 6,000 CPS, In – 30,000 CPS, and U – 20,000 CPS.
- Oxide (Ce) and ++ (Ba) levels, approximately 3% or lower are preferred.

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APPENDIX D.
INTERNAL STANDARD TABLES, ELEMENT ISOTOPE, & EQUATION

Table 1. Internal Standards and Limitations of Use

Internal Standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Gallium	71	c

NOTES:
Internal standards recommended for use with this method are shown in underlined text.
Internal standards typically used by the Region 9 Laboratory are shown in **bold** text.

a May be present in environmental samples.
b In some instruments, Yttrium may form measurable amounts of YO^{+} (105 amu) and YOH^{+} (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.
c Gallium is recommended by the manufacturer of the Elan DRC instrument being used at the EPA Region 9 Laboratory.

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Table 2. Element Equations for Data Calculations - Standard Mode

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{123}C) - (0.127189)(^{125}C)$	1
As	$1.000(^{75}C) - (3.127)[(^{77}C) - (0.815)(^{82}C)]$	2
Ba	$1.000(^{137}C)$	
Be	$1.000(^{9}C)$	
Cd111	$1.000(^{111}C) - (1.073)[(^{108}C) - (0.712)(^{106}C)]$	3
Cd114	$1.000(^{114}C) - 0.026826(^{118}C)$	4
Cr	$1.000(^{52}C)$	5
Co	$1.000(^{59}C)$	
Cu63	$1.000(^{63}C)$	
Cu65	$1.000(^{65}C)$	6
Pb	$1.000(^{206}C) + 1.000(^{207}C) + 1.000(^{208}C)$	7
Mn	$1.000(^{55}C)$	
Mo	$1.000(^{98}C) - 0.11058(^{101}C)$	8
Ni60	$1.000(^{60}C)$	
Ni62	$1.000(^{62}C)$	9
Se78	$1.000(^{78}C) - 0.1869(^{76}C)$	10
Se82	$1.000(^{82}C)$	11
Ag	$1.000(^{107}C)$	
Tl	$1.000(^{203}C)$	
Th	$1.000(^{232}C)$	
U	$1.000(^{238}C)$	
V	$1.000(^{51}C) - (3.127)[(^{53}C) - (0.113)(^{52}C)]$	12
Zn	$1.000(^{66}C)$	
Ga	$1.000(^{71}C)$	
Ho	$1.000(^{165}C)$	
In	$1.000(^{115}C) - 0.014032(^{118}C)$	13
Li^{6}	$1.000(^{6}C)$	

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Element	Elemental Equation	Note
Rh	$1.000(^{103}C)$	
Sc	$1.000(^{45}C)$	
Tb	$1.000(^{159}C)$	
Y	$1.000(^{89}C)$	

NOTES:

C Calibration blank subtracted counts at specified mass.

1 Isobaric correction for Te

2 Isobaric correction for ArCl, Se

3 Correction for MoO. Isobaric mass 106 must be from Cd only, not ZrO. An additional isobaric elemental correction should be made if palladium is present.

4 Isobaric correction for Sn. Used as primary mass for reporting.

5 The background for ClOH will normally be small and can be estimated from the reagent blank.

6 Used as alternate mass when ArNa interference apparent at Cu63.

7 Allowance for isobaric variability of lead isotopes

8 Isobaric elemental correction for Ru

9 Used as alternate mass when CaO and CaOH interferences at Ni60.

10 Used as alternate mass when HBr interference apparent at Se82, Isobaric correction for Ar2 dimer.

11 Some Ar supplies contain Kr as an impurity. Se is corrected for ^{82}Kr by background subtraction.

12 Correction for chloride interference with adjustment for ^{53}Cr. ClO 51/53 ratio may be determined from the reagent blank. Isobaric mass 52 must be from Cr only, not ArC^{+}.

13 Isobaric correction for Sn

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Table 3. Analytical Isotope and Additional Masses that are monitored

Element of Interest	Isotope
Aluminum	27
Antimony	121, 123
Arsenic	75
Barium	135, 137
Beryllium	9
Cadmium	106, 108, 111, 114
Chromium	52, 53
Cobalt	59
Copper	63, 65
Lead	206, 207, 208
Manganese	55
Molybdenum	95, 97, 98
Nickel	60, 62
Selenium	76, 77, 78, 82
Silver	107, 109
Thallium	203, 205
Thorium	232
Uranium	238
Vanadium	51
Zinc	66, 67, 68
Bromine	79, 81
Krypton	83
Palladium	105
Ruthenium	101
Tellurium	125
Tin	118

NOTE: Isotopes used for analytical determination are underlined.

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Table 4. Analytical Isotopes For DRC Analysis

Element of Interest	Isotope
Arsenic as Arsenic Oxide	91
Chromium	52

NOTE: Isotopes used for analytical determination are underlined.

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Table 5. Internal Standard Groups - Standard Mode

Element	Internal Standard Group	Internal Standard
Be	1	Sc
Al	1	
V	1	
Cr	1	
Mn	1	
Co	1	
Ni	1	
Cu	1	
Zn	2	Y
As	2	
Se	2	
Mo	3	In
Ag	3	
Cd	3	
Sb	3	
Ba	4	Tb
Tl	4	
Pb	4	
U	4	
Th	4	

Table 6. Internal Standards - DRC Mode

Element	Internal Standard Group	Internal Standard
Cr	5	Ga
As as AsO	5	Rh

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APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

Nebulizer Gas Flow:	0.85 - 1.05 mL/min (~0.90 typical)
Auxiliary Gas Flow:	1.20 mL/min
Plasma gas Flow:	12.0 mL/min
ICP RF Power:	1,100 - 1,500 watts (1,350 typical)
Pulse Stage Voltage:	700 - 2,500 (increases with age of detector to meet sensitivity parameters)
Analog Stage Voltage:	1,300 - 2,500 (increases with age of detector to meet sensitivity parameters)
Argon Line Pressure:	51 psi ± 1

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the Elan ICP-MS

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	As needed	Fill with 2% $HN0_3$.
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
Cones	Daily Weekly	Inspect for sample residues. Wipe clean or replace with clean cone as needed. Remove and inspect condition of cones. Replace if needed.
Torch Tip	Daily	Check for sample residues. Replace with clean glassware if needed.
Argon Dewar	Daily	Check for sufficient amount and pressure. Order as needed.
Autodiluter	Daily	Rinse thoroughly with reagent water after each use.
Auto-sampler and Peristaltic Pump	Weekly	Wipe spills or residues.
Nebulizer Spray	Weekly	Check, unclog or replace if needed.
Glassware	Weekly	Inspect and clean if needed.
Glassware & Cone alignment	Weekly	Perform X-Y alignment, if needed.
Air filters	Monthly	Clean or replace as needed.
Chiller Coolant	Monthly	Check level and top off as needed.
Vacuum Oil	Monthly	Check level and color, replace with fresh one if needed.

