Quality Assurance Documentation and Quality Control Measures in the Volatile Organics Laboratory

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

CHEMISTRY PROGRAM

2600 BLAIR STONE ROAD

TALLAHASSEE, FLORIDA 32399

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION....2
2. DEFINITIONS AND ACRONYMS....3
3. DAILY LABORATORY QUALITY CONTROL COMPONENTS....5
4. EXTERNAL QUALITY CONTROL COMPONENTS....7
5. PERIODIC LABORATORY QUALITY CONTROL COMPONENTS....8
6. QC CALCULATIONS AND REPORTING CONVENTIONS....10
7. MDL/PQL DETERMINATION AND METHOD VALIDATION....13
8. INTERFERENCE MANAGEMENT....14
9. QUALITY ASSURANCE REQUIREMENTS....15
10. CORRECTIVE ACTIONS....17
11. REFERENCES....18
12. APPENDIX....20
13. SOP UPDATE REVISION SUMMARY....22

1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure (SOP) details the Quality Assurance (QA) and Quality Control (QC) procedures for the Volatiles Workgroup. Virtually all aspects of this SOP are dispersed among the method SOPs, thus this document is a summary and tabulation of QA/QC definitions, practices, acceptance criteria, and corrective actions.

1.2. Quality Assurance consists of all the practices undertaken in the laboratory to ensure that quality of the data generated is known and documented. It includes not only quality control measures, but can be as specific as the cleaning of glassware, maintenance of equipment, and preparation of analytical standards. This SOP will concentrate on general Quality Control elements that are used to measure and track the Quality Assurance in the Volatiles laboratory. Refer to the specific preparation or analysis SOPs and EPA methods for more specific details on QA/QC.[1-6]

1.3. The QA/QC practices should be uniform throughout the Chemistry Section, except those specific to the Volatile and other laboratory operations.

1.4. Acceptance criteria for the quality control measures are tabulated in Table 1 of this SOP and are within the text of the analytical SOPs or references identified within the analytical SOPs.

1.5. Corrective actions are tabulated in Table 2 of this SOP and are also listed within the text of the individual method SOPs.

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1.6. The following analysis and preparation methods apply: [7-13]

1.6.1. SOP **VO-002** Analysis of VOCs in Water by EPA Method 624
1.6.2. SOP **VO-003** Analysis of VOCs in Sediment and Waste by EPA 8260C
1.6.3. SOP **VO-004** Analysis of Polar Organic Compounds in Sediment and Waste
1.6.4. SOP **VO-005** TCLP and SPLP Sample Preparation
1.6.5. SOP **VO-006** Analysis of Polar Organic Compounds in Water
1.6.6. SOP **VO-007** VOC Glassware and Equipment Standard Cleaning Procedures

2. DEFINITIONS AND ACRONYMS

2.1. DEFINITIONS:

2.1.1 Accuracy describes the degree of deviation (bias) between a known amount of analyte added to a sample and the actual recovery amount of the analyte. It is expressed as the percent recovery.

2.1.2. Aliquot is a discrete, measured, representative portion of a sample taken for analysis.

2.1.3. Analyte is the specific chemical(s) or components(s) for which a sample is analyzed.

2.1.4. Blank evaluation is used to assess the degree of contamination and interference occurring from the sample preparation and analysis steps. The blank level should 10 times below the reporting level or below the MDL.

2.1.5. Calibration is the process of comparing the output of a measurement instrument against a reference standard and reporting the results. Calibration in a pure sense does not include instrument adjustment, but practically is used to mean calibration plus adjustment.

2.1.6. Detection Limits (MDL/PQL) are established during the validation of a method and are verified at least annually. These limits define the sensitivity of a method. Because "zero" has no meaning when an analyte is not detected, a method analyte must have a limit set which defines the lowest concentration that can be reliably detected when it is present in the sample.

2.1.6.1. Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99 % confidence that the analyte concentration is greater than zero.

2.1.6.2. Practical Quantitation Limit (PQL): Usually set at 3-5 times the MDL, it is a more reliable quantitation limit. Although the MDL can be detected at a 99 % confidence, the PQL is a level where the analyte can be quantitated more accurately with confidence limits established by the analytical method.

2.1.7. Digestion is a process in which the sample is treated to convert the sample to a more easily measured form.

2.1.8. Duplicate – The analysis of two identically prepared subsamples of the same sample. The results of duplicate analysis are used to evaluate analytical precision, but not precision of sample, preservation or storage.

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2.1.9. False Negative – An analyte incorrectly identified as absent from a sample.

2.1.10. False Positive – An analyte incorrectly identified as present in the sample.

2.1.11. Internal Standard – A pure substance that is introduced in known amount into each sample. The ratio of the analyte-to-internal standard signal is used to determine analyte concentration.

2.1.12. Matrix – The collection of all of the various constituents making up an analytical sample.

2.1.13. Precision describes the degree of replication between duplicate samples. It is calculated and expressed as the Relative Percent Difference (RPD) between duplicate sample results or as the Relative Standard Deviation (RSD) for 3 or more results.

2.1.14. Sample Batch is a group of 20 or less samples that are analyzed sequentially, in association with a set of quality control samples.

