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USEPA CONTRACT LABORATORY PROGRAM

NATIONAL FUNCTIONAL GUIDELINES FOR ORGANIC DATA REVIEW

MULTI-MEDIA, MULTI-CONCENTRATION (ILMO 1.0) AND LOW CONCENTRATION WATER (OLCO 1.0)

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Multi-Media, Multi-Concentration (OLM01.0)

and

Low Concentration Water (OLC01.0)

DRAFT

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INTRODUCTION

This document is designed to offer guidance on EPA Contract Laboratory Program (CLP) analytical data evaluation and review. In some applications it may be used as a Standard Operating Procedure (SOP). In other, more subjective areas, only general guidance is offered due to the complexities and uniqueness of data relative to specific samples. For example, areas where the application of specific SOPs are possible are primarily those in which definitive performance criteria are established. These criteria are concerned with specifications that are not sample dependent; they specify performance requirements that should fully be under a laboratory's control. These specific areas include blanks, calibration standards, performance evaluation standard materials, and instrument performance checks (tuning).

These Guidelines have been updated to include the requirements in the Statement of Work (SOW) for Organic Analysis Multi-Media Multi-Concentration (SOW OLM01.0), and the SOW for Low Concentration Water Organic Analysis (SOW OLC01.0). *To ensure that the data review guidelines that are unique to the Low Concentration Water SOW are easily identified, these requirements and procedures are presented in italics and contained within brackets ([ ]) throughout the document.*

This update includes changes to instrument performance checks (formerly referred to as tuning) including changes to instrument performance checks and calibration criteria as a result of the Response Factor Workgroup. Minor revisions to the Data Qualifier Definitions from the previous National Functional Guidelines are also included in this document.

This document is intended to assist in the technical review of analytical data generated through the CLP. Determining contract compliance is not the intended objective of these guidelines or the regional data review process. The data review process provides information on analytical limitations of data based on specific quality control (QC) criteria. In order to provide more specific useability statements, the reviewer must have a complete understanding of the intended use of the data. For this reason, it is recommended that whenever possible the reviewer obtain usability issues from the user prior to reviewing the data. When this is not possible, the user should be encouraged to communicate any questions to the reviewer.

At times, there may be an urgent need to use data which do not meet all contract requirements and technical criteria. Use of these data does not constitute either a new requirement standard or full acceptance of the data. Any decision to utilize data for which performance criteria have not been met is strictly to facilitate the progress of projects requiring the availability of the data. A contract laboratory submitting data which are out of specification may be required to rerun samples or resubmit data even if the previously submitted data have been utilized due to urgent program needs; data which do not meet specified requirements are never fully acceptable. The only exception to this requirement is in the area of requirements for individual sample analysis; if the nature of the sample itself limits the attainment of specifications, appropriate allowances must be made. The overriding concern of the Agency is to obtain data which are technically valid and legally defensible.

Appendix A is based on the Multi-media Multi-concentration SOW and contains appropriate contractual requirements and equations for verifying various calculations. Appendix B contains the corresponding contractual requirements and equations from the Low Concentration Water SOW. Appropriate equations are presented for easy reference and to allow the reviewer to verify calculations as needed. Contractual requirements are provided to facilitate comparisons with the technical requirements. For each analytical fraction, Appendix C contains a table comparing contractual requirements of the Multi-media, Multi-concentration with those of the Low Concentration Water SOWs. Appendix D contains proposed guidance for Tentatively Identified Compounds (VOA and SV), and Appendix E contains a glossary of commonly used terms.

The data review should include comments that clearly identify the problems associated with a Case or Sample Delivery Group and to state the limitations of the data. Documentation should include the sample number, analytical method, extent of the problem, and assigned qualifiers.

A data review narrative generally accompanies the laboratory data forwarded to the intended data recipient (client) or user to promote communication. A copy of the data review narrative should be submitted to the CLP Quality Assurance Coordinator (QAC), the Regional CLP Technical Project Officer (TPO) assigned oversight responsibility for the laboratory producing the data, and the Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV).

It is the responsibility of the data reviewer to notify the appropriate Regional CLP TPO concerning problems and deficiencies with regard to laboratory data. If there is an urgent requirement, the TPO may be contacted by telephone to expedite corrective action. It is recommended that all items for TPO action be presented at one time.

