STANDARD OPERATING PROCEDURES

DATA VALIDATION PROCEDURES FOR ROUTINE VOLATILE ORGANIC ANALYSIS

CONTENTS

CONTENTS (cont'd)

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CONTENTS (cont'd)

* These sections affected by Revision 1.0.

SUPERSEDES: SOP #1015; Revision 0.0; 09/23/03; U.S. EPA Contract 68-C99-223

DATA VALIDATION PROCEDURES FOR ROUTINE VOLATILE ORGANIC ANALYSIS

1.0 OBJECTIVE

The objective of this Standard Operating Procedure (SOP) is to establish a protocol for evaluation and validation of the volatile organic compound (VOC) data generated by the Response Engineering and Analytical Contract (SERAS) laboratory as well as VOC data generated by subcontracted laboratories.

2.0 APPLICABILITY

This SOP is applicable to the validation of all water and soil samples for VOC analysis submitted to the Data Validation and Report Writing (DVRW) Group. This SOP may also be applied to sample matrices not covered in SERAS SOPs (i.e., wipes, drum liquids, oil, or dust), analyses performed in mobile laboratories and/or with portable instrumentation, and to samples collected and/or extracted (i.e., solid phase extraction disks or other innovations) using techniques not addressed in SERAS SOPs as required.

Note: All criteria for data assessment detailed in this SOP must be adhered to unless otherwise directed by the SERAS DVRW Group Leader or Analytical Section Leader. All deviations are noted in the check records.

The data validator uses this SOP to review, verify and qualify VOC data. A deliverable checklist for VOC gas chromatograph/mass spectrometer (GC/MS) analyses that lists the required components of a data package (Figure 1, Appendix A) is used by the SERAS subcontract laboratories to provide a complete data package for validation. A VOC Data Assessment Form (Figure 2, Appendix A) is completed for each data package reviewed. This form provides the qualification information for the case narrative in the final analytical report. The VOC Data Assessment Form is included as part of the data validator's check records along with copies of the corrected and qualified VOC result and quality control (QC) tables.

The following qualifiers are always used in reporting blank, sample target compound, and tentatively identified compound (TIC) results in the final analytical report. These qualifiers, when applied as described below, are the only ones used in the results tables of the final analytical report. No qualifiers are applied to QC tables. If not applied by the laboratory, the data validator enters these qualifiers in red in the data validator's check records.

J - Indicates an estimated value when a target compound is identified using the mass spectral and retention time data based on the identification criteria, but the concentration is less than (<) the sample method detection limit (MDL). This flag is used when estimating a concentration for tentatively identified compounds where a response of 1.0 is assumed.

B - Indicates a reportable concentration of the same target compound found in a sample and the associated method blank. Target compound results in the method blank and all associated samples are flagged with a "B".

E - Indicates a target compound with a concentration exceeding the upper level of the associated initial calibration range. If a target compound has a response greater than (>) the upper level of the associated initial calibration range, the sample or extract must be diluted and re-injected according to the specifications of the method. All target compounds with concentrations greater than the associated

initial calibration range are considered estimated and flagged with an "E".

U - Indicates that the compound was analyzed for but not detected. No quantitation results of zero "0" are reported in any result or QC table. A "U" indicating that the compound was not detected appears in all tables for all target compounds not detected.

Several additional data validation (DV) qualifiers are entered in green in the data validator's check records. These DV qualifiers appear only in the data validator's check records and/or in a separate DV report (DVR) requested by the client. This is done so the report writer can differentiate the laboratory qualifiers added to the result table for the final analytical report from those which only appear in the data validator's check records and/or in a DV report requested by the client.

UJ - Indicates that the reported detection limit is estimated.

J - Indicates that the reported value is estimated.

R - Indicates that the reported value is rejected and unusable.

3.0 DESCRIPTION

3.1 Sample Containers, Preservative, Storage and Holding Times

3.1.1 Objective

The objective is to assess the quality of results based on the types of containers used, preservative added, sample storage and holding time of the sample from the time of collection to the time of analysis.

3.1.2 Requirements

Water samples must be collected in glass containers having a total volume of at least 40 mL with a Teflon®-lined septum and an open top screw cap, and must be completely filled with no air bubbles present. SERAS field personnel do not preserve water samples to pH<2 (with sulfuric or hydrochloric acid) for either in-house or subcontracted (SW-846 Method 8260B) analyses. Soil samples should be collected in wide mouth glass containers completely filled with minimal head space present and fitted with a Teflon®-lined cap. All samples must be protected from light and refrigerated at 4 ± 2 degrees Celsius (°C) from the time of collection to the time of analysis.

Samples Analyzed at SERAS

The analysis for VOC must be performed within seven days from the date of collection for all water and soil samples.

SW-846 Method 8260B

SW-846 requires that water samples be preserved to pH <2 at the time of collection. A holding time of seven days from the date of collection is used for water samples not preserved to pH <2. Water samples preserved to pH <2 at the time of collection and soil samples must be analyzed within 14 days from the date of collection.

3.1.3 Evaluation Procedure

Compare the date of sample collection on the chain of custody record with the date of analysis as noted on the laboratory instrument log and sample chromatogram. Review the chain of custody and data package for sample container, preservation and temperature receipt comments.

Note: High level soil samples may undergo a solvent (methanol) extraction. This solvent extraction does not extend the holding time of the sample.

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3.1.4 Action

Any deviations from the requirements listed in section 3.1.2 shall be noted in the case narrative. Soil samples analyzed at SERAS are only qualified if they exceed the SW-846 14-day holding time for soils.

If the unpreserved water holding time of 7 days prior to analysis is exceeded or the soil and preserved water holding time of 14 days prior to analysis is exceeded, all positive results are qualified estimated and flagged “J” and all non-detects are flagged “UJ”.

If the holding time prior to analysis was exceeded, but is < two times the respective holding time (14 days for a 7-day holding time and 28 days for a 14-day holding time); professional judgement is used to determine if all non-detects should be qualified unusable and flagged “R”.

If the holding time prior to extraction was exceeded by more than two times the respective holding time (14 days for a 7-day holding time and 28 days for a 14-day holding time); all non-detects are qualified unusable and flagged “R”.

Professional judgement is used to determine if sample results should be qualified when the sample containers and storage conditions (i.e., air bubbles in vials, cooler temperatures outside criteria) vary from the specifications in section 3.1.2.

3.2 GC/MS Tuning and Performance

3.2.1 Objective

Tuning and performance criteria are established to ensure that the data produced by the GC/MS are correctly qualified according to the requirements of the method used. These criteria are not sample specific; conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

3.2.2 Requirements

The GC/MS system must be tuned prior to every 12-hour analytical period using 4-Bromofluorobenzene (BFB). The 12-hour time period for GC/MS system tuning begins at the moment of injection of the BFB. The time period ends after 12 hours have elapsed according to the system clock. Additionally, the criteria must be achieved during every 12-hour period that standards, blanks and samples are analyzed. The following ion abundance criteria must be met prior to the analysis of any standards, blanks, or environmental samples:

SERAS Analysis (SERAS SOP #1806 & 1807)

m/z	Ion Abundance Criteria
50	8.0 - 40 % of mass 95
75	30.0 - 66 % of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0 % of mass 95
173	Less than 2.0 % of mass 174
174	50.0 - 120 % of mass 95
175	4.0 - 9.0 % of mass 174
176	93.0 - 101.0 % of mass 174
177	5.0 - 9.0 % of mass 176

NOTE: 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 up to 120.0% that of m/z 95.

Subcontract Analysis (Method 8260B)
(From the Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, U.S. EPA, SW-846, Revision 2, December 1996)

m/z	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	Less than 2.0 % of mass 174
174	Greater than 50 % of mass 95
175	5 - 9 % of mass 174
176	Greater than 95 and less than 101 % of mass 174
177	5 - 9 % of mass 176

Method 8260B (section 7.3.1.1) states that *in the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. Do not subtract part of the BFB peak.*. The background subtraction should be designed only to eliminate column bleed or instrument background ions.

3.2.3 Evaluation Procedure

Compare the data presented for each BFB Tuning and Mass Calibration Form with each mass listing submitted to ensure achievement of ion abundance criteria.

Ensure the following:

- A form has been submitted for each 12-hour tune
- The laboratory has not made any transcription errors between the data and form
- The appropriate number of significant figures has been reported
- The laboratory has not made any calculation errors

Verify that all information required on each BFB Tuning and Mass Calibration Form has been supplied.

Verify that all samples, blanks and standards associated with a given instrument tune were analyzed within 12 hours of BFB injection. This is done by comparing the date and time of analysis for each sample listed on the BFB Tuning and Mass Calibration Form against the time and date of the BFB injection.

Verify that spectra were generated using appropriate background subtraction techniques. Since the BFB spectra are obtained from chromatographic peaks that should be free of co-elution problems, background subtraction should be straight-forward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions

resulting in spectral distortions for the sole purpose of meeting the method specifications are contrary to Quality Assurance objectives and are considered unacceptable.

3.2.4 Action

If the ion abundance criteria are not met, the tune is not acceptable and associated data are qualified unusable and flagged "R".

If there are calculation or transcription errors, the results are recalculated and the necessary corrections are made. If all the criteria are now met, the tune and all associated data are considered acceptable. If after recalculation or correction ion abundance criteria are not met, the tune is not acceptable and all associated data are qualified unusable and flagged "R".

If any of the information required on the BFB Tuning and Mass Calibration is missing, this information must be obtained from the laboratory.

If any standards, blanks or samples, except QC samples [such as matrix spike/matrix spike duplicates (MS/MSDs), blank spike/blank spike duplicates (BS/BSDs) and laboratory control samples (LCSs)] were analyzed between 12 and 13 hours after the associated instrument tune, all data are qualified estimated and flagged "UJ" or "J". If they were analyzed more than 13 hours after the instrument tune, the data are rejected and flagged "R".

QC sample analyses [i.e., MS/MSDs, BS/BSDs and LCS/laboratory control sample duplicate (LCSDs)] performed more than 12 hours after the instrument tune may be accepted at the discretion and professional judgement of the data validator. All anomalies are noted in the case narrative.