2.1.15. Standard Samples are comprised of a known amount of standard reference material in the matrix undergoing analysis.

2.1.16. Standard Reference Material (SRM) is a certified reference material that has been characterized for absolute content, independent of analytical test method, usually produced by the US National Institute of Standards and Technology (NIST).

2.2. ACRONYMS:

- **AMU**: Atomic Mass Unit
- **BETX**: Benzene, Ethyl benzene, Toluene and Xylenes
- **BFB:** Bromofluorobenzene used for mass spectral tuning
- **ºC:** Degrees Celsius
- **CAS Number:** Chemical Abstract Services Number
- **CCC:** Calibration Check Compounds
- **CCV:** Continuing Calibration Verification
- **CFR:** Code of Federal Regulations
- **CI:** Chemical Ionization
- **CLP:** Contract Laboratory Program
- **cm:** centimeter
- **CV:** Coefficient of Variation
- **DF:** Dilution Factor
- **DOT:** Department of Transportation
- **EI:** Electron Ionization
- **EICP:** Extracted Ion Current Profile (plot of ion abundance vs. time)
- **EPA:** Federal Environmental Protection Agency
- **FDEP:** Florida Department of Environmental Protection
- **GC:** Gas Chromatography
- **GC/MS:** Gas Chromatography/Mass Spectrometry
- **GLP:** Good Laboratory Practice
- **Hz:** Hertz
- **ICAL:** Initial Calibration
- **ID:** Identification

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- **I.D.:** Internal Diameter
- **IS:** Internal Standard
- **L:** Liter
- **LCS:** Laboratory Control Sample
- **LFB:** Laboratory Fortified Blank
- **LIMS:** Laboratory Information Management System
- **LOD:** Limit of Detection
- **LOQ:** Limit of Quantitation
- **m:** Meter
- **MDL:** Method Detection Limit
- **MS:** Matrix Spike or Mass Spectrometry
- **MSD:** Matrix Spike Duplicate or Mass Selective Device
- **MW:** Molecular Weight
- **NELAP:** Nation Environmental Laboratory Accreditation Program
- **NIOSH:** National Institute of Occupational Safety and Health
- **NIST:** National Institute for Standards and Technology
- **PE:** Performance Evaluation
- **ppb:** Parts per billion
- **ppm:** Parts per million
- **ppt:** Parts per trillion
- **PQL:** Practical Quantitation Limit
- **PT:** Proficiency Testing
- **PTFE:** Polytetrafluoroethylene
- **QA/QC:** Quality Assurance/Quality Control
- **QAP:** Quality Assurance Plan
- **RCRA:** Resource Conservation and Recovery Act
- **RF:** Response Factor
- **RF:** Radio Frequency
- **RL:** Reporting Limit
- **RPD:** Relative Percent Difference
- **RRF:** Relative Response Factor
- **RRT:** Relative Retention Time
- **RT:** Retention Time
- **RSD:** Relative Standard Deviation
- **SARA:** Superfund Amendments and Reauthorization Act
- **SD:** Standard Deviation
- **SIM:** Selective Ion Monitoring
- **S/N:** Signal-to-Noise Ratio
- **SOP:** Standard Operating Procedure
- **SPCC:** System Performance Check Compound
- **TCLP:** Toxicity Characteristic Leaching Procedure
- **TIC:** Total Ion Current
- **TIC:** Tentatively Identified Compound
- **VOA:** Volatile Organic Analysis
- **VOC**: Volatile Organic Compound
- **ZHE**: Zero Headspace Extraction

3. DAILY LABORATORY QUALITY CONTROL COMPONENTS

For every batch of 20 samples, the following quality control samples are prepared and analyzed. A summary of the acceptance criteria is provided in Table 1.

3.1. Laboratory Blanks

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Laboratory blanks are prepared using laboratory reagent water and are treated exactly as a sample, including exposure to all glassware, equipment, solvents and reagents used with other samples. A lab blank is the first sample analyzed in each sample batch and is used to determine if the method analytes or other interferences are present in the lab environment, reagents, or equipment. A lab blank is prepared for every 10 samples analyzed.

If contaminants are present that interfere with the determination of any analyte, then detection limits must be elevated or affected compounds must be qualified accordingly. If a blank is contaminated with target compounds, then the source of contamination must be identified and eliminated. The blank recovery must be 10 times below the sample data or below the MDL. Otherwise, the data must be qualified with "V" and commented. A comment example is "Lab blank detected methylene chloride at 10 µg/L."

3.2. Continued Calibration Verification

The continued calibration verification (CCV) standard is included at the beginning of every analytical batch after the blank and is made from the same source as the initial calibration standard. The CCV includes all compounds to be reported. The CCV is normally spiked at a mid-range level and must meet the criteria given in the analytical SOP or referenced method. Unless otherwise specified in the method, a CCV is prepared and analyzed at the beginning of the sampling batch, for every 12 hours of analysis time, and at the end of each sampling batch.

3.3. Calibration Verification Standard

The calibration verification standards must come from a source different from the initial calibration standards. The compounds making up the calibration verification and their required recovery and relative response are specified in each method SOP. In EPA Method 8260C and 624, each CCV compound must meet the criteria given in the analytical SOP or referenced method, where all analytes must meet the 20% difference or drift criterion.