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APPENDIX G.
DECISION TREE FOR REPORTING METALS

Aluminum (Al)	x		xxx
Antimony (Sb)	x		
Arsenic (As)	x		
Barium (Ba)	x		xxx
Beryllium (Be)	x		xxx
Boron (B)		xx	
Cadmium (Cd)	x		
Calcium (Ca)		xx	
Chromium (Cr)	x		
Cobalt (Co)	x		xxx
Copper (Cu)	x		xxx
Iron (Fe)		xx	
Lead (Pb)	x		
Magnesium (Mg)		xx	
Manganese (Mn)	x		xxx
Molybdenum (Mo)	x		
Nickel (Ni)	x		xxx
Potassium (K)		xx	
Selenium (Se)	x		
Silica (SiO_2)		xx	
Silver (Ag)	x		
Sodium (Na)		xx	
Strontium (Sr)		xx	
Thallium (Tl)	x		
Thorium (Th)	x		
Tin (Sn)		xx	
Titanium (Ti)		xx	
Uranium (U)	x		
Vanadium (V)		xx	
Zinc (Zn)	x		xxx

Where:

x = reported by ICP-MS
xx = reported by ICP-AES
xxx = If all 200.7 QC passes and the concentration is above the 200.7 QL, an element may be reported from the 200.7 analysis.

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APPENDIX H.
TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms
- EPA Review Form
- ESAT technical review guide
- Discrepancy Reports (if applicable)
- Work Order Memo (if applicable)
- Daily folder review forms or checklists
- Analysis matrix listing all analytical runs (for organics only)

Tracking Forms
- Work Order(s)
- COC(s)

Sample Preparation (for projects that require extraction or digestion)
- Bench Sheets (and copies of notebooks, where used)
- Sample cleanup data and records (e.g. GPC logs)
- Sample homogenization records (for solid/waste/tissue samples)
- Moisture data (when applicable)

[Analysis Method] Data (For each method where multiple methods in package)
- Bench sheet(s) where not used in Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, when only one analysis is reported, separate calibration and sample data as:
- Initial Calibration Data (sorted by instrument and then by date)
- Sample Data (sorted by instrument and then by date)

Miscellaneous Data
- Other data as applicable (e.g. conductivity for perchlorate)
- Canister certifications (for volatiles in air analysis)

Standard Records
- Standards records from LIMS (and certificates of analysis, if required)

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APPENDIX I.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 507
Revision: 7, Effective: 02/01/12

DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-MS

Revision	Effective Date	Description
7	02/01/12	1. Updated format to current EPA Region 9 Laboratory requirements. 2. Updated procedure to follow current internal COC practices. 3. Removed reference to instrument runlog. 4. Lowered reporting limits for some analytes and updated corresponding QLS concentrations. 5. Internal standard for Be changed from Li^6 to Sc. 6. Added fish tissue analysis. 7. Change cadmium primary reporting mass from 111 to 114 8. Minor edits throughout.

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USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 530
ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

Revision 9
Effective Date: June 14, 2013

Reviewed by: _____ 5/30/13
Richard Bauer — Date
Chemistry Team Leader/Technical Director

Reviewed by: _____ 5-31-13
Lucrina Jones, Laboratory QA Officer — Date

Approved by: _____ 6/5/13
Brenda Bettencourt, Laboratory Director — Date

Periodic Review:

Signature	Title	Date
_____	ESAT QA Officer	4/28/15

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-06-041). ESAT Document Control Number: 01305020-15971

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1 SCOPE AND APPLICABILITY

This method is applicable for drinking, ground, surface, and saline water, domestic and industrial wastes, and solids leached with reagent water. This method applies to the determination of the inorganic anions fluoride, chloride, nitrite, bromide, nitrate, orthophosphate, and sulfate by ion chromatography for use in the USEPA Region 9 Laboratory, Richmond, California. This SOP is based on EPA Method 300.0, *Determination of Inorganic Anions by Ion Chromatography*, Revision 2.1, August 1993. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) for this analysis are listed in Appendix B.

2 METHOD SUMMARY

A small volume of sample is injected onto a series of ion-exchange columns. The anions of interest separate on the basis of their relative affinities to a low capacity, strongly basic anion exchanger. The separated anions are directed into a strongly acidic cation suppressor exchanger where they are converted to their highly conductive acid forms. The carbonate and bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are detected by electrical conductivity and are qualitatively determined on the basis of retention time as compared to the standards. Quantitation is based on peak areas. A quadratic calibration is used to determine concentrations in environmental samples for fluoride, nitrite, bromide, nitrate, chloride, orthophosphate, and sulfate.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

There are no analysis-specific definitions in this SOP.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample

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handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses, and gloves must always be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager (LaSHEM) to determine if additional treatment is required.

4.2 Equipment and Instrument Hazards

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact

of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Anions analysis waste (aqueous carbonate, bicarbonate solution)	Hazardous Waste	Not applicable

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned plastic or glass bottles. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 100 mL sample volume of water or 20 g of solid sample should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Anions samples may initially be received in either Room 207 or Room 503. Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Sample Storage

Samples should be received and stored at > 0 °C to ≤ 6 °C. If not already noted in the LIMS login record, record any discrepancies in the LIMS memo field.

Retain samples for 60 days after the final analytical report is sent to the data user.

5.4 Holding Time

The maximum sample holding time for nitrite-N, nitrate-N, and *ortho*-phosphate-P is 48 hours from the time of sample collection. For fluoride, chloride, bromide, and sulfate, the holding time is 28 days from the date of sample collection.