If the tuning criteria were achieved using techniques at variance with accepted practices, the associated runs are considered unacceptable, all associated data are qualified unusable and flagged "R".

3.3 Initial Calibration

3.3.1 Objective

The objective in establishing compliance requirements for satisfactory instrument calibration is to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run.

3.3.2 Requirements

Initial calibration of volatile compounds and surrogates requires the analysis of a minimum of 5 standard concentration levels after a compliant tune and within 12 hours. SERAS VOC

SOPs require 6 standards for all compounds except acetone, which uses 5 standards. Surrogate and internal standards must be added to each of the calibration standards. If an analyte saturates at the highest concentration level and the GC/MS system is calibrated to achieve a detection sensitivity of no less than the routine MDL, the laboratory must document the standard saturation in the Case Narrative, and attach a quantitation report and Reconstructed Ion Chromatogram (RIC). In this instance, the laboratory should calculate the results based on an initial calibration without the highest standard for the specific analyte that saturates.

SERAS Analysis

The average relative response factor (RRF) for all compounds must be greater than or equal to (≥) 0.050 and have a percent relative standard deviation (%RSD) of ≤30.0%. Optionally, a linear or non-linear equation with a correlation coefficient (r) ≥0.99 may be used.

SW-846, Method 8260B Analysis

SW-846, Method 8260B requires that all target compounds should have a %RSD ≤15.0, with the exception of six individual calibration check compounds (CCCs) that must be ≤30.0%RSD for calibrations based on the average response factor. The method allows the use of a linear or non-linear (e.g., a polynomial) equations for non-CCC target compounds having a %RSD >15.0%. An acceptable linear or non-linear equation must have a correlation coefficient (r) ≥0.99. In these cases, the analyst should not force the line through the origin. Instead, the intercept is calculated from the data points. The CCC compounds are: 1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Ethylbenzene, Toluene and Vinyl chloride.

SW-846 Method 8260B requires only the system performance check compounds (SPCCs) to meet minimum (mean of the initial calibration) RRFs because these compounds are typically the first to exhibit poor response. However, SERAS criteria requires all target compounds to have a mean RRF of ≥ 0.050 or the results are qualified. The minimum RRFs required by SW-846 for the SPCC compounds are:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

All samples and blanks must be analyzed within 12 hours following a compliant tune and calibration. All calibration standard lot numbers are recorded on the respective injection or instrument logs, and all SERAS standards are prepared and used according to SERAS SOP #1012, *Preparation of Standard Solutions*.

3.3.3 Evaluation Procedure

Review the results on the initial calibration summary, the standard chromatograms and the associated quantitation reports to verify the following:

- Time(s), date(s) and instrument ID of calibration standard analyses are consistent on all forms and raw data sheets.
- Calibration standard analyses are associated with an acceptable instrument tune.
- An initial calibration was conducted using the proper number of standard concentrations.

Verify that all calibration standard lot numbers are recorded on the respective injection log and that all SERAS standards are prepared and used according to SERAS SOP #1012, *Preparation of Standard Solutions*. Review the subcontracted laboratory standard preparation logs and verify the lot numbers, concentrations and expiration dates.

Check and recalculate the RRF or equation for one or more analytes quantitated for the 5 or 6 calibration standards; verify that the recalculated values agree within 10% of the laboratory reported values. Generally, the validator should select a minimum of one surrogate and the analyte with the highest concentration and/or toxicity reported in the associated samples for verification. Additional analytes should be selected as needed so that ten percent of the analytes with positive results in the associated samples are verified. The RRF for a compound can be calculated as follows:

$$RRF = \frac{(A_X)(C_{IS})}{(A_{IS})(C_X)}$$

where:

A_X	=	Area of quantitation ion for the compound to be measured
C_{IS}	=	Concentration of the internal standard in micrograms/liter (µg/L)
A_{IS}	=	Area of quantitation ion for the specific internal standard
C_X	=	Concentration of the compound to be measured (µg/L)

Check and recalculate the average RRF for the same analytes selected for RRF validation; verify that the recalculated values agree with the laboratory reported values. The average RRF for a compound can be calculated as follows:

$$RF_{ave} = \frac{RF_1+...+RF_n}{n} \quad \text{and} \quad n = \text{number of standards}$$

For Method 8260B, verify that all SPCCs meet the minimum (mean of the initial calibration) RRF criteria in section 3.3.2 and all non-SPCC compounds have mean RRF values greater than or equal to (≥) 0.050.

For SERAS data, verify that all compounds have an average RRF value of ≥0.050.

Check and recalculate the %RSD for the same analytes selected for average RRF validation; verify that the recalculated value agrees with the value reported by the laboratory. The percent relative standard deviation for each compound is calculated as follows:

$$\%\ RSD = \frac{SD}{\overline{X}} \times 100$$

where:

%RSD	=	Percent relative standard deviation
SD	=	Standard deviation of initial relative response factors (per compound)
$\overline{X}$	=	Average initial relative response factor (per compound)

where:

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (\overline{X} - x)^2}{N-1}}$$

where:

N	=	number of response factors
X	=	average RRF
x	=	individual RRF
SD	=	standard deviation

If quantitation was performed using a linear or non-linear (e.g., a polynomial) equation, verify that the correlation coefficients (r) are ≥0.99. Verify the linear equation and r of one compound by calculating the equation and r using the compound's standard concentrations (as the independent variable x) and area of quantitation ion for the compound (as the dependent variable y). The linear equation is defined as:

$$y = mx + b$$

where:

y	=	Instrument response
m	=	Slope of the line or coefficient of x
x	=	Concentration of the calibration standard
b	=	y intercept

If compounds were quantitated using a linear or non-linear (e.g., a polynomial) equation, then verify that the correlation coefficients (r) are $\geq$0.99. For a linear equation r is defined as:

$$r = \frac{n\sum XY - \sum X \sum Y}{\sqrt{[n\sum X^2 - (\sum X)^2][n\sum Y^2 - (\sum Y)^2]}}$$

where:

X	=	value of the compound's standard concentrations
Y	=	value of the area of the quantitation ion for the compound
n	=	the number of calibration standards

Currently, non-linear (e.g., a polynomial) equations and their correlation coefficients are accepted without verification. However, in all cases verify that the line was not forced through the origin.

Verify that all analytes in the initial calibration have a %RSD ≤30.0%. Verify that all samples and blanks analyzed following the initial calibration standards were within 12 hours of a compliant tune.

3.3.4 Action

If there are inconsistent time(s), date(s), or instrument ID(s) on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies must be resolved.

If the calibration standard analyses are not associated with an acceptable instrument tune, all calibration data are qualified unusable and flagged "R".

If the initial calibration did not consist of six points (SERAS analysis), determine if a five-point calibration is applicable (SERAS acetone or Method 8260B analysis in Section 3.3.2). If a three or four-point (other than those described in Section 3.3.2) initial calibration was performed, determine the range of concentrations used in the calibration. Review the QC and

sample results. Use professional judgement to determine if the data should be qualified. Two- and one-point initial calibrations are unacceptable; all results from these calibrations are qualified as estimated, flagged "J" and labeled as usable for screening purposes only.

Verify that all analytical results reported outside the calibration concentration range for samples or blanks are flagged with the laboratory qualifier "E". If the "E" qualifier is missing, enter it in red for all affected results. Additionally, all affected results are qualified as estimated and are flagged with a green "J".

If secondary ion quantitation is performed, the reasons are documented in the Case Narrative.

If recalculation of average RRF and %RSD reveal laboratory calculation errors, close examination of all calculations is required. If additional recalculations of average RRF and %RSD reveal more laboratory calculation errors, the laboratory must be contacted and the problem must be resolved.

If recalculation of a linear equation and "r" reveal calculation errors, close examination of all calculations is required. Recalculate all regressions and results for compounds where the line was forced through the origin instead of calculating the y intercept from the five data points. If additional recalculations of linear equations and correlation coefficients reveal more laboratory calculation errors, the laboratory must be contacted and the problem must be resolved.

If any Method 8260B SPCC does not meet the minimum (mean of the initial calibration) RRF criteria, or a Method 8260B non-SPCC or SERAS compound has an mean RRF 0.050, then all positive results for that compound in samples and blanks associated with the initial calibration are qualified estimated and flagged "J". Additionally, all non-detected results for that analyte in samples and blanks associated with the initial calibration are qualified unusable and flagged "R".

For linear and nonlinear equations, if any "r" are < 0.99, then the validator must calculate the %RSD of each compound that fails and qualify the data using %RSD criteria. Recalculate equations and all associated results if the y intercept was forced through the origin.

If any analyte has a %RSD > 30.0%, or for Method 8260B non-CCC compounds with a %RSD >15.0% but ≤50.0%, all positive results for that analyte in samples and blanks associated with the initial calibration are qualified estimated and flagged "J"; no action is required for non-detects when the %RSD is ≤50.0%. When the %RSD is >50.0% but ≤90.0%, all non-detects are qualified estimated and flagged "UJ". If the %RSD is >90.0%, then non-detects are qualified unusable and flagged "R".

Contact the laboratory and obtain any calibration standard lot numbers not recorded on the respective injection or instrument log. Inform the DVRW Group Leader of any discrepancies.

3.4 Continuing Calibration

3.4.1 Objective

The objective in establishing compliance requirements for satisfactory continuing calibration is to document the ability of the instrument to produce acceptable quantitative calibration on a day-to-day basis.

3.4.2 Requirements

Continuing calibration of target analytes is required at 50 µg/L or mid-range of the initial calibration range. Surrogate and internal standards are added to the continuing calibration standard.

SERAS Analyses: The percent difference (%D) must be ≤25.0% for all compounds and all RRFs must be ≥0.050.

Method 8260B Analyses: All SPCCs must meet the minimum RRF criteria listed in section 3.3.2 and all non-SPCC compounds must have RRF values ≥0.050. All CCCs (section 3.3.2) must have a %D ≤20.0% and non-CCCs must be ≤25.0%. If linear or non-linear (e.g., a polynomial) equations are used, the percent difference between the certified and recovered concentration of the continuing calibration standard must be ≤25.0%.