PRELIMINARY REVIEW

In order to use this document effectively, the reviewer should have a general overview of the sample delivery group (SDG) or case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analysis are essential information. Background information on the site is helpful but often this information may be difficult to locate. The site manager is the best source for answers to questions or further direction.

Contract Compliance Screening (CCS) is a source of summarized information regarding contract compliance. If available, it can be used to alert the reviewer to problems in the SDG data package.

Sample cases (SDGs) routinely have unique samples which require special attention by the reviewer. These include field blanks, field duplicates, and performance audit samples which need to be identified. The sampling records should provide:

1. Project Officer for site.

2. Complete list of samples with information on:

    a. sample matrix,
    b. field blanks,
    c. field duplicates,
    d. field spikes,
    e. QC audit samples,
    f. shipping dates, and
    g. laboratories involved.

The chain-of-custody record includes sample descriptions and date(s) of sampling. The reviewer must take into account lag times between sampling and receipt for analysis when assessing technical sample holding times.

The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, and unusual events should be found in the SDG Narrative.

The SDG Narrative for the sample data package must include a Laboratory Certification Statement (exactly as stated in the SOW), signed by the laboratory manager or his designee. This statement authorizes the validation and release of the sample data results. In addition, the laboratory must also provide comments in the SDG narrative describing in detail any problems encountered in processing the samples in the data package.

For every data package, the reviewer must verify that the laboratory certification statement is present, exactly stated as in the SOW (i.e., verbatim to the statement in the SOW), and signed by the Laboratory Manager or designee. The reviewer must further verify that the data package is consistent with the laboratory's certified narrative. Also, the reviewer should check the comments provided in the narrative to determine if they are sufficient to describe and explain the associated problem.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process. If the Regions choose to use additional qualifiers, a complete explanation of those qualifiers should accompany the data review.

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

VOLATILE DATA REVIEW

**** Data review guidelines that are unique to data generated through the Low Concentration Water SOW are contained within brackets ([ ]) and written in italics. ****

The volatile data requirements to be checked are listed below

I. Technical Holding Times (CCS - Contractual holding times only)

II. GC/MS Instrument Performance Check (CCS)

III. Initial Calibration (CCS)

IV. Continuing Calibration (CCS)

V. Blanks

VI. System Monitoring Compounds (Surrogate Spikes) (CCS)

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Laboratory Control Samples (CCS)

IX. Regional Quality Assurance and Quality Control

X. Internal Standards (CCS)

XI. Target Compound Identification

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XIII. Tentatively Identified Compounds

XIV. System Performance

XV. Overall Assessment of Data

NOTE: "CCS" indicates that the contractual requirements for these items will also be checked by CCS; CCS requirements are not always the same as the data review criteria.

I. Technical Holding Times

A. **Review Items:** Form I VOA *[Form I LCV]*, EPA Sample Traffic Report and/or chain-of-custody, raw data, and SDG Narrative.

B. **Objective**

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of analysis.

C. **Criteria**

Technical requirements for sample holding times have only been established for water matrices. The holding times for soils (and other non-aqueous matrices such as sediments, oily wastes, and sludge) are currently under investigation. When the results are available they will be incorporated into the data evaluation process. Additionally, results of holding time studies will be incorporated into the data review criteria as the studies are conducted and approved.

The holding time criteria for water samples, as stated in the current 40 CFR Part 136 (Clean Water Act) is as follows:

> For non-aromatic volatile compounds in cooled (@ 4°C) water samples, the maximum holding time is 14 days from sample collection.
>
> Maximum holding times for purgeable aromatic hydrocarbons in cooled (@ 4°C ± 2°C), acid-preserved (pH 2 or below) water samples is 14 days from sample collection.
>
> Water samples that have not been maintained at 4°C (± 2°C) and preserved to a pH of 2 or below should be analyzed within 7 days from sample collection. If insufficient ice is used to ship samples, the laboratory may receive samples with no ice left in the cooler. Under these circumstanes, the temperature of the samples may exceed 4°C.

It is further recommended that volatile compounds in properly preserved non-aqueous samples be analyzed within 14 days of sample collection.