3.4. Laboratory Fortified Blank (LFB)

An LFB is a reagent blank that is fortified with a known amount of the analyte(s) of interest and with any surrogates used. An LFB may be prepared singly or in duplicate. The analysis of duplicate LFBs is routinely required per our SOPs for volatile analysis. It is used to assess the method accuracy (i.e., analyte % Recovery) without the effects that a true sample matrix may contribute. When prepared in duplicate, the LFB data can also be used to assess method precision (as Relative Percent Difference.

3.5. Matrix Spike Samples

Sample matrix spikes are samples that are fortified with a known amount of the analyte(s) of interest. They are prepared for assessing method accuracy and, when performed in duplicate, for assessing precision on "real" samples in the presence of matrix effects. Matrix spikes samples are routinely prepared in duplicate with each sample batch to assess the true method precision in the presence of matrix effects. Spike recoveries are used as indicators for potential sample matrix interference and may be used to monitor analyte losses or other matrix effects. Historical percent recoveries are used to calculate method bias and the confidence range of the bias.

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3.6. Laboratory Duplicate Samples

A laboratory duplicate sample is prepared for every sample batch to assess precision for each matrix type. Unless otherwise specified in the method, the precision of the duplicate sample must be less than 30% RPD. Duplicate samples outside of the criteria must be reanalyzed or qualified if required (the result is not qualified if a mechanical error affecting only one of the samples can be identified).

3.7. Daily MDL/PQL Verification Samples

The MDL/PQL may be verified daily with a spike prepared within 4 times of the MDL level. It is the policy of the volatiles group to include a PQL level spike with each instrument batch to verify the method MDL/PQL. This is different than the initial instrument calibration which is normally updated at least monthly.

3.8. Internal Standards

Internal standards are pure analytes of known amount that are added to every sample prior to VOC analysis. An internal standard is used to measure the relative response of other analytes and surrogates and is useful in correcting for system variations. It is also used as a reference peak, to correct for retention time drift, not to exceed 20 seconds, during an analysis sequence. The internal standards must be compounds that are not found naturally in the sample. The internal standards must also not vary more than -50% or +100% from the mid-point standard level in the most recent calibration sequence. Any samples with recoveries for internal standards out of this range must be reanalyzed.

3.9. Surrogates

Surrogates are pure analyte(s) that are added to all samples, blanks, and spikes at sample analysis. Surrogates must be similar in behavior and chemical structure to the method analytes, but not found naturally in the sample. To assure this, deuterated analogs of some of the target analytes are frequently selected as surrogates. Surrogate recoveries give an indication of method accuracy and are a good check for gross inaccuracy (i.e., incorrect volumes, concentration problems, etc.) in all the samples.

4. EXTERNAL QUALITY CONTROL COMPONENTS

In addition to the daily laboratory quality control samples, there are also field and external proficiency quality control samples that may be assessed. A summary of the acceptance criteria is provided in Table 1.

4.1. Field Duplicate Samples are two separate samples collected at the same time and from the same site under identical circumstances and are treated the same through all field and laboratory procedures. Duplicate analysis gives a measure of the accuracy and precision associated with the sample collection, preservation, and storage, as well as with the laboratory procedures.

4.2. Field Blank is reagent water added to a sample bottle at the time of sample collection. It is treated exactly as a sample, including exposure to the sampling site conditions, storage, preservation, and all lab procedures. It is used to determine if method analytes and/or other interferences are present in the field sampling environment.

4.3. Equipment Blank is reagent water rinsed through the equipment (baler, etc.) and collected

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as a sample. This blank is evaluated to ensure the field sampling environment and equipment did not contaminate the samples.

4.4. Trip Blank is a reagent water sample prepared in the lab and accompanies the other associated sample bottles to the sample collection site and back to the laboratory. The trip blanks travel on the entire sampling "trip" and are exposed to all aspects of sample storage and transportation. The trip blank sample bottles remain closed at all times and are used to determine if any method analytes or interferences have diffused into the sample bottle.

4.5. Field Spikes are fortified samples that are used to assess the stability and method performance of the analyte(s). These may be "blind" spikes that are unlabeled as spikes and are therefore unknown to the laboratory personnel. This is an excellent way to determine true method performance including both field and lab operations.

4.6. Proficiency Testing (PT) Samples are fortified samples used to evaluate the proficiency of the laboratory for each method. The PT samples may also be used to evaluate a particular analyst or to evaluate a laboratory group. The testing entity establishes the acceptance criteria. The NELAC program, analytical methods and Quality Control Manual stipulate the frequency and type of PTs required.

5. PERIODIC LABORATORY QUALITY CONTROL COMPONENTS

The following laboratory quality control tests are performed on an annual or periodic basis. A summary of the acceptance criteria is provided in Table 1.

5.1. Annual MDL/PQL Verification Samples

The MDL must be verified at least once annually for each analytical instrument and method by analyzing samples spiked within 4 times of the MDL level. It is also the policy of the volatiles group to include MDL and PQL level spikes with each instrument calibration to verify the method MDLs. Instrument calibrations are normally updated at least monthly. The MDL verification data is tabulated at least annually to determine a calculated MDL. The verification data are logged-in as samples in a job and kept on file in the labs data storage.