6 INTERFERENCES

1. Interferences can be caused by substances with retention times that are similar to an overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification with concentrated eluent can be used to solve most interference problems associated with retention times. See Section 8.3.4.4 for procedures employed to prevent reporting false negative results for nitrite in the presence of chloride.

2. The water dip or negative peak elutes near and can interfere with the fluoride peak. This effect does not typically occur under conditions described in this SOP. When other measures fail, this interference can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100x) to 100 mL of each standard and sample. See Section 8.3.3 for measures to address interference from the water dip.

3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4. Samples and reagents that contain particulates require filtration to prevent damage to instrument columns and flow systems.

5. Large concentration of acetate anion, which elutes early during the chromatographic run, affects retention times of target analytes. This method is therefore not recommended for acetic acid leachates.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Ion Chromatograph - The Dionex Ion Chromatograph System including Advance Chromatography Module, Pump, Conductivity Cell Detector, Dionex Advance Computer Interface, Dionex AS40 Autosampler, and Dionex PeakNet 6/Chromeleon 6 Data System or equivalent that meets the requirements of the method.
- Anion Guard Column, AG14-4mm from Dionex or equivalent
- Anion Separator Column, AS14-4mm from Dionex or equivalent
- Anion Self-Regenerating Suppressor ASRS, Ultra 4mm from Dionex or equivalent
- Analytical Balance - capable of weighing accurately to ± 0.001 g
- ASTM Class 1 weights
- Desiccator
- Drying oven, capable of being controlled at 105 ± 5°C
- Stirrer Plate and Stirring Bars

7.2 Reagents

Reagents may contain impurities that affect analytical data. Only materials that conform to the American Chemical Society (ACS) reagent grade specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Record all chemical and reagent preparations in the LIMS database. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

- Reagent water - As defined in USEPA Region 9 Laboratory SOP 825, *Deionized Water*.
- Degassed reagent water - Reagent water that has been purged with helium or nitrogen for at least 2 minutes.

- Blank solid matrix - Acid washed sand
- Sodium bicarbonate ($NaHCO_3$), ACS reagent grade
- Sodium carbonate (Na_2CO_3), ACS reagent grade
- Sodium bromide (NaBr), ACS reagent grade
- Sodium chloride (NaCl), ACS reagent grade
- Sodium fluoride (NaF), ACS reagent grade
- Sodium nitrate ($NaNO_3$), ACS reagent grade
- Sodium nitrite ($NaNO_2$), ACS reagent grade
- Potassium phosphate (KH_2PO_4), ACS reagent grade
- Potassium sulfate (K_2SO_4), ACS reagent grade
- Helium, ultra high purity grade (UHP)
- Nitrogen

7.2.1 Eluent Stock Solutions

- 0.5 M Sodium Carbonate

  Prepare by dissolving 26.49 g of sodium carbonate in 400 mL of reagent water and diluting to final volume of 500 mL, or equivalent purchased commercially (e.g.; Dionex).

- 0.5 M Sodium Bicarbonate

  Prepare by dissolving 8.40 g of sodium bicarbonate in 100 mL of reagent water and diluting to final volume of 200 mL, or equivalent purchased commercially (e.g.; Dionex).

7.2.2 Eluent Working Solution, 8 mM Na_2CO_3 / 1 mM $NaHCO_3$

Prepare working eluent solution by pipetting 32 mL of 0.5 M Na_2CO_3 and 4 mL of 0.5 M $NaHCO_3$ into a 2-L volumetric flask and diluting to volume with degassed reagent water.

7.3 Standards

Record all standard and standard preparations in the LIMS database.

7.3.1 Stock Standards

Stock standard solutions may be purchased as certified solutions (ex.: 1,000 mg/L from Inorganic Ventures) or prepared from ACS reagent grade materials (dried at 105 °C for 30 minutes) and are stable for at least a year when stored at 4 °C. The stock standards are also used to make calibration and quality control standards as needed.

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- 1,000 mg/L Fluoride standard is prepared by dissolving 1.105 g NaF in reagent water to a final volume of 500 mL.

- 1,000 mg/L Chloride standard is prepared by dissolving 0.824 g of NaCl in reagent water to a final volume of 500 mL.

- 1,000 mg/L Nitrite-N standard is prepared by dissolving 2.463 g $NaNO_2$ in reagent water to a final volume of 500 mL.

- 1,000 mg/L Bromide standard is prepared by dissolving 0.644 g NaBr in reagent water to a final volume of 500 mL.

- 1,000 mg/L Nitrate-N standard is prepared by dissolving 3.034 g $NaNO_3$ in reagent water to a final volume of 500 mL.

- 1,000 mg/L Orthophosphate-P standard is prepared by dissolving 2.197 g of KH_2PO_4, in reagent water to a final volume of 500 mL.

- 1,000 mg/L Sulfate standard is prepared by dissolving 0.9070 g of K_2SO_4 in reagent water to a final volume of 500 mL.

7.3.2 Working Standards

Intermediate standards may be prepared and used to make calibration and quality control standards as needed.

- 100 mg/L Fluoride and Bromide

  Prepare by adding 50 mL each of the 1,000 mg/L F and Br into a 500-mL volumetric flask and diluting to volume with reagent water.

- 100 mg/L Nitrite-N and Nitrate-N

  Prepare by adding 50 mL each of the 1,000 mg/L NO_2-N and NO_3-N into a 500-mL volumetric flask and diluting to volume with reagent water.

- 250 mg/L Chloride, Orthophosphate-P, and Sulfate

  Prepare by adding 50 mL each of the 1,000 mg/L Cl, O-PO_4-P, and SO_4 into a 200-mL volumetric flask and diluting to volume with reagent water.