3.4.3 Evaluation Procedure

Review the results on the standard chromatograms and the associated quantitation reports to verify the following:

- Time(s), date(s) and instrument ID(s) of continuing calibration standard analyses are consistent on all forms and raw data sheets
- Continuing calibration standard analyses are associated with acceptable instrument tunes and are within 12 hours following a tune.

Verify that the correct internal standards (Bromochloromethane, 1,4-Difluorobenzene, Chlorobenzene-d5 or other internal standards as appropriate to the method) were used.

Check and recalculate the RRF for the same analytes selected for initial calibration RRF validation for each continuing calibration standard and verify that the recalculated value agrees with the value reported by the laboratory. Use the RRF equation in section 3.3.3 for calculations.

Check and recalculate the %D for either each continuing calibration RRF or equation selected for validation. Verify that the recalculated value agrees with the value reported by

the laboratory. The %D for a compound is calculated as follows:

$$\%\ Difference = \left| \frac{A_I - A_C}{A_I} \right| \times 100$$

where:

A_I = average relative response factor from initial calibration or standard concentration

A_C = relative response factor or recovered concentration from current continuing calibration check standard

Verify that all analytes in the continuing calibration have a %D ≤25.0%.

Verify that all samples and blanks were analyzed within 12 hours of a compliant tune.

3.4.4 Action

If there are inconsistent time(s), date(s), or instrument ID(s) on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies must be resolved.

If the calibration standard analyses are not associated with an acceptable instrument tune, all calibration data are qualified unusable and flagged "R".

If incorrect internal standards are used, all calibration data for the compounds associated with the incorrect internal standards are qualified unusable and flagged "R".

If recalculation of RRF and %D reveal laboratory calculation errors, close examination of all calculations is required. If additional recalculations of RRF and %D reveal more laboratory calculation errors, the laboratory must be contacted and the problem must be resolved.

If any analyte has a relative response factor of < 0.050, all positive results for the analyte in associated samples and blanks are qualified estimated and flagged "J"; and all non-detected results for the analyte in the associated samples and blanks are qualified unusable and flagged "R".

SERAS Analyses: If any analyte has a %D >25.0%, the positive results for that compound in all samples and blanks associated with the continuing calibration are qualified estimated and flagged "J". No action is taken for non-detects when the %D is ≤50.0%. For %D >50.0% but ≤90.0% non-detects are qualified estimated and flagged "UJ", and for %D > 90.0% non-detects are qualified unusable and flagged "R".

8260B Analyses: All CCCs must have a %D ≤20.0%. Although there is no method criteria

for non-CCC compounds in this method, SERAS applies the QC criteria of %D ≤25.0%. If linear or non-linear (e.g., a polynomial) equations are used, the %D between the certified and recovered concentration of the continuing calibration standard must be calculated. If any analyte has a %D >20.0% for CCCs and >25.0 for all other compounds, all positive results are qualified estimated and flagged "J". For %D >50.0 but ≤90.0% non-detects are qualified "UJ", and for %D > 90.0% non-detects are qualified unusable and flagged "R".

Contact the laboratory and obtain any calibration lot numbers not recorded on the respective injection or instrument log. Inform the DVRW Group Leader of any deficiencies.

3.5 Blanks

3.5.1 Objective

The assessment of results for blank analyses is for the purpose of determining the existence and magnitude of contamination problems. The criteria for evaluation of blanks applies to all blanks, including reagent blanks, method blanks, field blanks, trip blanks, etc. If problems with any blanks exist, all data associated with the project must be carefully evaluated to determine whether or not there is an inherent variability in the data for the project or the problem is an isolated occurrence not affecting other data.

3.5.2 Requirements

The only in-house blank the laboratory is responsible for reporting is the method blank. The method blank for aqueous samples is a volume of reagent water, free of target compounds, subsequently carried through the entire analytical procedure. The aqueous method blank volume must be approximately equal to the sample volumes being analyzed. For soil/sediment samples, the method blank consists of a purified solid matrix of the same approximate weight as the highest weight sample associated with the method blank and five milliliters (mL) of reagent water subsequently carried through the entire analytical procedure. For medium level samples (methanol dilutions), the method blank consists of the largest volume of the methanol used for dilutions in five mL of reagent water subsequently carried through the entire analytical procedure.

The method blank must be analyzed immediately prior to every 12-hour group of samples, for each matrix and/or methanol dilution, for each type of analysis (heated versus non-heated purge) and for each instrument used for sample analysis.

An instrument or system blank (typically prepared identically to the method blank) may be run after a sample containing a high concentration of target or non-target compounds. These blanks and associated samples are evaluated using the same criteria as the method blanks.

SERAS Analysis

Current SERAS laboratory practices do not require reanalysis of a sample batch if the method

blank contains < five times the MDL for the common laboratory contaminants methylene chloride, acetone, and 2-butanone, and < the MDL for all other target analytes. Additional blank analyses (instrument blanks) may be analyzed to check for carryover of contamination from one sample to another.

Method 8260B Analysis

The method blank must contain < the MDL for all target analytes. Additional blank analyses (instrument blanks) may be analyzed to check for carryover of contamination from one sample to another.

Method blank results must not be subtracted from associated sample results.

3.5.3 Evaluation Procedure

Review the results recorded on the methanol extraction log, instrument injection logs, method blank chromatograms and associated quantitation reports to verify the following:

- Time(s), date(s) and instrument ID(s) for method blank analyses are consistent on all forms and raw data sheets.
- Method blank analyses are associated with an acceptable instrument tune and within 12 hours of the tune.
- Verify that a method blank was analyzed immediately prior to each 12 hour group of samples, for each matrix and/or methanol dilution, and for each instrument used for sample analysis.
- Check to see if an instrument blank was run immediately following a high concentration sample to ensure no carryover occurs.
- Verify that if the method blank contains reportable concentrations of target compounds, that the results for the analyte are flagged with the laboratory qualifier "B" in the method blank and all associated samples.

Verify that each SERAS method blank contains less than or equal to (≤) ten times the MDL of methylene chloride, acetone, and 2-butanone, and < the MDL for all other volatile compounds and each Method 8260B method blank contains < the MDL for all target analytes.

Verify that the method blank results were not subtracted from associated sample results.

First evaluate the method blank(s) against all associated samples including trip blank, field blank, and rinsate blank. Trip blank, rinsate blank, and field blank are evaluated against the method blank utilizing the same criteria as the samples. If, however, trip blank, rinsate blank

and/or field blank contain analytes that cannot be attributed to method blank contamination, the trip blank, rinsate blank and/or field blank results must be evaluated against associated samples.

Next, evaluate the trip blank against the associated samples, field blank and rinsate blank. If, the rinsate blank and/or field blank contain analytes that cannot be attributed to method blank contamination or trip blank contamination, then the rinsate blank and/or field blank results must be evaluated against associated samples.

Then evaluate the field blank against the rinsate blank and associated samples.

Finally, if the rinsate blank contains analytes that cannot be attributed to method blank contamination, trip blank contamination, or field blank contamination, the rinsate blank results must be evaluated against the associated samples if they are in the same concentration units [i.e., liquid rinsate blank results (µg/L) can not be evaluated against solid sample results (µg/kg)] and the relationship between an aqueous sample and the rinsate blank is understood (i.e., both are the same volume of water pulled through a bailer).

3.5.4 Action

If there are inconsistent times, dates or instrument ID on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies must be resolved.

If results for the method blank were subtracted from associated sample results, the laboratory must be notified of the data reporting error and submit a revised data report package.

If a VOC is present in a method blank but not in any associated samples, no action is taken.

The trip blank, rinsate blank, and field blank are evaluated against the method blank utilizing the same criteria as the samples. If contaminants are present in a method blank, then the following action is taken: If the concentration of a given analyte in a sample is < five times the concentration of that analyte in the associated method blank, (10 times for common laboratory contaminants methylene chloride, acetone, or 2-butanone) the presence of that analyte in the sample is qualified as not detected and flagged with a green “U” and the “B” flag is crossed out with a green line. Additionally, if the sample concentration is >MDL, then the MDL is crossed out with a green line and the sample concentration is elevated to the concentration found in the sample. These actions are noted in the case narrative.

Repeat the action described above when evaluating the trip blanks, field blanks, and rinsate blanks if the associated samples are in the same concentration units [i.e., liquid rinsate blank results (µg/L) can not be evaluated against solid sample results (µg/kg)] and the relationship between the sample and the rinsate blank is understood (i.e., both are the same volume of water pulled through a bailer). If they are not in the same units or the sample and rinsate blank are different volumes, then estimate all the positive results in all associated samples for the analytes found in the rinsate blank.

If a common laboratory contaminant is present in a SERAS method blank at concentrations > 5 times the MDL or if any other analyte is present at concentrations > the MDL in a SERAS or 8260B method blank, the data validator notes in the case narrative that the method criteria was exceeded.

3.6 Surrogates

3.6.1 Objective

Laboratory performance on individual samples is established by means of spiking the samples with known concentrations of specific compounds. All samples are spiked with surrogates just prior to sample purging. Surrogate recoveries are used to evaluate laboratory system performance. However, factors such as sample matrix interference effects and high concentrations of analytes in the sample may affect the surrogate recoveries. The data validator must employ professional judgement in conjunction with the analytical results to evaluate the surrogate results and consequently qualify sample results based on laboratory performance.

3.6.2 Requirements

SERAS Analysis

All environmental samples including matrix spike, matrix spike duplicate, and method , trip, field and rinsate blank are fortified with surrogates prior to purging or extraction. The surrogates shown below are used to fortify each sample, MS, MSD, and blank to the proper concentrations.

Surrogate	Concentration Added to Sample/Extract	
	Water	Soil
Toluene-d_8	50 µg/L	50 µg/L
4-Bromofluorobenzene	50 µg/L	50 µg/L
1,2-Dichloroethane-d_4	50 µg/L	50 µg/L

Surrogate recoveries for all samples, blanks, and MS/MSD must be within the following control limits:

Surrogate	% Recovery Limits Low/Medium	
	Water	Soil
Toluene-d_8	88-110	84-138
4-Bromofluorobenzene	86-115	59-113
1,2-Dichloroethane-d_4	76-114	70-121

If sample surrogate recoveries do not meet criteria, the laboratory is required to reanalyze the sample to establish whether the non-conformance was due to the sample matrix interference or due to a deficiency in the laboratory system.