The contractual maximum holding times, which differ from the technical maximum holding times, state that water and soil samples are to be analyzed within 10 days from the validated time of sample receipt (VTSR) at the laboratory.

D. **Evaluation**

Technical holding times are established by comparing the sampling dates on the EPA Sample Traffic Report with dates of analysis on Form I VOA *[Form I LCV]* and the raw data. Information contained in the complete SDG file (formerly called the purge file) should also be considered in the determination of holding times. Verify that the analysis dates on the Form Is and the raw

data/SDG file are identical. Examine the sample records to determine if samples were preserved. If adequate documentation on sample preservation is not available, contact the sampler. If the sampler cannot be contacted, then it must be assumed that the samples are unpreserved. If there is no indication in the SDG narrative or the sample records that there was a problem with the samples (e.g., samples not maintained @ 4°C or containing headspace in the samples), then the integrity of samples can be assumed to be good. If it is indicated that there were problems with the samples, then the integrity of the sample may have been compromised and professional judgement should be used to evaluate the effect of the problem on the sample results.

E. Action

1. If technical holding times are exceeded, document in the data review narrative that holding times were exceeded and qualify the sample results as follows (also see Table 1):

   a. If there is no evidence that the samples were properly preserved and the technical holding times exceeded 7 days, qualify positive results for aromatic compounds with "J" and sample quantitation limits with "UJ". Use professional judgement to determine if and how non-aromatic volatile compounds should also be qualified.

   b. If the samples were properly preserved but the technical holding times exceeded 14 days, qualify positive results with "J" and sample quantitation limits with "UJ".

Table 1. Qualification of Volatile Analytes Based on Technical Holding Times

MATRIX	PRESERVED	> 7 DAYS	> 14 DAYS
Water	No	All Aromatics*	All Compounds
	Yes	None	All Compounds
Non-aqueous	No/Yes	Professional Judgement	Professional Judgement

* Reviewer should use professional judgement to determine if data for additional compounds require qualification.

2. If technical holding times are grossly exceeded (e.g., by greater than two times the required time for volatiles) either on the first analysis or upon re-analysis, the reviewer must use professional judgement to determine the reliability of the data and the effects of additional storage on the sample results. Should the reviewer determine that qualification is necessary, non-detected volatile target compounds may be qualified unusable (R). Positive results are considered approximates and are qualified with "J".

3. Due to limited information concerning holding times for non-aqueous samples, it is left to the discretion of the data reviewer to apply water holding times or other information that is available.

4. Whenever possible, the reviewer should comment on the effect of the holding time exceedance on the resulting data in the data review narrative.

5. When contractual and/or technical holding times are grossly exceeded, this should be noted for TPO action.

6. The reviewer should also be aware of the scenario in which the laboratory has exceeded the technical holding times, but met contractual holding times. In this case, the data reviewer should notify the Regional TPO (where samples were collected) and/or RSCC that shipment delays have occurred so that the field problem can be corrected. The reviewer may pass this information on to the laboratory's TPO, but should explain that contractually the laboratory met the requirements.

II. GC/MS Instrument Performance Check

A. **Review Items:** Form V VOA *[Form V LCV]*, BFB mass spectra and mass listing.

B. **Objective**

Gas chromatograph/mass spectrometer (GC/MS) instrument performance checks (formerly referred to as tuning) are performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. **Criteria**

The analysis of the instrument performance check solution must be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, bromofluorobenzene (BFB) for volatile analysis, must meet the ion abundance criteria given below.

Bromofluorobenzene (BFB)

m/z	ION ABUNDANCE CRITERIA
50	8.0 - 40.0% of m/z 95
75	30.0 - 66.0% of m/z 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of m/z 95
173	Less than 2.0% of m/z 174
174	50.0 - 120.0% of m/z 95
175	4.0 - 9.0% of mass 174
176	93.0 - 101.0% of m/z 174
177	5.0 - 9.0% of m/z 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 percent that of m/z 95.

D. **Evaluation**

1. Compare the data presented for each Instrument Performance Check (Form V VOA *[Form V LCV]*) with each mass listing submitted to ensure the following:

   a. Form V VOA *[Form V LCV]* is present and completed for each 12-hour period during which samples were analyzed.

b. The laboratory has not made transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.

c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.

d. The laboratory has not made calculation errors.