7.3.3 Calibration Standard 6 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

Analyte	*Final Concentration, mg/L*	*Volume of Working Standard*	*Final Volume, mL*
Fluoride	10	5 mL of 100 mg/L F and Br	50
Bromide	10		
Nitrite-N	25	12.5 mL of 100 mg/L NO_2-N and NO_3-N	
Nitrate-N	25		
Chloride	50	10 mL of 250 mg/L Cl, O-PO_4-P, and SO_4	
o-Phosphate-P	50		
Sulfate	50		

7.3.4 Calibration Standard 5 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

Analyte	*Final Concentration, mg/L*	*Volume of Working Standard*	*Final Volume, mL*
Fluoride	2.0	1 mL of 100 mg/L F and Br	50
Bromide	2.0		
Nitrite-N	10	5 mL of 100 mg/L NO_2-N and NO_3-N	
Nitrate-N	10		
Chloride	25	5 mL of 250 mg/L Cl, O-PO_4-P, and SO_4	
o-Phosphate-P	25		
Sulfate	25		

7.3.5 Calibration Standard 4 / CCV / LCS - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

Analyte	*Final Concentration, mg/L*	*Volume of Working Standard*	*Final Volume, mL*
Fluoride	1.0	1 mL of 100 mg/L F and Br	100
Bromide	1.0	, ,	
Nitrite-N	5.0	5 mL of 100 mg/L NO_2-N and NO_3-N	
Nitrate-N	5.0		
Chloride	10	4 mL of 250 mg/L Cl,	

		O-PO_4-P, and SO_4
o-Phosphate-P	10	
Sulfate	10	

7.3.6 Calibration Standard 3 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

Analyte	*Final Concentration, mg/L*	*Volume of Working Standard*	*Final Volume, mL*
Fluoride	0.5	0.25 mL of 100 mg/L F and Br	50
Bromide	0.5		
Nitrite-N	1.0	0.5 mL of 100 mg/L NO_2-N and NO_3-N	
Nitrate-N	1.0		
Chloride	5.0	1 mL of 250 mg/L Cl, O-PO_4-P, and SO_4	
o-Phosphate-P	5.0		
Sulfate	5.0		

7.3.7 Calibration Standard 2 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

Analyte	*Final Concentration, mg/L*	*Volume of Working Standard*	*Final Volume, mL*
Fluoride	0.25	0.125 mL of 100 mg/L F and Br	50
Bromide	0.25		
Nitrite-N	0.5	0.25 mL of 100 mg/L NO_2-N and NO_3-N	
Nitrate-N	0.5		
Chloride	1.0	0.2 mL of 250 mg/L Cl, O-PO_4-P, and SO_4	
o-Phosphate-P	1.0		
Sulfate	1.0		

7.3.8 Calibration Standard 1 - Dilute working standards (Section 7.3.2) or working standard to volume with reagent water as shown in the following table. Prepare daily.

Analyte	*Final Concentration, mg/L*	*Volume of Working Standard*	*Final Volume, mL*
Fluoride	0.1	0.05 mL of 100 mg/L F and Br	50

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Bromide	0.1	
Nitrite-N	0.1	0.05 mL of 100 mg/L NO_2-N and NO_3-N
Nitrate-N	0.1	
Chloride	0.5	0.1 mL of 250 mg/L Cl, O-PO_4-P, and SO_4
o-Phosphate-P	0.5	
Sulfate	0.5	

7.3.9 QLS

Pipet 0.05 mL of the 100 mg/L F, Br, NO_2-N, and NO_3-N working standard, 0.05 mL of the 1,000 mg/L chloride and orthophosphate-P stock standard, and 0.025 mL of 1,000 mg/L sulfate stock standard into a 50-mL volumetric flask and dilute to volume with reagent water. Prepare daily. QLS concentrations are shown in the following table:

Analyte	*Concentration, mg/L*
Fluoride	0.10
Chloride	1.0
Nitrite-N	0.10
Bromide	0.10
Nitrate-N	0.10
o-phosphate-P	1.0
Sulfate	0.50

7.3.10 SCV

Prepare or obtain an SCV from a source external to the laboratory and different from the source of the calibration standards. A Multi-Anion solution from Alltech is available in the concentrations shown in the following table. Dilute by a factor of four prior to analysis to get all analytes within calibration range.

Analyte	*Concentration, mg/L*
Sulfate	30
Bromide	20
Chloride	20
Fluoride	10
o-Phosphate-P	10
Nitrite-N	6.0
Nitrate-N	4.5

7.4 Supplies

- Clean sand (used as a blank for solid matrix)
- 100-mL beakers or Erlenmeyer flasks
- Disposable beaker cups
- Disposable syringe filters, 0.20-micron and 0.45-micron
- Disposable syringes with Luer-lock fittings
- Plastic or Teflon spray bottle
- Polyvials, 5 mL capacity with filter caps (Dionex P/N 38141)
- Volumetric Class A Flasks - 2000 mL, 500 mL, 100 mL, 50mL, 25ml, and 10mL
- Volumetric Class A Pipettes - 10 mL, 5 mL, and 4 mL

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the ion chromatograph following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point. Appendix E provides instrumental startup information.

Ensure that all appropriate waste containers are properly connected and labeled. Ensure that waste containers will not overflow.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration using a minimum of six calibration standards to establish a quadratic curve. Analyze calibration standards as described in Section 8.3.3. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze a calibration blank immediately after the initial calibration. If the value of the CB is less than one-half the QL, the calibration is acceptable. If the value of the blank result equals or exceeds one-half the QL, the cause of the high CB result must be determined, the problem corrected, and the instrument re-calibrated.

Analyze an SCV standard to confirm the initial calibration. Meet QC criteria and take corrective action as needed as described in Section 9.2.1 and Appendix C.

NOTE: Update retention time windows in the instrument software after each initial calibration. Five percent of Standard 4 retention times should generally

be used to define calibration retention time windows. Print a record of the retention time windows and retain for inclusion in the data package.

8.2.2 Continuing Calibration Verification

At the beginning of each analytical sequence, verify calibration with a CCV standard. Prepare the CCV as described in Section 7.3.4 and analyze according to Section 8.3. Follow requirements and take corrective action as described in Section 9.2.2.

NOTE: After the first CCV analysis, update retention times in the instrument software to correspond to the first CCV and adjust retention time window to 5% of the retention times.

8.3 Analysis

8.3.1 Water Sample Preparation

1. Prepare MS and MSD samples by fortifying the source sample with primary stock or working standards. The MS/MSD spike levels in the following table are recommended for most projects:

Parameter	*Recommended MS/MSD Spiking Levels, mg/L*
Fluoride	1
Chloride	10
Nitrite-N	5
Bromide	1
Nitrate-N	5
o-Phosphate-P	10
Sulfate	10

2. Filter samples that are turbid or contain particulates to prevent damage to instrument columns and flow systems. Filter samples following this procedure:

   Transfer an aliquot of a well-mixed unfiltered sample into a disposable beaker cup. Draw approximately 5 mL of the sample into a disposable syringe. Attach a 0.45-micron disposable syringe filter to the syringe. Apply pressure to the plunger and filter the sample through the syringe filter and into a 5-mL vial. Repeat the procedure until the 5-mL vial is filled close to the 5-mL mark. Discard the remaining sample from the beaker cup into the liquid waste container and the syringe assembly into a solid waste container.