If method blank surrogate recoveries do not meet criteria, the laboratory is required to determine the source of the problem, take any corrective action which may be required to resolve the problem, and subsequently analyze an additional method blank.

Method 8260B

All environmental samples including MS, MSD, QC samples, and method, trip, field and rinsate blanks must be fortified with surrogates prior to purging as dictated by the method. The recommended surrogates are Toluene-d8, 4-Bromofluorobenzene, 1,2-Dichloroethane-d4 and Dibromofluoromethane prepared at concentration levels of 5 - 25 mg/L and using a spiking volume of 10µL per sample. The laboratory must prepare and update surrogate control limits for each matrix and surrogate compound according to SW-846 Method 8000B, Section 8.7.

Surrogate recoveries for volatile samples, blanks, and MS/MSD must all be within the control limits. If sample surrogate recoveries do not meet criteria, the affected sample must be re-injected.

If method blank surrogate recoveries do not meet criteria, corrective action is required or an additional method blank may be analyzed.

3.6.3 Evaluation Procedure

Verify that all samples, blanks, MS/MSDs have been spiked with the appropriate surrogates at the correct concentrations.

Review the surrogate recovery summary table and verify that outliers are marked correctly with an asterisk.

Check raw data (i.e., chromatograms, quantitation reports, etc.) to verify that the surrogate recoveries were calculated correctly by using the following equation:

$$\%\ Recovery = \frac{concentration\ amount\ recovered}{concentration\ amount\ spiked} \times 100$$

The following should be determined from the surrogate recovery summary table:

- Verify that if any surrogate is out of specification, the sample was reanalyzed to

confirm the non-compliance.

NOTE: When there are unacceptable surrogate recoveries followed by successful re-analyses, the laboratories are required to report only the successful run, if within holding time.

- Verify that no blanks have surrogates outside the criteria.

3.6.4 Action

If any sample, blank, MS/MSD were not spiked with surrogates or were spiked with incorrect surrogates, all data are qualified usable for screening purposes only and flagged "J". Additionally, all data for samples, MS/MSDs associated with a method blank that do not contain any surrogates are usable for screening purposes only. A statement to this effect is made in the Data Validator's VOC data assessment form for the case narrative.

If surrogate recoveries are out of specification in the initial analysis, but meet criteria on reanalysis, the laboratory must report results based on results of the reanalysis. If surrogate recoveries are out of specification in the initial analysis and the reanalysis, this may be indicative of sample matrix interference effects or surrogate standard spiking problems. The laboratory is not required to perform any additional analyses on that particular sample. Both sets of analyses must be submitted by the laboratory.

If surrogate recoveries exceed the QC limits in the initial run and reanalysis, the following actions are taken:

- Samples - If one or more surrogate percent recoveries is out of specification and are > 10%, all positive results are qualified as estimated and flagged "J". If one or more surrogate percent recoveries is < the lower acceptance limit, but > 10%, all non-detected results are qualified as estimated and flagged "UJ". If one or more surrogate percent recoveries is < 10%, all positive results are qualified as estimated and flagged "J" and all undetected results are qualified as unusable and flagged "R".

- Method blanks - If one or more surrogates are out of specification, all method blank data and associated sample data are qualified unusable and flagged "R".

3.7 Matrix Spike/Matrix Spike Duplicate Analysis

3.7.1 Objective

These data are generated to determine long term precision and accuracy of the analytical method and laboratory on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples.

3.7.2 Requirements

SERAS Analysis

A MS/MSD must be performed on the following according to whichever is more frequent:

- Every group of samples of a similar matrix
- Every group of field samples received (by project)
- Every 10 samples in a group of samples

Limits for MS/MSD recoveries and relative percent differences (RPDs) are listed below [United States Environmental Protection Agency (U.S. EPA) Contract Laboratory Program Statement of Work (SOW) for Organic Analysis OLM 4.2 May 1999]:

	Percent Recovery Limits	
Matrix Spike Compound	Water	Soil/ Sediment
1,1-Dichloroethene	61-145	59-172
Trichloroethene	71-120	62-137
Benzene	76-127	66-142
Toluene	76-125	59-139
Chlorobenzene	75-130	60-133

	Percent RPD	
Matrix Spike Compound	Water	Soil/ Sediment
1,1-Dichloroethene	14	22
Trichloroethene	14	24
Benzene	11	21
Toluene	13	21
Chlorobenzene	13	21

Method 8260B Analysis

A matrix spike and matrix spike duplicate must be performed on the following according to whichever is more frequent:

- Every group of samples of a similar matrix.
- Every group of field samples received (by project).
- Every 20 samples in a group of samples (or as specified by the method).

The compounds spiked, percent recovery and RPDs are evaluated against any requirements in the analytical method.

3.7.3 Evaluation Procedure

Determine if the proper number of MS and MSD samples were analyzed.

Review the MS/MSD recovery forms, chromatograms and quantitation reports to verify reported matrix spike recoveries and the RPD between the MS and MSD.

Verify an individual compound recovery. MS/MSD recoveries are calculated as follows:

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

where:

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

RPDs for each compound are calculated as follows:

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

where:

RPD	=	Relative percent difference
D_1	=	Spike concentration
D_2	=	Duplicate spike concentration

All MS/MSD concentrations must be in the same units used for reporting sample results.

3.7.4 Action

No action is taken on MS/MSD data alone to qualify or reject an entire group of samples.

The results of the MS and MSD can be used in conjunction with other QC criteria to aid the validator in applying more informed professional judgement when necessary.

Typically, when a subcontract laboratory uses a non-SERAS sample for the MS/MSD in an analytical batch, the results of this MS/MSD are not included in the final analytical report or used in conjunction with other QC criteria to qualify the data.

If the percent recovery is greater than the upper control limit, then a positive result for this compound in the sample is considered estimated and flagged "J". If the percent recovery is < the lower control limit, but ≥10%, then the result for this compound in the sample is considered estimated and flagged "J" or "UJ". If the percent recovery is <10%, then the result for this compound in the sample is qualified as estimated and flagged "J" for positive results and qualified as unusable and flagged "R" for non-detects.

If MS/MSD recovery ranges are not provided, then the validator uses professional judgement in applying the following recommended actions: If the percent recovery >150%, then a positive result for this compound in the sample is qualified as estimated and flagged "J". If the percent recovery <30%, but ≥10%, then the result for this compound in the sample is qualified as estimated and flagged "J" or "UJ". If the percent recovery is <10%, then the result for this compound in the sample is qualified as estimated and is flagged "J" for positive results and qualified as unusable and flagged "R" for non-detects.

3.8 Internal Standard Area Evaluation

3.8.1 Objective

The assessment of changes in the absolute area of internal standards is for the purpose of determining GC performance quality and/or loss of instrument sensitivity that may affect compound quantitation. The criteria for evaluating internal standard areas applies to all samples, blanks, MS/MSDs and QC samples.

3.8.2 Requirements

Samples Analyzed at SERAS and Subcontract Laboratories

The internal standards are the ones specified in the SERAS SOP #1806, *Volatile Organic Analysis in Water by GC/MS* and SOP #1807, *Volatile Organic Analysis in Soil/Sediment by GC/MS,* or by the method used by the subcontracted laboratory.

The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, MS and MSD.

If samples, blanks or MS/MSDs are analyzed immediately following an initial calibration but before another BFB tune and a continuing calibration, evaluation is conducted on the basis of the internal standard areas of the 50 µg/L initial calibration standard.

If samples, blanks or MS/MSDs are analyzed immediately following a BFB tune and a continuing calibration, evaluation is conducted on the basis of the internal standard areas in the continuing calibration standard.

The EICP area for each internal standard in all samples, blanks and matrix spike/matrix spike duplicates must be between 50% and 200% of the respective internal standard EICP area in the associated calibration standard.

The retention time (RT) of the internal standards in samples, MS/MSD and blanks must not vary by more than ±0.5 minutes from the retention time of the associated calibration standard.

3.8.3 Evaluation Procedure

Review the Internal Standard Area Summary Form and verify that the internal standards recommended by the method or equivalent (as defined by the method) were used and that outliers are noted by the laboratory.

Check raw data (i.e., chromatograms, quantitation reports, etc.) to verify the internal standard EICP areas and RT on the Summary Forms.

3.8.4 Action

If internal standard EICP areas or RT are out of specification on initial analysis, but meet criteria on reanalysis, the laboratory must report results based on the results of the reanalysis. If the internal standards recommended by the method or equivalent (as defined by the method) were not used, the laboratory must be contacted and corrective action taken; the data validator documents the anomalies in the VOC Data Assessment Form and uses professional judgement in qualifying or rejecting data.

If internal standard EICP areas or RT are out of specification on initial analysis and also out of specification on reanalysis, the sample may be exhibiting a matrix effect. The laboratory does not have to perform any additional analyses of the particular sample. Both sets of data must be submitted by the laboratory.

If an internal standard retention time varies by more than 0.5 minutes, the chromatographic profile for associated samples must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the validator may consider rejecting some or all of the analytical results associated with that internal standard.

If internal standard EICP areas or RTs are out of specification, the following action must be taken:

For each internal standard that does not meet criteria, all positive results for compounds quantified using that particular internal standard are qualified estimated

and flagged "J".

If the internal standard area is below the QC limits and is $\geq$ 25.0% of the respective internal standard EICP area in the associated calibration standard, then non-detects for compounds quantified using that particular internal standard are qualified estimated and flagged "UJ".

If the internal standard area is < 25.0% of the respective internal standard EICP area in the associated calibration standard, then non-detects for compounds quantified using that particular internal standard are qualified unusable and flagged "R".

If the RT exceeds QC limits, then review the chromatogram and associated spectra to determine if any false positives or negatives exist and use professional judgement to determine if positive results should be estimated and if negative results should be estimated or rejected.