5.2. Annual Analyst Continued Calibration Verification

A set of 4 CCV samples or 1 unknown PT sample are used to certify each lab analyst on an annual basis to ensure they can perform the applicable method.
The CCV standard is made from the same source as the initial calibration standard and includes all compounds to be reported. The CCV is normally spiked at a mid-range level and must meet the criteria given in the analytical SOP or referenced method.

5.3. Periodic Proficiency Testing (PT) Samples

PT samples may be used to evaluate a particular analyst or to evaluate a laboratory group. The testing entity establishes the acceptance criteria. The NELAC program and Laboratory Comprehensive QA Manual stipulate the frequency and type of PTs required.

5.4. Quarterly Pipet Calibration Check

The calibration of dispensing pipettes must be verified at least once a quarter and the results

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recorded in the pipette and syringe calibration notebook. The procedure for the pipette calibration check may be found is SOP **CM-032**. The acceptance criteria are the same as provided by the manufacture.

5.5. Annual Fixed-Syringe Replacement or Recertification

All fixed syringes should be replaced or recertified on an annual basis. Syringes typically last only a few months, so this is normally not an issue. However, syringes that are not replaced should be recertified and the result recorded in the pipette and syringe calibration notebook. The acceptance criteria are the same as provided by the manufacture or, if different, are specified in the calibration notebook.

5.6. Annual DI Water System Continuity Calibration

Verify the continuity calibration on the DI water system using a continuity standard from the general laboratory. The calibration must meet the acceptance criteria as provided by the manufacture of the DI water system. The results of the calibration test must be stored in the Temperature and DI Water Calibration Verification notebook.

Table 1

Summary of Frequency and Acceptance Criteria, for QC Checks
(Refer to Table 2 for corrective actions)

QC Check	Minimum Frequency	Acceptance Criteria
Initial Instrument Demonstration of Capability	Prior to putting instrument into service and at any time a significant change is made in instrument type or test method.	A minimum of 7 replicate spike samples meeting the QC acceptance criteria established by laboratory or method.
MDL Study	At initial instrument set-up and annually	See 40 CFR, Part 139 Appendix B.
BFB MS Tuning	Prior to analyzing calibration standards and every 12 hours thereafter.	See Appendix 12.2. -Verify MS calibration per analytical SOP.
Analyst Demonstration of Capability	Prior to Analyst reporting data, once a year, and at any time a significant change is made in instrument type or test method.	A minimum of 4 QC spikes or a PT sample meeting the QC acceptance criteria established by laboratory or method.
RT Windows	At method set-up and prior to calibration.	Verify per analytical method requirements. RT Window must be within 0.06 RRT units for analysis with internal standards and ±10 sec for other methods.
Initial 5 Point Calibration (ICAL)	At method set-up and any time 20% of compounds do not pass criteria. Must contain all analytes of interest.	RSD ≤ 20%, Minimum Correlation Coefficient 0.995.
Continuing Calibration Verification (VOCs)	Daily before sample analysis and every 12 hours of analysis time. Must contain all analytes.	% Difference or Drift ≤ 20%. Mid-point spike level.
Internal Standard Verification	In all laboratory samples, standards, and field samples	RT window ± 30 sec; EICP areas are within -50% to + 100% of ICAL area
Method Blank	Daily before sample analysis and every 20 samples; at least every 12 hours of analysis time.	No analyte greater than ½ the reporting limit or less than MDL.

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Table 1 continued.

QC Check	Minimum Frequency	Acceptance Criteria
Laboratory Control Sample	Duplicate LCS per analytical batch of 20 samples.	QC acceptance criteria specified in LIMS QC Manager Tables typically between 70–130%.
Matrix Spikes	Duplicate MS per analytical batch of 20 samples.	QC acceptance criteria specified in LIMS QC Manager Tables typically between 70–130%.
LCS or MS Duplicate	One per preparatory batch per matrix.	QC acceptance criteria specified in LIMS QC Manager Tables typically RPD ≤ 30%.
Surrogate Spike	Added to all samples for EPA Methods 8260C and 624.	Recovery must be between 70–130% using single point calibration, as applicable.
Periodic PT Samples	Per requirement of laboratory QA Manual. Once annually for each analyst/method.	Criteria established by testing entity.

6. CALCULATIONS AND REPORTING CONVENTIONS

6.1. Accuracy is expressed as % Recovery for the LFBs and matrix spikes and is calculated as follows:

$$\%\ \text{Recovery} = \frac{\text{Spike Sample Conc.} - \text{Original Sample Conc.}}{\text{Actual Spike Concentration}} \times 100\%$$

6.2. Precision is expressed as Relative Percent Difference (RPD) or Relative Standard Deviation (RSD) for a set of measurements obtained for the LFBs, matrix spikes, or duplicate sample results. The precision is calculated as follows:

$$RPD = \frac{|\,A - B\,|}{A + B} \times 200\%$$

and

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

where

A = Measure concentration from spike 1
B = Measure concentration from spike 2
SD = Standard deviation
RF = Response factor for each of the calibration standards

6.3. Acceptance Limits are in some instances established by the specific analytical method. Otherwise, the limits are determined for accuracy and precision by a statistical evaluation of the blank, LFB, and matrix spike recoveries. These limits are used to assess the acceptability of accuracy and precision in subsequent spikes and in determining if the spike recovery values are a true and accurate reflection of the method performance. Limits are established for each matrix type (i.e., sediment, water, and waste) and are updated quarterly throughout the year. The acceptance limits consist of both Warning Limits and Control Limits:

6.3.1. **Accuracy Warning Limits:** are defined as the mean from a set of 20-25 data points (recovery values), +/- 2 Sigma. Sigma is the standard deviation of the n-1 population. This calculation will give an upper and a lower warning limit for the accuracy values. Warning Limits are used in evaluating data trends.