If sample is still turbid or colored, filter the sample again following the procedure above using the 0.20-micron disposable syringe filter.

NOTE: A separate MB must be filtered if any sample in the batch is filtered. Use corresponding filter that was used for the sample. Record any sample filtrations in the comments section of the LIMS benchsheet.

3. Fill 5-mL polyvials with each well-mixed sample. Attach a filter cap to each vial and push down the filter cap with the supplied tool until it is flush with the top of the vial. Label the contents of the vial.

8.3.2 Solid Sample Preparation

1. For homogenization of solid samples, follow SOP 150, *Soil and Sediment Homogenization.*

2. Weigh out approximately 2.0 g of each solid sample. Sample weights may be adjusted to meet project requirements, if necessary. Add reagent water equal to ten times the weight of solid material taken as sample. (Example: To 2.2 g of solid sample, add 22 mL of reagent water).

3. Prepare MS, MSD, and LCS samples. For MS and MSD samples, fortify the source sample with primary stock or working standards. Prepare the LCS by fortifying a blank solid matrix with primary stock or working standards. The following table provides MS/MSD and LCS spike levels suitable for most projects:

Parameter	*Recommended MS/MSD & LCS Spiking Levels, mg/L*
Fluoride	1
Chloride	10
Nitrite-N	5
Bromide	1
Nitrate-N	5
o-Phosphate-P	10
Sulfate	10

4. Mix each sample with a shaker table or a magnetic stirrer for 10 to 15 minutes. Filter the resulting mixture with a 0.45-micron or 0.20-micron filter as described in Section 8.3.1.

5. Fill 5-mL polyvials with each well-mixed sample filtrate. Attach a filter cap to each vial and push down the filter cap with the supplied tool until it

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is flush with the top of the vial. Label the contents of the vial.

6. From a separate sample aliquot, determine moisture following SOP 460, *Percent Solids Determination*.

8.3.3 Analytical Sequence and Sample Analysis

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument software and the LIMS sequence.

Include all batch QC samples as described in Section 9.3.

1. Enter sample sequence in the instrument software. (Refer to Appendix E for details regarding entering the sequence). Load the samples to be analyzed in the autosampler according to their designated positions in the sequence file.

2. The following table shows an example of a typical sample sequence. If not calibrating the instrument, start with Seq. #9.

Seq.	*Description*	*Seq.*	*Description*	*Seq.*	*Description*
1	Cal Std 1	15	S1-MS **	29	S12
2	Cal Std 2	16	S1-MSD **	30	S13
3	Cal Std 3	17	S2	31	S14
4	Cal Std 4	18	S3	32	S15
5	Cal Std 5	19	S4	33	CCV
6	Cal Std 6	20	S5	34	CB
7	CB	21	CCV	35	S16
8	SCV	22	CB	36	S17
9	CCV/LCS	23	S6	37	S18
10	CB/MB	24	S7	38	S19
11	QLS *	25	S8	39	S20
12	MB (for filtered or solid samples)	26	S9	40	CCV
13	LCS (for solid samples)	27	S10	41	CB
14	S1	28	S11	42	

* A QLS must be analyzed daily at the beginning of the analytical run and every subsequent 40 analytical samples.
** Alternatively, analyze MD as specified in Section 9.3.4.

3. If any water sample is filtered, analyze a separate filtered MB. If no sample is filtered, the CB serves as the MB.

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4. Start the autosampler (Dionex AS40) by pressing the 'Hold/Run' button until the light on the side of the word 'Run' is lighted. Initiate the analysis by clicking on the 'Start' button in the Batch list section of the software. The analysis will stop automatically by inserting a 'Sample' positioned at the end of the sequence file and changing the Program name (Anions Program) under the 'Program' column to 'StopMethod', and re-saving the edited sequence file.

5. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

6. If the water dip interferes with the fluoride peak, try the following:

   - Optimize instrument condition to maximize fluoride peak resolution.
   - If using an old column, clean or replace the analytical column.
   - If the first two steps fail, add the equivalent of 1 mL of concentrated eluent (100x) to 100 mL of each standard and sample.

8.3.4 Analyte Identification and Quantitation

8.3.4.1 Peak Identification

Review all chromatograms to ensure that the correct peaks are integrated. The instrument is typically set to identify peaks as target analytes if the retention times are within ± 5% of retention times from the first CCV.

8.3.4.2 For water samples, report results in mg/L using the following equation:

$$C = M \, x \, D$$

Where
C = final reported concentration, in mg/L
M = measured concentration reported by software, in mg/L
D = sample analysis dilution factor, to account for any dilution

8.3.4.3 For solid samples, report results in mg/kg using the following equation:

$$C = M \times \frac{Vf}{Vi} \times D \times 100 / S$$

Where

C = final reported concentration, in mg/kg
M = measured concentration reported by software, in mg/L
V_f = final volume of sample solution after sample preparation, in liters
V_i = initial weight of sample used in sample preparation, in kilograms
D = sample analysis dilution factor, to account for any dilution
S = percent of solids in the sample used

8.3.4.4 Nitrite results in the presence of chloride

Quantitation of nitrite may be affected by the chloride concentration. Therefore, apply the following rules:

- For undiluted samples where nitrite is not detected, report nitrite as follows:

  1. If chloride concentration ≤50 mg/L, report nitrite QL = 0.1 mg/L.
  2. If chloride concentration >50 mg/L, dilute and reanalyze sample. In this case, the nitrite QL is 0.1 mg/L multiplied by the dilution factor used for chloride analysis.