3.9 Compound Identification, Quantitation and Sample Evaluation

3.9.1 Objective

The objective of the criteria for qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can be either a false positive (finding a compound present when in actuality it is not) or a false negative (not finding a compound that is actually present). The objective of the criteria for sample quantitation is to verify that the sample results were calculated correctly. The objective of the criteria for sample evaluation is to assess the impact of sample dependent (i.e., surrogate compound analysis, internal standard area evaluation) and independent (i.e., system tuning, calibration, blanks) variables on the individual sample results according to the required standards. Additionally, a completeness check is performed verifying that all requested and/or method required target compounds are reported.

3.9.2 Requirements

Samples are analyzed only upon successful completion of the initial QC activities of tuning and calibration. When 12 hours have elapsed since the initial tune was completed, it is necessary to perform an instrument tune and continuing calibration analysis. Any major system maintenance, such as a source cleaning or installation of a new column, necessitates a re-tune and re-calibration irrespective of the 12-hour requirement. Minor maintenance should necessitate only the continuing calibration.

Each analytical run must also be checked for saturation and for analyte concentrations exceeding the initial calibration range. The level at which an individual compound will saturate the detection system is a function of overall system sensitivity and the mass spectral characteristic of that compound. The initial method calibration requires that the system

should not be saturated at 200 µg/L for target analytes.

If any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample re-injected, as described in the specific methodologies. Secondary ion quantitation is only allowed when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, the laboratory must document the reasons in the case narrative.

If the dilution of the sample causes any compound detected in the first analysis to be undetectable in the second analysis, then the results of both analyses are submitted.

Compounds are identified by an analyst competent in the interpretation of mass spectra, by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

For establishing correspondence of the GC relative retention time (RRT), the sample analyte RRT must compare within ±0.06 RRT units of the respective standard RRT. The reference standard should be analyzed on the same shift as the sample.

For comparison of standard and sample component mass spectra, mass spectra obtained on the GC/MS instrument are required.

If any target analytes, surrogates, and internal standards are manually integrated, a copy of the manual integration shall be submitted for review. The manual integration results shall be flagged with "m" in the sample report form and shall be initialized and dated by analyst indicating that the integration was performed appropriately. Documentation of the manual integration of quantitation ion peaks must be included in the data package. For SERAS analysis, refer to SERAS SOP# 1001, *Chromatographic Peak Integration Procedures*.

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

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

- SERAS Analyses-The relative intensities of ions specified above must agree within ±20% between the standard and sample spectra. (i.e., For an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).

  Method 8260B Analyses-The relative intensities of ions specified above must agree within ±30% between the standard and sample spectra.

- Ions with a relative intensity > 10% in the sample spectrum but not present in the

standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated.

The comparison of sample and standard mass spectra for tentative identification must be made for compounds (up to a maximum of the 20 largest peaks) in a sample having an area > 10% of the closest internal standard based on the GC analysis. Sample and standard mass spectra must be provided for both positive identifications and unknowns.

A National Institute of Standards and Technology (NIST) library search is executed for nonsurrogate and sample components for the purpose of tentative identification.

Guidelines for making tentative identification:

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

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

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

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

If all of the above conditions for a compound are met and if the Q value (software generated goodness of fit criterion) of the search is ≥80%, that compound will be reported as a tentatively identified compound (TIC). If the Q value is < 80% or the mass spectral interpretation specialist indicates that no valid tentative identification can be made, the compound should be reported as *unknown*. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown organic acid type, unknown chlorinated compound). The molecular weight should be included in the TIC report if it can be distinguished from the library search. Only one compound or unknown is reported per RT and no siloxanes (column bleed compounds) or carbon dioxide are reported.

Target components identified are quantitated using the internal standard method or linear and non-linear equations. The internal standards are those specified in section 3.8.2. Quantitation is based on the EICP area of the quantitation ions specified in the method for both the IS and target compounds. Target compound concentrations are calculated as

follows:

Water

$$Concentration\ \mu g/L = \frac{(A_X)(I_S)(DF)}{(A_{IS})(RRF)}$$

where:

A_X	=	Area of the quantitation ion for the compound to be measured
I_S	=	Amount of internal standard added (µg/L)
DF	=	Dilution factor
A_{IS}	=	Area of the quantitation ion for the specific internal standard associated with the compound to be measured
RRF	=	Initial calibration average RRF or associated continuing calibration RRF for the compound (from ambient purge)

$$Where:\ RRF = \frac{(A_X)(C_{IS})}{(A_{IS})(C_X)}$$

where:

A_X	=	Area of the quantitation ion for the compound
C_{IS}	=	Concentration of the internal standard (µg/L)
A_{IS}	=	Area of the quantitation ion for the specific internal standard associated with the compound
C_X	=	Concentration of the compound measured (µg/L)

Alternatively, if I_S is used in ng instead of µg/L, V_0, the volume of water purged in mL, is added to the formula for unit conversion as follows:

$$C_c(\mu g/L) = \frac{(A_c)(I_{is})(DF)}{(A_{is})(RRF)(V_0)}$$

where:

C_c	=	Compound concentration in µg/L
A_c	=	Area of the characteristic ion for the compound
I_{is}	=	Amount of internal standard in nanograms (ng)
DF	=	Dilution factor
A_{is}	=	Area of the characteristic ion for the internal standard

RRF	=	Relative Response Factor from the ambient temperature purge
V_0	=	Volume of water purged in milliliters (mL)

Sediment/Soil (low level)

$$Dry\ Weight\ Concentration\ (\mu g/kg) = \frac{(A_X)(I_S)(DF)}{(A_{IS})(RRF)(W_S)(D)}$$

where:

A_X	=	Area of the quantitation ion of the compound
I_S	=	Amount of internal standard injected in nanograms (ng)
DF	=	Dilution factor
A_{IS}	=	Area of the quantitation ion of the associated internal standard
RRF	=	Initial calibration average RRF or associated continuing calibration RRF for the compound (from heated purge)
W_S	=	Weight of sample extracted (g) or purged
D	=	Decimal percent solids

Sediment/Soil (medium level)

$$C_c(\mu g/kg) = \frac{(A_c)(I_{is})(V_t)(1000)(DF)}{(A_{is})(RRF)(W_s)(V_a)(S)}$$

where:

C_c	=	Compound concentration in µg/kg dry weight if *S* is used.
A_c	=	Area of the characteristic ion for the compound
I_{is}	=	Amount of internal standard in nanograms (ng)
DF	=	Dilution factor
A_{is}	=	Area of the characteristic ion for the internal standard
RRF	=	Relative Response Factor
W_s	=	Mass of sample (g) purged (gm sample/mL methanol x mL methanol added to purge)
S	=	Decimal percent solid = (100 - % moisture)/100
Vt	=	Total volume of methanol extract in mL (typically 5 to 10 mL)
Va	=	Volume in µL of methanol extract added to 5 mL reagent water
1000	=	Conversion factor from mL to µL

For linear equations the soil and water sample concentrations are calculated using:

$$x = \frac{y - b}{m}$$

where:

y	=	Area of the compound's quantitation ion
m	=	Compound's slope or coefficient of x
x	=	Compound concentration (same units as the calibration standards)
b	=	y intercept

Non-linear equations must be clearly described by the lab along with one example of sample concentration calculation. The validator should check calculations of both low and high sample results of compound's calculated with non-linear equations.

The reported concentration is corrected for dilution and percent solids (if applicable) for each sample as follows:

$$\textit{Sample specific reported concentration} = \frac{x}{S} \times DF$$

where:

x = Compound concentration from the linear or non-linear equation (same units as the calibration standards)
S = (% Solids)/100 (S = 1.0 for liquid samples)
DF = Dilution factor (including changes in sample size)

All results are rounded to 2 significant figures for concentrations >10 and to one significant figure for concentrations <10, rounding down all values less than or equal to (≤)4 and up all values ≥5 (i.e., 42.54 is rounded to 43 and 0.0245 is rounded to 0.02). Concentrations < 25% of the MDL are not be reported.

An estimated concentration for non-target compounds is quantitated by the internal standard method. For quantification, the nearest internal standard free of interferences must be used.

The formula for calculating non-target concentrations are the same as those described above. Total area counts from the total ion chromatograms are to be used for both the compound quantitated and the associated internal standard. A relative response factor (RRF) of 1.0 is assumed. All TIC quantitation results are qualified as estimated and flagged "J". An

estimated concentration is calculated for all TICs and unknowns.

SERAS MDLs are determined on an annual basis for each instrument and for each matrix by the laboratory and kept on file. Subcontracted laboratories must provide copies of MDL studies for reported MDLs derived by this method. Alternately, both laboratories may report an MDL calculated as half of the concentration of the lowest associated calibration standard for the respective analyte.

The only time all sample compound MDLs are adjusted using a dilution factor is if a sample is not analyzed undiluted or the undiluted analysis exhibits significant matrix interference making all results unusable (as determined by the analyst or data validator), and an acceptable diluted sample analysis is performed. In this case, all sample compound MDLs are adjusted using the dilution factor. MDLs are never adjusted by the dilution factor if the dilution analysis is performed to bring an analyte's concentration within the calibration range. Some subcontract laboratories report both the entire undiluted and diluted results if a dilution is performed to bring an analyte's concentration within the calibration range. In this case, the undiluted MDLs and results are reported with the diluted results replacing any undiluted results that were outside the calibration range. The MDL is corrected for dilution and percent solids (if applicable) for each sample as follows:

$$Sample\ specific\ MDL = \frac{MDL}{S} \times DF$$

where:

S = (% Solids)/100 (S = 1.0 for liquid samples)
DF = Dilution factor (including changes in sample size)

All MDLs are reported to 2 significant figures.

No quantitation results of zero "0" are reported in any result or QC table. "U" is used to indicate that the compound was not detected in all tables for all target compounds not detected. Only the laboratory qualifier symbols J, B, and E are used in the result tables and are not added to any QC tables.

A completeness check is performed verifying that all requested and/or method required target compounds are reported. This is done by comparing the method target compound list or the subcontract award letter target compound list against the reported compounds in the result tables.