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Upper Warning Limit (UWL) = Mean + 2 Sigma
Lower Warning Limit (LWL) = Mean - 2 Sigma

6.3.2. **Accuracy Control Limits:** are defined as the mean from a set of 20-25 data points (recovery values), +/- 3 Sigma. Sigma is the standard deviation of the n-1 population. This calculation will give an upper and a lower control limit for the accuracy values. Limits are used in accepting or rejecting recovery data and in determining whether a system is out of control. EPA defines an out-of-control system as one in which there is seven successive data points on the same side of the mean value.

Upper Control Limit (UCL) = Mean + 3 sigma
Lower Control Limit (LCL) = Mean - 3 sigma

6.3.3. **Precision Warning Limits:** are defined as the mean from a set of 20-25 RPD values + 2 Sigma. This calculation will give an upper warning limit for the precision values. For precision, only the upper limit is relevant.

6.3.4. **Precision Control Limits:** are defined as the mean from a set of 20-25 data points (RPD values), + 3 Sigma. This calculation will give an upper control limit for the precision values. This limit is used in accepting or rejecting precision data and in determining whether a system is out of control.

Upper Control Limit (UCL) = Mean + 3 sigma

6.3.5. The accuracy and precision limits are calculated from the latest 20-25 data points. These ranges are used in assessing the next 20-25 data points as they in turn are generated. Once 20-25 new data points have been generated, new limits are calculated. If a particular method does not generate 20 data points within 3 months, then a minimum of 7 data points may be used in the calculations. If any data point is outside of the acceptance control limits, the batch of samples must be re-analyzed provided samples are not expired. A comment is added to the final report detailing the reporting of outlier data and the affected analytes are denoted with a "J" qualifier.

6.4. Retention Times and Relative Retention Times

Evaluate retention time of each compound when setting up the method and with each new calibration. The absolute retention time of analytes in methods without internal standards must be within a 20 second window (±10 seconds). The relative retention time (RRT) should agree within 0.06 RRT for methods with internal standards. The RRT is calculated as follows:

$$\text{RRT} = \frac{\text{Retention Time of Analyte}}{\text{Retention Time of Internal Standard}}$$

6.5. Rounding of Numbers

6.5.1 In routine reporting, round the final results to 2 significant figures. Round the second significant number up if the third significant figure is greater than 5 and round down if it is less than 5. For those instances where the third significant figure is 5, round the second significant number up if the second significant figure

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is an odd number or truncate to 2 significant figures if the second significant figure is an even number. For example:

Calculated Result	Reported Result
128	130
133	130
135	140
125	120

6.5.2. Results with 4 digits or more must be converted to scientific notation and reported with 2 significant figures. For example:

Calculated Result	Reported Result
1350	1.4 E+03
12,548	1.2 E+04

6.6. Sample Reporting Codes/Conventions

See the **SOP LB-027** for additional details. The laboratory uses the following sample reporting codes and conventions:

6.6.1. For sample results that are below the MDL, report the MDL followed by the letter U.

6.6.2. Sample results that are ≥ MDL and < PQL are report with the qualifier letter I.

6.6.3. Samples analyzed in duplicate (in-lab duplicates, NOT field duplicates) may be reported as an average followed by the qualifier letter A.

6.6.4. For samples that are analyzed after expiration, report the result followed by the qualifier letter Q.

6.6.5. For analytes that were not analyzed, use the qualifier O.

6.6.6. For values above the calibration range or have associated QC outside of the acceptance limits, use the qualifier J.

6.6.7. For analytes detected with recoveries closer than a factor of 10 in both the sample and method blank, use the qualifier V.

6.6.8. Some conditions may require two or more qualifiers. Use the list below to assign priorities (#1 has highest) and order in which they are listed in reports:

1. U or I
2. Q
3. J
4. V
5. A

6.6.9. Request approval by the supervisor before using any qualifiers that are not listed above.

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6.6.10. Report all full-scan VOC water and TCLP results in µg/L, all VOC sediment and waste samples in µg/kg, and SIM VOC water results in ng/L. Sediment samples are reported on a dry weight basis and waste samples are reported on a wet weight basis.

7. MDL/PQL DETERMINATION AND METHOD VALIDATION

The Method Detection Limit (MDL) and Practical Quantitation Limit (PQL) are also referred to as Limit of Detection (LOD) and Limit of Quantitation (LOQ), respectively. The MDL and PQL values are initially determined during validation of a new method and are verified annually. Refer to the SOP **LB-007** *Procedure and Policy for Method and Instrument Validation* and refer to SOP **LB-031** *Limit of Detection Verification* for specific procedural details.