- For undiluted samples where nitrite is present, nitrite must be reported regardless if chloride is detected. Report nitrite as follows:

  1. If nitrite is present from 0.05 mg/L to 0.09 mg/L, report result as estimated (J).
  2. If nitrite is present from 0.1 mg/L to 0.25 mg/L and chloride is ≤100 mg/L, report nitrite result without qualification. If chloride is >100 mg/L and <400 mg/L, the nitrite result is estimated with low bias (L) due to interference from chloride.
  3. If nitrite is present at >0.25 mg/L to ≤0.5 mg/L and chloride is ≤200 mg/L, report nitrite without qualification. If chloride is >200 mg/L to ≤400 mg/L, the nitrite result estimated with low bias (L) due to interference from chloride.
  4. If nitrite is present at >0.5 mg/L, report without qualification.

8.3.4.5 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be

stamped, initialed and dated by the analyst, and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.5 Data and QC Review

- Review results of instrument QC (CCV, CB, QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

- Review results of batch QC (MB, LCS, MS/MSD/MD). See Section 9.3 for corrective action requirements and Appendix C for QC limits.

8.3.6 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS. The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

8.4 Maintenance

Column maintenance prolongs column life and reduces retention time shifts. Shorter retention time and smaller peaks are indications that a column is degrading and maintenance is necessary. Refer to manufacturer's requirements for column maintenance.

Monitor retention time shift. Retention time drift, as indicated by the first CCV, of >5% is an indication that instrument maintenance may need to be performed.

Routine instrument maintenance is summarized in Appendix F.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

The following sections describe quality control measures, criteria, frequency, and corrective action. Appendix C summarizes QC measures and criteria.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in USEPA Region 9 Laboratory SOP 880, *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 Initial Calibration

An initial calibration is performed by analysis of a minimum of six standards. Calibration for all analytes is calculated using a quadratic fit. The coefficient of determination for the initial calibration must be ≥ 0.995 for the calibration to be valid. The calibration is verified by analyzing a SCV standard. Refer to Appendix C for acceptance criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If the calibration does not meet coefficient of determination and SCV criteria, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

9.2.2 Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze a CCV standard. The CCV is analyzed prior to analyzing each analytical batch, at a frequency of one per 10 analytical samples, and at the end of the analytical run.

The recovery of analytes in the CCV is calculated as follows:

$$\%R = \frac{M}{T} \times 100$$

Where

$\%R$ = percent recovery of the standard
M = measured concentration of analyte, mg/L

T = true concentration of the analyte in the CCV, mg/L

If the CCV recovery is not within QC criteria, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the poor recovery must be determined and the problem corrected. All samples not bracketed by acceptable CCV results must be reanalyzed.

NOTE: If it is suspected that the CCV was prepared incorrectly, it may be re-prepared and reanalyzed. If it passes, the analysis may continue.

9.2.3 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after everyCCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds ½ the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. All samples not bracketed by acceptable CB results must be reanalyzed.

NOTE: If it is suspected that there is contamination in the vial used for the CB, the blank may be re-poured and reanalyzed. If it passes, the analysis may continue.

9.2.4 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run (typically just after the CCV and CB) and every subsequent 40 analytical samples.

The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
%R = percent recovery of the standard
M = measured concentration of the analyte, mg/L
T = true concentration of the analyte in the QLS, mg/L

If the QLS recovery does not meet criteria in Appendix C, determine the cause, take corrective action, and reanalyze the QLS.

NOTE: Any samples analyzed in an autosampler sequence after a failing QLS must be reanalyzed after the system has been corrected and the standard meets acceptance criteria

9.3 Batch QC

9.3.1 Method Blank

Analyze one MB with each batch of 20 or fewer field samples of the same matrix. MB values ≥ ½ QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared and reanalyzed:

a) If the MB analyte value ≥ ½ QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and reanalyzed. If either the holding time is expired or no more sample volume is available, the associated sample results may be reported but will be qualified as estimated "J" and a note must be entered in the Work Order Memo field explaining the situation.

b) If the MB analyte value ≥ ½ QL and the sample result is non-detected or is greater than or equal to five times the MB analyte concentration, report sample results without qualification.

NOTE: The first CB analyzed meets the requirement of the MB if no sample preparation was performed. If sample preparation was performed (e.g. filtration), a filtered MB must be prepared and analyzed separately.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer field samples of the same matrix. NOTE: For analysis of water samples, the LCS is equivalent to a CCV. Analysis of a CCV serves as both a CCV and the batch LCS.

LCS recovery is calculated as:

$$\%R = \frac{C_m}{C_t} \times 100$$

Where
$\%R$ = percent recovery
C_m = measured analyte concentration in the LCS
C_t = true analyte concentration in the LCS

If the LCS recovery does not meet recovery criteria, reanalyze once to verify, if still does not meet criteria provided in Appendix C, determine the cause, take corrective action, and reanalyze all samples associated with the out-of-control LCS. If either the holding time is expired or no more sample volume is available, the associated sample results may be reported but will be qualified as estimated "J", in this case a note must be entered in the Work Order Memo field explaining the situation.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be analyzed for each 20 or fewer field samples of the same matrix in an SDG. If the analyte concentration of the MS/MSD source sample is more than four times the MS/MSD spike level, an MD sample is analyzed and reported instead of the MS/MSD samples.

Samples identified as field blanks cannot be used for MS and MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$ = percent recovery

C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions

C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions

s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where

RPD = relative percent difference

C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions

C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions

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If the value of C is less than four times the value of s, apply accuracy and precision criteria in Appendix C. If the MS/MSD does not meet the acceptance criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy or precision is likely to be matrix-related. Flag any out-of-control results as estimated (J).

9.3.4 Matrix Duplicate

Sample homogeneity can affect the quality and interpretation of the data. MD results can be used to assess sample homogeneity.

A matrix duplicate is analyzed only if the original sample concentration is more than four times the matrix spike level. A sample and a matrix duplicate are diluted, if needed, and analyzed for every MS and MSD that falls outside of the calibration range.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmd - C|}{(Cmd + C)/2} \times 100$$

Where

RPD = relative percent difference

C_{md} = measured concentration in the MD, corrected for sample preparation and any dilutions

C = measured concentration in the routine sample, corrected for sample preparation and any dilutions

The RPD for any analyte must be $\leq$ 20 for samples with analyte levels $\geq$ QL. If the control limits are exceeded, flag all associated analyte results as estimated (J).

9.4 Method Performance

The following table summarizes method performance by matrix for the period 04/01/2012 to 05/03/2013.