3.9.3 Evaluation Procedure

DATA VALIDATION PROCEDURES FOR ROUTINE VOLATILE ORGANIC ANALYSIS

Verify that all required deliverables for each sample have been delivered for both target and nontarget compounds, methanol extraction and instrument logs, sample chromatograms, quantitation reports and mass spectra, and standard reference mass spectra.

A completeness check is performed verifying that all requested and/or method required target compounds are reported. This is done by comparing the method target compound list or the subcontract award letter target compound list against the reported compounds in the result tables. If some requested or required target compounds are not reported in the result tables, then the laboratory is contacted and results for these compounds are requested and/or the laboratory may be required to reanalyze the samples for these compounds.

Verify that all sample results are within the associated initial calibration range and review each sample chromatogram for system saturation. Verify that for any analysis that exceeds the associated initial calibration range or that resulted in system saturation, a diluted sample analysis was also conducted and both sets of data were reported.

Verify that the RRT of reported compounds is within ±0.06 RRT units of the reference standard and that the reference standard was analyzed within 12 hours of the sample analysis.

Verify all target qualitative identifications by comparing the sample compound mass spectra with the laboratory standard spectra.

The validator should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carryover is a possibility and should use professional judgement to determine if instrument cross-contamination has affected any positive compound identifications.

Verify that all nontarget peaks on the sample chromatogram (up to a maximum of the 20 largest peaks) that have peak heights/area that are > 10% of the nearest internal standard have undergone a nontarget library search.

Verify all nontarget qualitative identification by comparing the sample compound mass spectra with the library search mass spectra.

Verify that all TIC results are qualified as estimated concentrations.

Verify target and nontarget compound quantitation by verifying the correct quantitation ion was used and recalculating the quantitation of a percentage (up to 5%) of the compounds reported in all result and QC tables.

Check all QC parameters (i.e., sample holding time, GC/MS tuning, calibration, blanks, surrogates, matrix spike/spike duplicate analysis, internal standard area, etc.) to determine if any or all of the sample data requires qualification and/or rejection.

Verify that the laboratory has properly applied the data qualifier symbols J, B, and E to the

result tables. Additionally, verify that no quantitation results of zero "0" are reported and that a "U" indicating that the compound was not detected appears in the result table for all target compounds not detected. Verify that concentrations < 25% of the MDL are not reported.

Verify that the laboratory reported the proper MDLs and results including any adjustments for sample dilution, change in sample size and/or percent solids content and rounding to two significant figures.

Any time there are two or more analyses for a particular sample, the validator must determine which are the best data to report. Considerations should include but are not limited to:

- Surrogate and internal standard area recoveries.
- Technical holding times.
- Comparison of the values of the target compounds reported in each sample analysis.
- Other QC information, such as%RSD, %D, and RRF.

3.9.4 Action

If any required deliverables are missing (i.e., sample chromatograms, sample mass spectra, target compound, etc.), the laboratory must be contacted for delivery of the missing information. If the information is not provided, the data validator uses professional judgement in qualifying or rejecting the results. These actions must be documented in the analytical report case narrative, and the DVRW Group Leader must be immediately informed.

If some requested or required target compounds are not reported in the result tables, and the laboratory can not provide results and the required documentation for these compounds, then the unreported compounds must be documented in the analytical report case narrative and the DVRW Group Leader must be immediately informed.

If a sample concentration exceeds the associated initial calibration range or a chromatogram reveals system saturation, and a dilution analysis was not conducted, the chromatogram and associated quantitation report must be closely examined. All target compounds with quantitation values exceeding the upper concentration of the associated initial calibration curve are qualified estimated and flagged with the laboratory qualifier "E" (red in DV check records) and the DVqualifier (entered in green) "J".

If the relative retention time (RRT) of a reported target compound is not within ±0.06 RRT units of the reference standard, the mass spectrum of the affected sample must be closely examined (i.e., single ion scans may be requested). If the sample mass spectrum matches the reference standard mass spectrum, the semi-qualitative identification (some isomers or

similar non-target compounds may produce like spectra) may be made. All results are qualified estimated and flagged "J". The excessive RRT shift, the fact that a semi-qualitative identification has been performed, and any qualifications by the data validator must be noted in the case narrative.

If it is determined that incorrect identifications of target compounds were made, all affected data are corrected by the data validator and noted in the check records. This must include the reasons for making a change in the qualitative identification.

An effort should be made to ensure that no duplicate reporting of the same compound occurs (i.e., a BNA target compound which is identified as a VOC TIC).

If the laboratory failed to conduct a nontarget library search for all applicable nontarget peaks on a chromatogram, no action is taken. The deficiency is noted in the case narrative.

If incorrect identifications of nontarget compounds were made, all affected data are corrected, and the actions noted in the check records including the reasons for making a change in the qualitative identification.

If spot check calculations of compound quantitation do not match the concentrations reported by the laboratory or if incorrect quantitation ions were used, the laboratory must be contacted and the quantitation problem resolved.

If the result tables have improperly used or are missing data qualifiers, then the correct data qualifier symbols J, B, and E are added to, and any improperly used qualifiers deleted from, the result tables. No qualifiers are added to any QC tables and any added by the laboratory are removed. Additionally, all reported quantitation results of zero "0", in all result and QC tables, are replaced with a "U" indicating that the compound was not detected.

If the laboratory reported incorrect MDLs or reported MDLs that cannot be verified with a MDL study, the laboratory must be contacted in order to resolve the discrepancies in the MDLs. If the reported MDLs can not be verified, the data validator calculates and reports MDLs using half of the concentration of the lowest associated calibration standard for the respective analyte. MDLs higher than those calculated as described in section 3.9.2 may be reported with approval of the DVRW Group Leader. The results may require addition or deletion of qualifiers based on the corrected MDLs.

During DV the ten percent rule is applied to all reported results and MDLs. That is if the reported result or MDL is within ten percent of the data validator's calculated value, then the value reported by the laboratory is reported (not corrected) in the final analytical report.

The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgement. It is up to the data validator's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, all affected data are qualified as not detected "U" or unusable "R".

Data is qualified as described in section 3.5 if any blank contamination has been identified.

4.0 RESPONSIBILITIES

4.1 Data Validator

- Verifies that the laboratory is in compliance with the method, that all documents are included and complete (see Appendices A and B), that all obligations pertaining to the method and reporting requirements are met, and that all requested analyses were performed
- Responsible for performing DV of the VOC data package according to this SOP and the applicable analytical method, completing the appropriate checklists and data assessment forms, and providing a written report of all data and QC anomalies and qualifications
- Responsible for immediately informing the DVRW Group Leader of any major non-compliance of the method that may affect the usability of the data
- Responsible for preparing a written log of all communications, including all verbal communications, with the laboratory

4.2 Data Validation and Report Writing Group Leader

- Responsible for periodically updating this DV SOP to reflect all procedural changes
- Periodically audits the review process to ensure compliance with review requirements
- Responsible for communication of any major non-compliance of the method that may affect the usability of the data to the Task Leader of the project and the Analytical Section Leader. If the usability of the data is due to the subcontracted laboratory's non-compliance to the method specified, then the DVRW Group Leader is responsible for notifying the purchasing department of adjustments to the payment to the subcontract laboratory.
- Concurs with the data validator's comments and qualifications by reviewing the final report, DV data assessment forms and qualified result tables, and signing the final analytical report check list and the peer review document control sheet.

4.3 Task Leader

- Responsible for verifying that all sample numbers and locations are correct in the final result tables and chain of custody. The Task Leader verifies that all requested analyses were performed on all samples and that the sample results are reported only once. Additionally, Task Leader verifies the site name and location, Work Assignment Manager, U.S. EPA work assignment (WA) number and Lockheed Martin WA number.

4.4 Analytical Section Leader

- Ensures adherence to this SOP prior to authorizing the release on analytical deliverables. The Analytical Section Leader concurs with the data validator's comments and qualifications by signature of the title page of the analytical report and on the peer review document control sheet

- Initiates updating of this SOP on a timely basis.

4.5 Quality Assurance Officer

- Responsible for ensuring adherence to this SOP by conducting routine audits of analytical reports and check records.

- Reviews and approves any revisions to this SOP.

APPENDIX A
Figures
SOP #1015
January 2004

FIGURE 1. Deliverable Checklist for VOC GC/MS Analyses

All the following information must be included in the data package.
(Please check all blanks and submit the list together with the report)

_____ Legible print on all pages of report, including instrument and raw data printouts.

_____ Case narrative

_____ Method numbers and any modifications

_____ Chain of custody (signed with date of receipt)

_____ All sample preparation logs (initial and re-extractions), if applicable

_____ Documentation of the composition, concentration and the volume of the spike solutions (surrogate, calibration standards, matrix spike, laboratory control standards and internal standards) used on the extraction and injection log.

_____ Worksheet of % solid or % moisture

_____ Analysis logs for all instruments used for analyses (For VOA analysis, the sample size used for analysis must be clearly documented)

_____ Copies of all manual integrations performed on all compounds (including internal std and surrogates).

Tuning and Mass Calibration
(for all instruments used for analyses, dilutions, and initial/continuing calibrations)

_____ Summary table _____ Ion chromatogram

_____ Spectrum _____ Mass listing

Initial Calibration Data - in order by instrument, if more than one instrument used

_____ Analysis logs

_____ Summary table of calibration results

_____ Chromatograms for all calibration standards

_____ Quantitation reports for all calibration standards

FIGURE 1. Deliverable Checklist for VOC GC/MS Analyses (cont'd)

Continuing Calibration Data - in order by instrument, if more than one instrument used (continuing calibration for sample dilution should also be submitted)

_____ Summary table of % difference of relative response factors

_____ Ion chromatograms

_____ Quantitation reports

_____ Internal standard area summary table for all Method Blanks, sample and dilution analyses, MS/MSDs and all associated QC analyses.