The LOD and Demonstration of Capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials, and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD determinations and DOCs where there is evidence that the method performance will not be affected by sub-matrix distinctions within these group, Otherwise LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matrix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc.

7.1 Quality System Matrices:

7.1.1. Aqueous – all aqueous samples, excluding drinking water (see below) and salt or estuarine waters;

7.1.2. Drinking Water – water from a designated potable source;

7.1.3. Saline/Estuarine – aqueous sample from an ocean or estuarine. The effects of this matrix type may vary with salt content. Therefore, the decision to what extent, if any, this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff.

7.2. MDL Determination

Method Detection Limits (MDLs) are set such that the risk of reporting a false positive at the detection limit is ≤ 1%. The MDLs are determined using the method specified in the Federal Register, 40CFR, Part 139, Appendix B unless the possibility exists for significant systematic bias from analytical steps. In that case (primarily inorganic constituents) the IUPAC method will be followed, accounting for systematic bias.

7.2.1. Estimate the MDL by analyzing a standard on the appropriate instrument and examining the chromatographic peaks. The analytical peaks must have a signal to noise ratio (S/N) of approximately, but not less than, 10.

7.2.2. After obtaining the estimated MDL, at least 7 replicate lab fortified blanks (LFBs) are prepared using laboratory pure water, Ottowa sand or other pure matrix spiked at 1-5 times the estimated MDL. These LFBs are then analyzed. The standard

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deviation (SD) and relative standard deviation (RSD) for the measurements are calculated. The relative standard deviation should be acceptable, based on EPA method or other references results (usually less than 30%). If this was achieved, the MDL is calculated using the formula:

$$MDL = t \times S$$

where: t is the Student coefficient (t=3.143 for 7 replicates; t=2.998 for 8 replicates) and S is the standard deviation calculated for at least 7 replicates

If the relative standard deviation requirement is achieved, then the MDL of the analyte is set at this level. If the criterion is not achieved, then prepare and analyze 7 replicates LFBs at higher concentrations until the criterion is achieved.

7.3. PQL Determination

Practical Quantitation Limits (PQLs) must be set at 3 to 5 times the reported MDL, unless otherwise noted. Because PQL level checks are part of the daily analytical regimen, ease of preparation from commercial analytical mixes may dictate to some extent the reported PQL. The PQL should not be set less than 3 times the MDL unless it can be demonstrated that a systematic bias causes the MDL to be elevated to quantifiable levels.

7.3.1. Prepare and analyze 7 replicate LFBs at the estimated PQL concentration. The relative standard deviation and average recovery must meet the applicable EPA requirements. If the RSD and % Recovery requirements are achieved, then set the PQL of that analyte at the spike level. If the criteria were not achieved, then prepare and analyze 7 replicate LFBs at a higher concentration until the criteria are achieved.

7.4. The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically on at least an annual basis to establish or update the MDLs and PQLs for each analyte and matrix. A list of MDLs and PQLs is given in the Laboratory Comprehensive Quality Control Plan, see Reference 11.22.

7.5. MDL and PQL Reporting

The MDL and PQL values are used when reporting data, however these values may be adjusted upward to account for differences in matrix interferences, sample wet/dry weight, and amount of sample analyzed. A comment is added to the final report for samples with an elevated MDL.

8. INTERFERENCE MANAGEMENT

The following general interference management guidelines are used to assure reliable and complete date is reported. This will not encompass a complete list for every method so refer to the analytical method procedures for additional requirements.

8.1. Most analytical interferences can be mitigated by good laboratory practices. Proper training and good instrument/work environment maintenance is necessary. All staff must be trained and qualified to perform the analytical tests to be reported.

8.2. Maintenance or analytical problems must be reported to a supervisor. Instrument repairs are included in instrument logs and analytical problems are recorded in a

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nonconformance report (NCR) for the affected samples.

8.3. Field sampling problems such as contamination, mislabeling, and sample expirations are reported to a supervisor. Unusually samples that may require special handling or alternative preparation techniques must be discussed with the supervisor. An NCR must be generated, if the sample analysis deviates from our standard operating procedures.

8.4. Method interferences may be caused by contaminants in reagents, glassware, instrumentation, and highly contaminated samples. All potential contaminants must be routinely monitored by daily analysis of laboratory water blanks. To avoid method interferences, take the following general precautions:

8.4.1. Solvent Interference Resolution

8.4.1.1. Use only the specified grade of solvents. If interferences from solvents are suspected, then analyze a concentrated aliquot of the solvent for verification. Remove any contaminated solvent from production immediately. Label solvents as contaminated.

8.4.1.2. Never use solvents from unlabeled bottles.

8.4.1.3. Never pipet solvents directly from bulk solvent containers. Always pour the required volume of solvent into a labeled container and pipet from the smaller volume. Dispose of the unused portion.

8.4.2. Reagent Interference Resolution

8.4.2.1. Use the purity of reagents required by the appropriate method SOPS

8.4.2.2. Store all the reagents appropriately in a clean environment, and with a proper label, which includes the date and initials of the person who prepared the reagent.