Method Performance

Analyte	*Matrix*	*Number of Measurements*	*Mean Recovery, %*	*95% Confidence Interval (2σ)*
Fluoride	Water	109	95.6	83.2 - 108
Chloride	Water	109	96.5	90.8 - 103
Nitrite-N	Water	109	97.2	89.9 - 105
Bromide	Water	109	98.7	88.6 - 109

Analyte	*Matrix*	*Number of Measurements*	*Mean Recovery, %*	*95% Confidence Interval (2σ)*
Nitrate-N	Water	109	98	91 - 105
Orthophosphate-P	Water	109	98.6	89.9 - 107
Sulfate	Water	109	99.9	90.4 - 110

The primary sources of analytical error are:

- Analytical balance
- Instrument calibration
- Pipette calibration
- Standard's accuracy
- Vial contamination

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the Element database or in the instrument sequence Log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.6 SOP Read and Understood

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Laboratory QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

U.S. Environmental Protection Agency, 1993. *EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. The scope of the SOP does not include the analysis of bromate, chlorate, chlorite, and sulfite.

2. The SOP requires that the MB be less than one-half the QL, while the reference method specifies that MB be less than the MDL. Region 9 Laboratory policy specifies that results be reported to one-half the QL.

3. The SOP specifies sample storage temperature of > 0 to ≤ 6 °C, while the reference method specifies 4 °C.

4. The SOP calculates the width of the retention time window used to make identifications based on ± 5% of the first CCV retention times. The reference method states that the width of the retention time window should be determined using three times the standard deviation of measurements of actual retention times of standards over the course of a day.

5. The SOP specifies six concentration levels and a quadratic fit for calibration, as recommended by the instrument manufacturer, while the reference method recommends a minimum of three concentration levels and a linear curve fit.

6. To improve chromatographic separation, the SOP specifies the working eluent solution to be 8 mM Na_2CO_3 / 1 mM $NaHCO_3$, while the reference method specifies it to be 1.8 mM Na_2CO_3 / 1.7 mM $NaHCO_3$.

7. The SOP uses the SCV standard to meet the requirements of the QCS specified in the reference method. While the method requires the QCS to be analyzed quarterly, the SOP requires an SCV standard be analyzed with each initial calibration, which may be more or less frequent than quarterly.

8. The SOP specifies MS/MSD recovery criteria to be 80 - 120%. The reference method specifies the initial limits to be 90 - 110% and allows 80 - 120% if control charts are used.

9. The reference method specifies that matrix QC frequency be prepared to a minimum of 10 percent of the routine samples; this SOP conforms to EPA Region 9 Laboratory policy for matrix QC frequency.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	*Chemical Abstracts Registry Number (CASRN)*	*Water Quantitation Limit, mg/L*	*Soil Quantitation Limit, mg/kg*
Fluoride	7681-49-4	0.1	1
Chloride	7647-14-5	1	10
Nitrite-N	7632-00-0	0.1	1
Bromide	7647-15-6	0.1	1
Nitrate-N	7631-99-4	0.1	1
Orthophosphate-P	7778-77-0	1	10
Sulfate	7778-80-5	0.5	5

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	*Frequency*	*Criteria*
Coefficient of Determination	Each ICAL	≥ 0.995
SCV	After ICAL	90 - 110%
CCV	Beginning, every 10 samples, and end of run	90 - 110%
CB	After every CCV	< ½ QL
QLS	Beginning and every subsequent 40 analytical samples	60 - 140%
MB	Each batch of 20 or fewer samples	< ½ QL
LCS	Each batch of 20 or fewer samples	90 - 110%
MS/MSD, accuracy	Every 20 or fewer samples in an SDG	80 - 120%
MS/MSD, MD precision	Every 20 or fewer samples in an SDG	≤ 20 RPD
CCV Retention Time Drift	Each batch	± 5% ICAL Std 4
Retention Time Window	Each batch	± 5% first CCV

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APPENDIX D.
TYPICAL ION CHROMATOGRAPH OPERATING PARAMETERS

General Parameters
Dimension of amounts: mg/L
Global Calibration Settings: Total
Auto Recalibrate: Select
Use Recently Detected Retention Times: Deselect
Reference Inject Volume: Fixed, 25.0 µL
Blank Run and Matrix Blank: No blank run subtraction

Detector Parameters
Detector Type: conductivity
Data Collection time (minutes): 13.5 for ICS1100; 12.0 for ICS2500
Data Collection Rate: 5.00 Hz
Real time plot scale maximum (µs): 15,100 for ICS1100; 3,000 for ICS2500

ICS1100 Integration Detection Parameters

Time	Description
0.00	Min. Area 0.003 "[Signal]*min"
0.00	Inhibit Integration ON
0.00	Peak Slice 1.50 s
0.00	Fronting Sensitivity Factor 4.0
2.3	Sensitivity 0.004 "[Signal]"
2.6	Tailing Sensitivity Factor 10.0
2.6	Minimum Height 0.0175 "[Signal]"
2.6	Valley to Valley On
2.6	Inhibit Integration OFF

ICS2500 Integration Detection Parameters

Time	Description
0.00	Min. Area 0.002 "[Signal]*min"
0.00	Inhibit Integration ON
0.00	Peak Slice 0.50 s
2.30	Valley to Valley On
2.30	Inhibit Integration OFF
2.30	Sensitivity 0.004 "[Signal]"
2.30	Fronting Sensitivity Factor 10.0
2.30	Tailing Sensitivity Factor 7.0
2.30	Minimum Height 0.015 "[Signal]"

NOTE: The sensitivity and the minimum area values may change overtime depending on baseline noise for both ICS1100 and ICS2500.

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Calibration Parameters
External or internal calibration: EXTERNAL
Number of replicates for calibration: 1
Update response: Yes
Default dilution factor: 1.00
Default response factor for unknown peaks: 0.00
Calculate unknowns by area or height: Area
Calibration Fit: Quadratic
Flow Rate, initial setup: 1.2 mL/min, adjust as needed.

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APPENDIX E.
TYPICAL STARTUP PROCEDURES

TYPICAL STARTUP PROCEDURE FOR THE ICS1100

1. Ensure that the helium and nitrogen regulator on the system is set at 5 ±1 psi and gas is on.

2. Turn on the computer system and printer connected to the instrument. Log into the network. Double click on the 'Server Monitor' icon and click on the 'Start' button to turn on the Chromeleon server. This will allow the instrument to transfer data into the computer. When the server is running, the message in the status box on the computer monitor should display "Chromeleon Server is running idle".