Method Blank Data - in chronological order(for VOA, each 12-hour period, for each GC/MS system)

_____ Result summary table (including detection limits)

_____ Surrogate recovery table

_____ Ion Chromatograms

_____ Quantitation reports

_____ Target compound spectra, which should include:

- _____ Raw target compound spectra
- _____ Enhanced or background subtracted spectra
- _____ Laboratory generated target compound standard spectra

_____ Tabulated results for Tentatively Identified Compounds, if applicable

_____ GC/MS library search spectra for Tentatively Identified Compounds, if applicable

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

_____ Spike recovery summary table (including sample concentrations, spiked concentrations, MS/MSD recovered concentrations, percent recoveries of MS/MSD, and RPDs)

_____ Ion Chromatograms

_____ Quantitation reports

_____ Surrogate recovery table

FIGURE 1. Deliverable Checklist for VOC GC/MS Analyses (cont'd)

Sample Data

_____ Result summary table (including a per sample method detection limit taking into account dilutions, sample size, extraction volumes, and % solids).

_____ Surrogate recovery table

_____ Ion Chromatograms (including dilutions)

_____ Quantitation reports (including dilutions)

_____ Target compound spectra, which should include:

- _____ Raw target compound spectra
- _____ Enhanced or background subtracted spectra
- _____ Laboratory generated target compound standard spectra

_____ Tabulated results for Tentatively Identified Compounds, if applicable

_____ GC/MS library search spectra for Tentatively Identified Compounds, if applicable

_____ _____
Signature Date

DATA VALIDATION PROCEDURES FOR ROUTINE VOLATILE ORGANIC ANALYSIS

FIGURE 2. VOC DATA ASSESSMENT FORM

PROJECT NAME_____ **WA#**_____ **PACKAGE#**_____**LAB**_____
 # OF SAMPLES_____**MATRIX**_____**CHAIN OF CUSTODY #**_____

DATA ASSESSMENT: SERAS method detection limits (MDL) are obtained from MDL studies performed by the laboratory (required yearly for each instrument and for each matrix) and kept on file. Subcontracted laboratories must provide the data validator with copies of MDL studies for reported MDLs derived by this method. Alternately, both labs may report an MDL calculated as half of the concentration of the lowest associated calibration standard for the respective analyte. The only time all sample compound MDLs are adjusted using a dilution factor is if a sample is not analyzed undiluted or the undiluted analysis exhibits significant matrix interference making all results unusable (as determined by the analyst or data validator), and an acceptable diluted sample analysis is performed; all sample compound MDLs are adjusted using the dilution factor. MDLs are never adjusted by the dilution factor if the dilution analysis is performed to bring an analyte's concentration within the calibration range. All MDLs are reported to 2 significant figures. All Results >10 are rounded to 2 significant figures and <10 to 1 significant figure, rounding down all values $\leq$4 and up all values $\geq$5 (i.e., 42.54 is rounded to 43 and 0.0245 is rounded to 0.02). Concentrations less than 25% of the method detection limit (MDL) are not be reported. The method detection limit (MDL) is corrected for dilution and percent solids (if applicable) for each sample as follows:

$$\text{Sample specific MDL} = \frac{MDL}{S} \times DF$$

where: S = (% solids)/100 (S = 1.0 for liquid samples) DF = Dilution factor (including changes in sample size)

The following qualifiers are always used in reporting blank and sample target compound and TIC results in the final analytical report. These laboratory qualifiers, when applied as described below, are the only ones used in the results tables of the final analytical report. No qualifiers are applied to QC tables. Generally, the data validator enters these qualifiers in red in the data validator's check records. All other qualifiers are entered in green in the data validator's check records. All other qualifiers discussed in this form only appear in the data validator's check records and/or in a data validation report requested by the client. This is done so the report writer can differentiate qualifiers added to the result table for the final analytical report from those which only appear in the data validator's check records and/or a data validation report requested by ERTC.

J - Indicates an estimated value when a target compound is identified using mass spectral data based on the identification criteria, but the concentration is less than the sample method detection limit. This flag is used when estimating a concentration for tentatively identified compounds where a response of 1.0 is assumed.

B - This flag is used when a reportable concentration of the same target compound is found in a sample and the associated method blank. The target compound result of the method blank and all associated samples are flagged with a "B".

E - This flag identifies target compounds with concentrations exceeding the associated initial calibration range. If target compounds have a response > the associated initial calibration range, the sample or extract must be diluted and re-injected according to the specifications of the method. All target compounds with concentrations > the associated initial calibration range are considered estimated and flagged with an "E".

U - Denotes that the compound was not detected.

No quantitation results of zero "0" are reported in any result or QC table. A "U" indicating that the compound was not detected appears in all tables for all target compounds not detected. Concentrations less than 25% of the method detection limit (MDL) are not be reported. Verify that only the data qualifier symbols J, B, and E are used in the result tables and that no qualifiers are added to any QC table.

Verify that all calibration and spike standard lot numbers are recorded on the respective injection or extraction log and that all SERAS standards are prepared and used according to ERTC/SERAS SOP 1012. Inform the Data Validation and Report Writing Group Leader of deviations from the ERTC/SERAS Preparation of Standard Solutions SOP 1012.

Validator's Signature:_____**Date:**____/____/____ Rev. 1/04

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

1. CONTAINERS, PRESERVATIVE, STORAGE and HOLDING TIME: Water samples should be collected in glass containers completely filled with no air bubbles present and fitted with a Teflon®-lined cap. SERAS does not preserve water samples at pH <2 (with H_2SO_4 or HCL) for both in-house and subcontracted (SW-846 Method 8260B) analysis. SW-846 requires that water samples be preserved at pH <2 at the time of collection. Soil samples should be collected in wide mouth glass containers completely filled with minimal head space present and fitted with a Teflon®-lined cap. All samples must be protected from light and refrigerated at 4°C (±2°C) from the time of collection to the time of analysis.

If the unpreserved water or the SERAS VOC method soil holding time of 7 days, or the 8260B preserved water and soil holding time of 14 days was exceeded, then the samples affected and the amount of time the holding time was exceeded are noted in the case narrative. Soil samples analyzed at SERAS are only qualified if they exceed a 14 day holding time. If the unpreserved water holding time of 7 days prior to analysis is exceeded or the soil and preserved water holding time of 14 days prior to analysis is exceeded, all positive results are considered estimated and flagged (J) and all non-detects are flagged (UJ). If the holding time prior to analysis was exceeded, but less is than two times the respective holding time (14 days for 7 day holding times and 28 days for 14 day holding time); professional judgement is used to determine if all non-detects should be considered unusable and flagged ®). If the holding time prior to extraction was exceeded by more than two times the respective holding time (14 days for 7 day holding times and 28 days for 14 day holding time); all non-detects are considered unusable and flagged ®).

Professional judgement is used to determine if sample results should be qualified if the sample containers and storage differ from the ones specified.

The following action was taken on the following samples and analytes:

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

2. BLANK CONTAMINATION: A method blank is required for each 12 hour group of samples. First evaluate the method blank against all associated samples including trip, field, and rinsate blanks. Trip blank, rinsate blank, and field blank are evaluated against the method blank utilizing the same criteria as the samples. If contaminants are present in a method blank, then the following action is taken: If the concentration of a given analyte in a sample is less than five times the concentration of that analyte in the associated method blank, (10 times for common laboratory contaminants methylene chloride, acetone or 2-butanone) the presence of that analyte in the sample is considered not detected (U), flagged with a green "U" and the "B" flag is crossed out with a green line and the concentration is elevated to the concentration found in the sample. These actions are noted in the case narrative.

Repeat the action described above when evaluating the trip blanks, field blanks, and rinsate blanks if the associated samples are in the same concentration units [i.e., liquid rinsate blank results (µg/L) can not be evaluated against solid sample results (µg/kg)] and the relationship between the sample and the rinsate blank is understood (i.e., both are the same volume of water pulled through a bailer).

If a common laboratory contaminant is present in a SERAS method blank at concentrations > 5 times the MDL or if any other analyte is present at concentrations > the MDL in a SERAS or 8260B method blank, the data validator notes in the case narrative that the method criteria was exceeded.

The following samples had analytes qualified as non-detects (U) for these reasons:

A) Method blank contamination:

B) Trip blank contamination:

C) Field or rinsate blank contamination (samples with locations labeled "water blanks" or "distilled water blanks" are validated like any other sample):

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

3. MASS SPECTROMETER TUNING: This criteria must be met in all circumstances. The tuning standard for volatile organics is bromofluorobenzene (BFB) and is required for each 12-hour group of samples. If any standards, blanks or samples (not QC samples such as MS/MSDs, BS/BSDs and LCSs) were analyzed more than 13 hours after the instrument tune or the mass calibration is in error, the data for the affected samples, blanks or standards are rejected and flagged ®). If any standards, blanks or samples (not QC samples such as MS/MSDs, BS/BSDs and LCSs) were analyzed between 12 and 13 hours after the associated instrument tune, all data are considered estimated and flagged (J).
Note: Currently, only the in-house SERAS method analysis of VOC in air (carbon tubes), PAH in air (XAD tubes) and methyl parathion (all matrices) adhere to a 24-hour clock.

4. CALIBRATION RELATIVE RESPONSE FACTOR: The relative response factor (RRF) is a measure of the instrument's response to specific chemical compounds. The RRF for the Target Compound List (TCL) must be $\geq$ 0.050 in both the initial (average RRF) and continuing calibrations. However, Method 8260B requires the system performance check compounds (SPCC) meet the minimum mean RRFs of:

Chloromethane	0.10	Chlorobenzene	0.30
1,1-Dichloroethane	0.10	1,1,2,2-Tetrachloroethane	0.30
Bromoform	0.10		

A value less than the required RRF indicates a serious detection and quantitation problem (poor sensitivity). Positive results for an analyte with a RRF less than the specified limit are qualified as estimated (J) all non-detects for that compound are rejected ®).

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

5. INITIAL CALIBRATION PERCENT RELATIVE STANDARD DEVIATION (%RSD):
SERAS Analyses: The %RSD must be ≤ 30.0% for all compounds. Optionally, a linear or non-linear equation with a correlation coefficient ®) ≥0.99 may be used.

Method 8260B Analyses: Requires all compounds to have a percent relative standard deviation (%RSD) ≤ 15.0% with the exception of individual calibration check compounds (CCC) which must be <30%RSD. Use of a linear or non-linear (e.g., a polynomial) equations for non-CCC target compounds having a %RSD >15.0% with a correlation coefficient (r) ≥0.99 is allowed. In these cases the analyst should not force the line through the origin, instead, the intercept is calculated from the five or six data points. If any rs are < 0.99, then the validator must calculate the %RSD of each compound that fails and qualify the data using %RSD criteria. The CCC compounds are:1,1-dichloroethene, chloroform, 1,2-dichloropropane, ethylbenzene, toluene and vinyl chloride.