2. Verify from the raw data (mass spectral listing) that the mass assignment is correct and that the mass listing is normalized to m/z 95.

3. Verify that the ion abundance criteria was met. The criteria for m/z 173, 176, and 177 are calculated by normalizing to the specified m/z.

4. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the BFB spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged and background subtraction must be accomplished using a single scan prior to the elution of BFB.

NOTE: All instrument conditions must be identical to those used in the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the quality assurance objectives and are therefore unacceptable.

E. Action

1. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, then the reviewer must use professional judgement to assess the data. The laboratory's TPO should be notified.

3. If mass assignment is in error (such as m/z 96 is indicated as the base peak rather than m/z 95), classify all associated data as unusable (R).

4. If ion abundance criteria are not met, professional judgement may be applied to determine to what extent the data may be utilized. Guidelines to aid in the application of professional judgement to this topic are discussed as follows:

The most important factors to consider are the empirical results that are relatively insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96, 174/175, 74/176, and 176/177 ratios. The relative abundances of m/z 50 and 75 are of lower importance.

5. Decisions to use analytical data associated with BFB instrument performance checks not meeting contract requirements should be clearly noted on the data review narrative.

6. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described in II.D.4, then additional information on the instrument performance checks should be obtained. If the techniques employed are found to be at variance with the contract requirements, the performance and procedures of the laboratory may merit evaluation. Concerns or questions regarding laboratory performance should be noted for TPO action. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the BFB peak), then this should be noted for TPO action.

III. Initial Calibration

A. **Review Items:** Form VI VOA *[Form VI LCV]*, quantitation reports, and chromatograms.

B. **Objective**

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the volatile target compound list (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.

C. **Criteria**

1. Initial calibration standards containing both volatile target compounds and system monitoring compounds are analyzed at concentrations of 10, 20, 50, 100, and 200 ug/L at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.

   [For data generated through the Low Concentration Water SOW: Initial calibration standards containing both volatile target compounds and surrogate are analyzed at concentrations of 1, 2, 5, 10, and 25 ug/L for non-ketones and 5, 10, 25, 50, and 125 ug/L for ketones at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated BFB tuning check.]

2. Separate initial calibrations must be performed for water samples (or medium level soil samples) and for low level soil samples. The calibration for water samples and medium level soil samples is performed with an unheated purge and the calibration for low level soil samples is performed with a heated purge.

3. Initial calibration standard Relative Response Factors (RRFs) for all volatile target compounds and system monitoring compounds (surrogates) must be greater than or equal to 0.05. (Contractual initial calibration RRF criteria are listed in Appendix A *[Appendix B])*

4. The Percent Relative Standard Deviation (%RSD) from the initial calibration must be less than or equal to 30.0% for all compounds.

D. **Evaluation**

1. Verify that the correct concentration of standards were used for the initial calibration (i.e., 10, 20, 50, 100, and 200 ug/L for water).

   [Verify that the correct concentration of standards were used for the initial calibration (i.e., 1, 2, 5, 10, and 25 ug/L for non-ketones and 5, 10, 25, 50, and 125 ug/L for ketones).]

2. Verify that the correct initial calibration was used for water and medium level soil samples (i.e., unheated purge) and for low level soil samples (i.e., heated purge).

3. If any sample results were calculated using an initial calibration, verify that the correct standard (i.e., the 50 ug/L standard) was used for calculating sample results and that the samples were analyzed within 12 hours of the associated instrument performance check.

[If any sample results were calculated using an initial calibration, verify that the correct standard (i.e., the 5 ug/L for non-ketones and 25 ug/L for ketones) was used for calculating sample results and that the samples were analyzed within 12 hours of the associated instrument performance check.]

4. Evaluate the initial calibration RRFs and $\overline{RRF}$ for all volatile target compounds and system monitoring compounds (surrogates):

   a. Check and recalculate the RRFs and $\overline{RRF}$ for at least one volatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that for all volatile target compounds and system monitoring compounds (surrogates), the initial calibration RRFs are greater than or equal to 0.05.