3. Double click on the 'Chromeleon' icon and find the 9L1207HWFM51_Local directory. Click on the ICS1100 and double click on ICS1100 pts. Maximize the screen by clicking on a "square box with arrows on each corner" icon.

   Click on Pump Settings and enter 1.2 mL/min on the flow rate box and click on the ON button. Then click CLOSE button.

   Click on the Detector Settings and enter 51 mA in the box for the suppressor current, press 'Enter' on the computer keyboard and then click on CLOSE button.

   The system pressure is typically around 2,000 psi and the baseline conductivity reading should be around 24 µS.

4. Open the browser section of the multi colored (red, blue, green, and yellow) button at the top of the control panel by clicking on it. Set up a sequence by clicking on a sequence file that contains the last calibration performed on the instrument. The sequence files are located in: C:\Chromel\9L207HWFM51_Local\ICS1100\Data\Year_Anions\[*sequence#*]

   The sequence number is a seven digit number containing the last two digit of the year, the month, the day, and the run number, ex. 1108191. Re-save the accessed file and save it as today's sequence file. Ensure that the small box 'Save Raw Data' is checked on prior to clicking the save button. Under the 'Status' column for each position to be analyzed in the sequence, change 'Finished' to 'Single'. This will enable the computer system to acquire the data for the standards and samples to their designated position in the sequence file. Ensure that the 'Status' column for the calibration standards (std1 thru std6) says 'Finished', which will prevent the computer from writing over the calibration data. If a new calibration is to be analyzed with the QC standards and samples, every entry in the 'Status' column should be 'Single'. Check for errors within the sequence file by clicking on 'Batch', 'Edit', 'Add', click on the sequence file you wish to run, click 'Open', click on the data file that was just added, click on 'Ready Check', when it says 'OK', click on the 'OK' box. Then click on the 'Start' button to start the analytical sequence.

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TYPICAL STARTUP PROCEDURE FOR THE ICS2500

1. Ensure that the helium or nitrogen regulator on the system is set at approximately at 5 ±1 psi and the gas is on.

2. Follow step #1 on the ICS1100 startup procedure.

3. Double click on the 'Chromeleon' icon and find the C:\Chromel\9L207HWFM51_Local\Data\Year_Anions\ directory. Double click on the last analytical sequence and double click on the 'Conductivity_A_Detector_Gradient_Pump_AS40_LC30.pan' panel and click on 'Connect', if not connected.

4. Turn the eluent on by clicking on the 'ON' button on the control panel. Set the oven temperature to 30°C by typing in '30' on the space beside the word 'Oven Temperature' and press 'Enter' on the computer keyboard. Then turn on the SRS current by typing in '51' mA in the space beside the word 'Current' and press 'Enter' on the computer keyboard. The system pressure is typically 2200 psi and the baseline conductivity at approximately 25 uS.

5. Follow step #4 on the ICS1100 startup procedure except the sequence files for the ICS2500 are located in: C:\Chromel\9L207HWFM51_Local\ICS2500\Data\Year_Anions\[*sequence#*]

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APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the ICS1100 and the ICS2500

Item	Frequency	Comments
Eluent Filter	As needed	Check filters for discoloration when preparing fresh eluent from new stocks, replace if needed.
Eluent Reservoir	As needed	Wash the reservoir thoroughly when preparing fresh eluent from new stocks.
Pump	Daily	Prime prior to starting the instrument to prevent air bubbles from entering columns.
High System Pressure	As needed	Check individual pressure of guard and analytical columns.
Guard Column	As needed	Condition guard column if pressure is more than ¼ of the analytical column, if still high, replace. If a false positive o-phosphate peak appears in the blank, replace the inlet frit on the guard column. If the o-phosphate peak persists, clean the guard column. If the o-phosphate still persists, replace the guard column.
Analytical Column	As needed	Condition analytical column if pressure is more than 4 times of the guard column, if still high replace.
Low System Pressure and/ or Leak Alarm	As needed	Tighten or replace leaky lines or fittings.
Piston/pump seals and o-ring in pump head	Annually	Replace
Inlet frit of guard column	As needed	Replace if system pressure has increased by more than 200 psi and there's solid residue on frit.
Suppressor	As needed	Replace if peak resolutions are not well defined and the baseline noise interfere with peak quantitation.
Check valves	Annually	Replace
Injection Valve	Annually	Rebuild with new rotor seal and stator phase.
Autosampler tip assembly	Annually	Replace

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APPENDIX G.
TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

ESAT Cover memorandum
TDF
Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms
- EPA Review Form
- ESAT technical review guide
- *Discrepancy Reports (if applicable)*
- *Work Order Memo (if applicable)*
- Daily folder review forms or checklists
- *Analysis matrix listing all analytical runs (for organics only)*

Tracking Forms
- Work Order(s)
- COC(s)

Sample Preparation (for projects that require extraction or digestion)
- Bench Sheets (and copies of notebooks, where used)
- Sample cleanup data and records (e.g. GPC logs)
- Sample homogenization records (for solid/waste/tissue samples)
- Moisture data (when applicable)

[Analysis Method] Data (For each method where multiple methods in package)
- Bench sheet(s) where not used in Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:
- Initial Calibration Data (sorted by instrument and then by date)
- Sample Data (sorted by instrument and then by date)

Miscellaneous Data
- Other data as applicable (e.g. conductivity for perchlorate)
- Canister certifications (for volatiles in air analysis)

Standard Records
- Standards records from LIMS (and certificates of analysis, if required)

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APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 530
Revision: 9, Effective: 06/14/2013

ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

Revision	Effective Date	Description
8	10/28/11	1. Removed all references to DX-120 and added ICS1100. 2. Updated format to current EPA Region 9 Laboratory requirements. 3. Updated procedure to follow current internal COC practices. 4. Removed reference to instrument runlog.
9	06/14/13	1. Allowed CCV and LCS requirements to be met with one analysis. 2. Added filtered MB requirement when a sample in the batch is filtered. 3. Changed calibration range, MS/MSD spike and SCV concentrations of fluoride and bromide. 4. Updated matrix QC frequency. 5. Minor edits throughout for clarity.

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