If any analyte has a %RSD > 30.0%, or for Method 8260B non-CCC compounds with a %RSD > 15% (and a linear or non-linear equation is not used), all positive results for that analyte in samples and blanks associated with the initial calibration are considered estimated (J); no action is required for non-detects when the %RSD is <50.0%. When the %RSD is > 50.0 but ≤ 90.0%, all non-detects are considered estimated and flagged (UJ). If the %RSD is > 90.0%, then non-detects are considered unusable and flagged "R".

If Method 8260B non-CCC compounds were quantitated using a linear or non-linear (e.g., a polynomial) equation, then verify that the correlation coefficients ®) are ≥0.99 and that the line was not forced through zero (0). Verify the linear equation of one compound by calculating the equation and R with spreadsheet software using the standard concentrations (independent variable x) and area responses (dependent variable y) for that compound. Recalculate equations and all associated results if the y intercept was forced through the origin. Currently, non-linear (e.g., a polynomial) equations and their "r's" are accepted without verification. If any "r" is < 0.99, then the validator must calculate the %RSD of each compound that fails and qualify the data using %RSD criteria.

The use of a secondary ion for quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, the laboratory must document the reasons in the case narrative. All anomalies are noted in the case narrative. Contact the laboratory and obtain any calibration or spike standard lot numbers not recorded on the respective injection or extraction log. Inform the Data Validation and Report Writing Group Leader of deviations from the SERAS Preparation of Standard Solutions SOP 1012.

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

6. CONTINUING CALIBRATION PERCENT DIFFERENCE (%D): The %D must be $\leq$ 25.0%. If linear or non-linear (e.g., a polynomial)) equations are used, the percent difference between the certified and recovered concentration of the continuing calibration standard must be $\leq$ 25.0%. If any analyte has a %D for its response factor or continuing calibration standard (in the case of linear and non-linear equations) of $>$ 25.0%, all positive results for the analyte in associated samples and blanks are considered estimated "J". For %D values > 25.0 but $\leq$ 50.0%, no action is taken for non-detects, for %D values > 50.0% but $\leq$ 90.0% non-detects are qualified (UJ), and for %D values > 90.0% non-detects are considered unusable "R".

.

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

7. SURROGATES: If any samples, blanks, matrix spikes or matrix spike duplicates were not spiked with surrogate compounds or were spiked with incorrect surrogates, all data are usable for screening purposes only. Additionally, all data for samples, matrix spikes and matrix spike duplicates associated with a method blank that does not contain any surrogate compounds are usable for screening purposes only.

If surrogate recoveries are out of specification in the initial analysis, but meet criteria on reanalysis, the reanalysis results are reported. If surrogate recoveries are out of specification in the initial analysis and are also out of specification on reanalysis, this may be indicative of sample matrix interference effects. The laboratory is not required to perform any additional analyses on that particular sample. The data from either analysis may be submitted by the laboratory.

When a surrogate has a %RSD or %D that exceeds QC limits, the surrogate is considered to be outside the % recovery criteria for all associated samples. The associated sample data are qualified accordingly.

If surrogate recoveries are out of specification in the initial and reanalysis the following actions are taken:

- Samples - If one or more surrogate percent recoveries is out of specification and are > 10%, all positive results are qualified as estimated and flagged (J). If one or more surrogate percent recoveries is less than the lower acceptance limit, but > 10%, all non-detected results are qualified as estimated (UJ). If one or more surrogate percent recoveries is less than 10%, all positive results are qualified as estimated (J) and all undetected results are qualified as unusable "R".

- Method blanks - If one or more surrogates are out of specification, all method blank data, QC samples and associated sample data are reviewed and qualified using professional judgement.

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

8. INTERNAL STANDARDS PERFORMANCE: If internal standard EICP areas or RT are out of specification on initial analysis, but meet criteria on reanalysis, the results of the reanalysis are reported. If internal standard EICP areas or RT are out of specification on initial analysis and also out of specification on reanalysis, the sample may be exhibiting a matrix effect. The laboratory does not have to perform any additional analyses of the particular sample. The data for either analysis may be submitted by the laboratory. A full data validation review must be conducted on either set of data. If the internal standards recommended by the method or equivalent (as defined by the method) were not used, the laboratory must be contacted and corrected action taken; the data validator uses professional judgement in qualifying or rejecting data.

If an internal standard retention time varies by more than 0.5 minute the chromatographic profile for associated samples must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the validator may consider rejecting some or all of the analytical results associated with that internal standard.

If internal standard EICP areas or RTs are out of specification the following action must be taken:

- For each internal standard that does not meet criteria, all positive results for compounds quantified using that particular internal standard are considered estimated (J).
- If the internal standard area exceeds QC limits and is $\geq$ 25.0% of the respective internal standard EICP area in the associated calibration standard, then non-detects for compounds quantified using that particular internal standard are considered estimated and flagged (UJ).
- If the internal standard area is < 25.0% of the respective internal standard EICP area in the associated calibration standard (UJ), then non-detects for compounds quantified using that particular internal standard are considered unusable and flagged "R".
- If the RT exceeds QC limits, then review the chromatogram and associated spectra to determine if any false positives or negatives exist and use professional judgement to determine if positive results should be estimated and if negative results should be estimated or rejected.

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

9. COMPOUND IDENTIFICATION: If any required deliverables are missing (i.e., sample chromatograms, sample mass spectra, target compound not reported, etc.), the laboratory must be contacted for delivery of the missing information. If the information is not provided, the data validator uses professional judgement in qualifying or rejecting the results. These actions must be documented in the data validation case narrative and the DVRW group leader must be immediately informed.

If some requested or required target compounds are not reported in the result tables, and the lab cannot provide results and the required documentation for these compounds , then the unreported compounds must be documented in the data validation case narrative and the DVRW group leader must be immediately informed.

If a sample concentration exceeds the associated initial calibration range or a chromatogram reveals system saturation, and a dilution analysis was not conducted, the chromatogram and associated quantitation report must be closely examined. All target compounds with quantitation values exceeding the upper concentration of the associated initial calibration curve are considered estimated and flagged "E".

If the relative retention time (RRT) of a reported target compound is not within ±0.06 RRT units of the reference standard, the mass spectrum of the affected sample must be closely examined (i.e., single ion scans may be requested). If the sample mass spectrum matches the reference standard mass spectrum, a semi-qualitative identification (some isomers or similar non-target compounds may produce like spectra) may be made. All results are considered estimated and flagged "J". The excessive RRT shift, the fact that a semi-qualitative identification has been performed and any qualifications or rejections by the data validator must be noted in the case narrative.

If it is determined that incorrect identifications of target compounds were made all affected data are corrected by the data validator and noted in the case narrative. This must include the reasons for making a change in the qualitative identification.

An effort should be made ro ensure that no duplicate reporting of the same compound occurs (i.e., a BNA target compound which is identified as a VOC TIC).

Guidelines for making tentative identification:

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

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

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

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

If all of the above conditions for a compound are met and if the Q value (software generated goodness of fit criterion) of the search is ≥80%, that compound will be reported as a tentatively identified compound (TIC).

If the TIC Q value is < 80% or the mass spectral interpretation specialist indicates that no valid tentative identification can be made, the compound should be reported as *unknown*. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown organic acid type, unknown chlorinated compound). The molecular weight should be included in the TIC report if it can be distinguished from the library search. Only one compound or unknown is reported per RT and no siloxanes (column bleed compounds) or carbon dioxide are reported.

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

If the laboratory failed to conduct a nontarget library search for all applicable nontarget peaks on a chromatogram, no action is taken. The deficiency is noted in the case narrative.

If incorrect identifications of nontarget compounds were made, all affected data are corrected and the actions noted in the case narrative including the reasons for making a change in the qualitative identification.

If spot check calculations of compound quantitation do not match the concentrations reported by the laboratory or if incorrect quantitation ions were used, then the laboratory must be contacted and the quantitation problem resolved.

If the result tables have improperly used or are missing data qualifiers, then the correct laboratory data qualifier symbols J, B, and E, as described in page 1, are added to, and any improperly used qualifiers, deleted from the result tables. No qualifiers are added to any QC tables and any added by the lab are removed. Concentrations less than 25% of the method detection limit (MDL) are not be reported. Additionally, all reported quantitation results of zero "0", in all result and QC tables, are replaced with a "U" indicating that the compound was not detected.

If the laboratory reported incorrect method detection limits (MDLs) or reported MDLs that cannot be verified with a MDL study, the laboratory must be contacted in order to resolve the discrepancies in the MDLs. If the reported MDLs cannot be verified, the data validator calculates and reports MDLs using half of the concentration of the lowest associated calibration standard for the respective analyte. MDLs higher than those calculated as described in the data assessment section may be reported with approval of the DVRW group leader. The results may require addition or deletion of qualifiers based on the corrected MDLs.

During data validation the ten percent rule is applied to all reported results and MDLs. If the reported result or MDL is within ten percent of the data validator's calculated value, then the value reported by the lab is reported (not corrected) in the final analytical report.

The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgement. It is up to the data validator's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, all affected data is qualified as not detected (U) or unusable ®) using professional judgement.

All TIC results are qualified as estimated concentrations.

FIGURE 2. VOC DATA ASSESSMENT FORM (cont'd)

10. MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): No action is taken on MS/MSD data alone to qualify or reject an entire group of samples. The results of the matrix spike and matrix spike duplicate can be used in conjunction with other QC criteria to aid the validator in applying more informed professional judgement when necessary. Generally, non-SERAS MS/MSD samples are not reported unless requested by .the Task Leader.

If a SERAS sample matrix spike or matrix spike duplicate have 0% Recovery, then the result for this compound in the sample selected for spiking is considered estimated (J) for positive results and unusable (R) for non-detects. All MS/MSD concentrations must be in the same units used for reporting sample results.