NOTE: Because historical performance data indicate poor response and/or erratic behavior, the volatile compounds in Table 2 have no contractual maximum %RSD criteria. Contractually they must meet a minimum RRF criterion of 0.01, however, for data review purposes, the "greater than or equal to 0.05" criterion is applied to all volatile compounds.

Table 2. Volatile Target Compounds Exhibiting Poor Response

Acetone	1,2-Dichloropropane
2-Butanone	2-Hexanone
Carbon disulfide	Methylene chloride
Chloroethane	4-Methyl-2-pentanone
Chloromethane	**Toluene-d8** †
1,2-Dichloroethene (total)†	**1,2-Dichloroethane-d4**†
trans-1,2-Dichloroethene ‡	*1,2-Dibromo-3-chloropropane* ‡
cis-1,2-Dichloroethene ‡	

† **Multi-media, Multi-concentration only**
‡ *Low Concentration Water only*

5. Evaluate the %RSD for all volatile target compounds and system monitoring compounds (surrogates):

   a. Check and recalculate the %RSD for one or more volatile target compound(s); verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. Verify that all volatile target compounds have a %RSD of less than or equal to 30.0%. The contractual criteria for an acceptable initial calibration specifies that up to any 2 volatile target compounds may fail to meet minimum RRF or maximum %RSD as long as they have RRFs that are greater than or equal to 0.010, and %RSD of less than or equal to 40.0%. For data review purposes, however, all compounds must be considered for qualification when the %RSD exceeds the ± 30.0% criterion.

c. If the %RSD is greater than 30.0%, then the reviewer should use professional judgement to determine the need to check the points on the curve for the cause of the non-linearity. This is checked by eliminating either the high point or the low point and recalculating the %RSD.

6. If errors are detected in the calculations of either the RRFs or the %RSD, perform a more comprehensive recalculation.

E. Action

1. All volatile target compounds, including the 12 "poor performers" will be qualified using the following criteria:

   a. If the %RSD is greater than 30.0% and all initial calibration RRFs greater than or equal to 0.05, qualify positive results with "J", and non-detected volatile target compounds using professional judgement.

   b. If any initial calibration RRF is less than 0.05, qualify positive results that have acceptable mass spectral identification with "J", using professional judgement, and non-detected analytes as unusable (R).

2. At the reviewer's discretion, a more in-depth review to minimize the qualification of data can be accomplished by considering the following:

   a. If any of the required volatile compounds have a %RSD greater than 30.0%, and if eliminating either the high or the low point of the curve does not restore the %RSD to less than or equal to 30.0%:

      i. Qualify positive results for that compound(s) with "J".

      ii. Qualify non-detected volatile target compounds based on professional judgement.

   b. If the high point of the curve is outside of the linearity criteria (e.g. due to saturation):

      i. No qualifiers are required for positive results in the linear portion of the curve.

ii. Qualify positive results outside of the linear portion of the curve with a "J".

iii. No qualifiers are needed volatile target compounds that were not detected.

c. If the low end of the curve is outside of the linearity criteria:

i. No qualifiers are required for positive results in the linear portion of the curve.

ii. Qualify low level positive results in the area of non-linearity with "J".

iii. Qualify non-detected volatile target compounds based on professional judgement.

3. If the laboratory has failed to provide adequate calibration information, the designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgement to assess the data.

4. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the data review narrative.

5. If calibration criteria are grossly exceeded, this should be noted for TPO action.

IV. Continuing Calibration

A. **Review Items:** Form VII VOA *[Form VII LCV]*, quantitation reports, and chromatograms.

B. **Objective**

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration establishes the 12-hour relative response factors on which the quantitations are based and checks satisfactory performance of the instrument on a day-to-day basis.

C. **Criteria**

1. Continuing calibration standards containing both target compounds and system monitoring compounds (surrogates) are analyzed at the beginning of each 12-hour analysis period following the analysis of the instrument performance check and prior to the analysis of the method blank and samples.

2. The continuing calibration RRF for volatile target compounds and system monitoring compounds (surrogates) must be greater than or equal to 0.05.

3. The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF must be within $\pm$ 25.0%.

   [For data generated through the Low Concentration Water SOW: The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF must be within $\pm$ 30.0%.]