8.4.3. Use scrupulously cleaned glassware. See **SOP VO-007** for further details, including the acceptance criteria for cleaned glassware.

8.5. BE SENSITIVE TO CONTAMINATION AT ALL TIMES! If a highly contaminated sample has been analyzed with other non-contaminated samples, be sure that any positives reported in the other samples are not due to carryover or cross-contamination.

8.6. Be aware of other activities occurring within the laboratory environment. It is possible other employees are handling neat solvents, waste products, paint, or other potential sources of interferences. Communication is key, so make sure you know what other staff members are doing within the lab and how it may impact your work.

8.7. Any sample determined to be positive for an unusual analyte must be confirmed. Unusual positive analytes include positives that (1) cross jobs, (2) appear out of norm for a particular site, (3) appear to have come from a standard and (4) are present in a blank. Both the retention time and mass spectra must meet the method criteria for positive identification.

9. QUALITY ASSURANCE REQUIREMENTS

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9.1. Document quality control from all analysis sets in the LIMS and in the Daily Instrument QC folder.

9.2. Document sample preparation information in the sample preparation log.

9.3. Document analytical results for each analysis in the LIMS and in the Job folder.

9.4. Document non-conformance by issuing a Non-Conformance Report (NCR) in the LIMS and notify the client. See **SOP LB-002** for details.

9.5. Document corrective actions that may be required. Rerun affected samples if possible. Otherwise, notify the client if an NCR is issued.

9.6. Record instrument maintenance in the Maintenance Log.

9.7. Document QC deviations in the final report by adding appropriate comments and by flagging any affected results with the proper code. See **SOP CH-008** for details.

9.8. Record appropriate hazard identification for sample handling and disposal. See **SOP OG-001** for details.

9.9. Document refrigerator and freezer temperature log information daily. Refer to specific SOP equipment and instrument sections for listing of applicable units. Use the

9.10. Document the Solution 2000 DI water quality information daily. Use the form DI Water Log Form 2011.docx (see Appendix 12.2)

10. CORRECTIVE ACTIONS

Corrective Actions for problems encountered in meeting specific QA/QC requirements are provided in Table 2 below. Refer to Table 1 for frequency and acceptance criteria.

Table 2

Summary of Corrective Actions, Flagging Criteria, and Comments for QC Checks.

QC Check	Corrective Action	Flagging Criteria	Comments
Initial Instrument Demonstration of Capability	Locate and fix problems if instrument did not meet method criteria.	NA	Performed for each instrument system. Data from instrument must not be reported without an Initial Demonstration of Capability on file.
MDL Study	Perform a new MDL study if the MDL verification checks fail. May need to be performed at a higher level to produce an instrumental S/N of 3.	NA	Samples must not be analyzed without a valid MDL.
BFB MS Tuning	Retune instrument and verify. Rerun affected samples.	Apply J flag to all analytes in the affected samples and comment.	Attempt to reanalyze samples.
Analyst Demonstration of Capability	Rerun demonstration for those analytes that did not meet the method criteria.	NA	Performed for each group or an individual analyst. Data must not be reported without an Initial Demonstration of Capability on file.

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RT Windows	Correct problem and rerun RT window mix.	Flagging criteria not appropriate.	
Initial 5 Point Calibration (ICAL)	Correct problem, then repeat initial calibration	Flagging criteria not appropriate	No samples should be analyzed until ICAL has passed criteria.
Second Source Calibration Verification for VOCs	Correct problem and verify 2nd source standard. If rerun fails, then repeat initial calibration.	Apply J flag to all analytes with RSD >20% and comment.	Apply to SOPs analyzing samples by EPA Methods 624 and 8260C.

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Table 2 (Continued)

Summary of Corrective Actions, Flagging Criteria, and Comments for QC Checks.
(Refer to Table 1 for frequency and acceptance criteria)

QC Check	Corrective Action	Flagging Criteria	Comments
Continuing Calibration Verification for VOCs	Correct problem, then rerun CCV. If that fails, repeat initial calibration.	Apply J flag to all analytes with RSD >20% and comment.	Apply to SOPs analyzing samples by EPA Methods 624 and 8260C.
Internal Standard Verification	Inspect instrument for malfunctions. Reanalysis of sample required (if available.)	Apply J flag to analytes associated to non-compliant IS and comment.	Every effort should be made to have valid internal standards. Dilution may be required to eliminate some matrix effects.
Method Blank	Correct problem. Re-prepare and reanalyze method blank and associated samples.	Apply V flag to compounds present in both sample and blank. Make comment.	
Laboratory Control Sample	Correct problem. Re-prepare and reanalyze LCS and associated samples (if available).	Apply J flag (1) in all cases for low LCS recovery and (2) to sample detects with high LCS recovery.	
Matrix Spikes	Correct problem. Re-prepare and reanalyze LCS and associated samples (if available). Contact client.	Apply J flag (1) in all cases for low MS recovery and (2) to sample detects with high MS recovery.	
LCS or MS Duplicate	Examine results for potential sample variation for MS samples. Re-prepare and reanalyze if problem can be identified.	Apply J flag to specific analytes exceeding criteria if there is a sample detect and comment.	The data should be evaluated to determine source of difference. In some cases, the field sample "duplicates" may not be the same matrix.
Surrogate Spike	Correct problem. Re-prep and reanalyze LCS and associated samples (if available).	Apply J flag to all analytes in the affected sample and comment.	
Results Reported between MDL and PQL	N/A	Apply I flag to all results between MDL and PQL.	
Periodic PT Samples	Retrain analyst for failing performance. Reanalyze PT sample.	Flagging criteria not appropriate.	Multiple failures can result in loss of accreditation.

11. REFERENCES

11.1. Meier, P.C. & R. Zund, "Statistical Methods in Analytical Chemistry", Vol. 123 of Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications, John Wily & Sons, Inc., New York, 1993.

11.2. "EPA: Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act", 40 CFR, Part 136, Oct. 1984.

11.3. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories",

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Environmental Protection Agency, EPA-600/4-79-019, March 1979.

11.4. Code of Federal Regulations, Title 40, Part 136, Vol. 49, No. 209, Method 624: 10/26/84.

11.5. Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8260C, Revision 3, 08/2006.

11.6. Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846, Method 8000C, March 2003.

11.7. Florida Department of Environmental Protection, Standard Operating Procedure **VO-002-4,** *Measurement of VOCs in Water by Gas Chromatography/Mass Spectrometry.*

11.10. Florida Department of Environmental Protection, Standard Operating Procedure **VO-003-4,** *Measurement of VOCs in Sediment and Waste by GC/MS.*

11.11. Florida Department of Environmental Protection, Standard Operating Procedure **VO-004-3,** *Analysis of Acrolein and Acrylonitrile in Sediment and Waste by GC/MS.*

11.12. Florida Department of Environmental Protection, Standard Operating Procedure **VO-005-3,** *TCLP and SPLP Preparation Using Zero-Headspace Extraction.*

11.13. Florida Department of Environmental Protection, Standard Operating Procedure **VO-006-3,** *Measurement of Polar Organic Compounds in Wastewater by GC/MS.*

11.14. Florida Department of Environmental Protection, Standard Operating Procedure **VO-007-3,** *VOC and Methyl Mercury Glassware and Equipment Cleaning Procedures.*

11.15. Florida Department of Environmental Protection, Standard Operating Procedure **VO-013-1,** *Ambient Air Sampling into Passivated Canisters for VOC Analysis.*

11.16. Florida Department of Environmental Protection, Standard Operating Procedure **CM-032-1,** *Calibration of Auto-Pipettes*

11.17. Florida Department of Environmental Protection, Standard Operating Procedure **LB-002-1,** *Non-Conformance Reporting System.*

11.18. Florida Department of Environmental Protection, Standard Operating Procedure **LB-027,** *SOP for Reporting Qualified Data.*

11.19. Florida Department of Environmental Protection, Standard Operating Procedure **LB-007-1,** *Procedure and Policy for Method and Instrument Validation*

11.20. Florida Department of Environmental Protection, Standard Operating Procedure **LB-031-1,** *Limit of Detection Verification*

11.21. Florida Department of Environmental Protection, Standard Operating Procedure **OG-001-3,** *Safety and Waste Management Practices in the Organic Analysis Groups.*

11.22. Florida Department of Environmental Protection, "Comprehensive Quality Assurance Plan" (2018).

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12. APPENDICES

12.1. GC/MS Tune Criteria for BFB in EPA Methods 624 and 8260C

Tuning criteria are established to ensure analytical results produced by instruments are correctly interpreted, according to requirements of the method being used. These criteria are not sample specific; conformance is determined using standard materials.

The GC/MS system is tuned using ≤50 ng bromofluorobenzene (BFB) or amount specified within the applicable method, if different. Obtain a background subtracted BFB spectra by taking the apex scan or average of three scans (apex scan and the preceding and following scans) and subtract a single background scan acquired within 20 scans of the elution of BFB. The background subtraction is designed to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak to achieve a passing tune.

The BFB m/z abundance criteria below are used to tune the mass spectrometer prior to other standard, blank, and sample analysis.

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

12.1.1. GC/MS Tune Verifications:

Verify that all samples, blanks, and standards associated with a given instrument tune are analyzed within twelve (12) hours of BFB injection, as applicable to the specific analytical method.

Verify that spectra were generated using appropriate background subtraction techniques, as applicable to the specific analytical method.

Verify the GC/MS Tune results are included in the instrument's daily QA/QC folder.

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12.2 De-ionized Water Quality Log

FDEP CHEMISTRY LAB VOC WORKGROUP

Type I Water Purification System ID: 102136 **Conductivity: 0.057 µS**
Accepted Line Pressure (psi): 25 to 50 **Calibration: Jan 31, 2017**
Accepted Resistivity Range (Mohm-cm): > 17 **Expiration: Jan. 31, 2018**

Date January 2011	*Time AM/PM*	*Resistivity* (Mohm-cm)	*Pressure (psi)*	*Staff Initials*	*Comments*
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
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13. SOP UPDATE REVISION SUMMARY

The following revisions were made to this SOP from the prior version.

13.1. SOP version number and date.
13.2. Remove methyl mercury references.
13.3. Added clarification language for GC/MS tuning requirements.
13.4. Corrected typos.
13.3. Reference section updates.

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