D. **Evaluation**

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for all volatile target compounds and system monitoring compounds:

   a. Check and recalculate the continuing calibration RRF for at least one volatile target compounds associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that all volatile target compounds and system monitoring compounds meet the RRF specifications.

NOTE: Because historical performance data indicate poor response and/or erratic behavior, the compounds listed in Table 2 (Section III.D.4) have no contractual maximum %D criteria. Contractually they must meet a minimum RRF criterion of 0.01, however, for data review purposes, the "greater than or equal to 0.05" criterion is applied to all volatile compounds.

3. Evaluate the %D between initial calibration $\overline{RRF}$ and continuing calibration RRF for one or more compound(s).

   a. Check and recalculate the %D for one or more volatile target compound(s) associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that the %D is within $\pm$ 25.0% for all volatile target compounds and system monitoring compounds. Note those compounds which have a %D outside the $\pm$ 25.0% criterion. The contractual criteria for an acceptable continuing calibration specifies that up to any 2 volatile target compounds may fail to meet minimum RRF or maximum %D as long as they have RRFs that are greater than or equal to 0.010, and %D of less than or equal to 40.0%. For data review purposes, however, all compounds must be considered for qualification when the %D exceeds the $\pm$ 25.0% criterion.

4. If errors are detected in the calculations of either the continuing calibration RRF or the %D, perform a more comprehensive recalculation.

E. **Action**

1. The reviewer should use professional judgement to determine if it is necessary to qualify the data for any volatile target compound. If qualification of data is required, it should be performed using the following guidelines:

   a. If the %D is outside the $\pm$ 25.0% criterion and the continuing calibration RRF is greater than or equal to 0.05, qualify positive results with "J".

   b. If the %D is outside the $\pm$ 25.0% criterion and the continuing calibration RRF is greater than or equal to 0.05, qualify non-detected volatile target compounds with "UJ".

   c. If the continuing calibration RRF is less than 0.05, qualify positive results that have acceptable mass spectral identifications with "J" or use professional judgement.

   d. If the continuing calibration RRF is less than 0.05, qualify non-detected volatile target compounds as unusable (R).

2. If the laboratory has failed to provide adequate calibration information, the designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgement to assess the data.

3. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the data review narrative.

4. If calibration criteria are grossly exceeded, this should be noted for TPO action.

V. Blanks

A. **Review Items:** Form I VOA *[Form I LCV]*, Form IV VOA *[Form IV LCV]*, chromatograms, and quantitation reports.

B. **Objective**

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, trip blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. **Criteria**

1. No contaminants should be found in the blanks.

2. A method blank analysis must be performed after the calibration standards and once for every 12-hour time period beginning with the injection of BFB.

3. The method blank must be analyzed on each GC/MS system used to analyze samples for each type of analysis, i.e., unheated purge (water and medium level soil) and heated purge (low level soil).

4. An instrument blank should be analyzed after any sample that has saturated ions from a given compound to check that the blank is free of interference and the system is not contaminated.

[5. For data generated through the Low Concentration Water SOW: A storage blank must be prepared upon receipt of the first samples from an SDG, and stored with samples until analysis. The storage blank must be analyzed once per SDG.]

D. **Evaluation**

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that a method blank analysis has been reported per matrix, per concentration level, for each 12-hour time period on each GC/MS system used to analyze volatile samples. The reviewer can use the Method Blank Summary (Form IV VOA *[Form IV LCV]*) to identify the samples associated with each method blank.

3. Verify that the instrument blank analysis has been performed following any sample analysis where a target analyte(s) is reported at high concentration(s).

[4. Verify that a storage blank has been analyzed and included with each SDG and that the storage blanks are free of contamination.]

E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2, 3, and 4, *[and 5]* then the data reviewer should use professional judgement to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should be noted for TPO action.

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. Positive sample results should be reported unless the concentration of the compound in the sample is less than or equal to 10 times (10x) the amount in any blank for the common volatile laboratory contaminants (**methylene chloride, acetone, and 2-butanone**), or 5 times (5x) the amount for other volatile target compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must <u>not</u> be corrected by subtracting any blank value.

Specific actions are as follows:

1. If a volatile compound is found in a blank but <u>not</u> found in the sample, no action is taken. If the contaminants found are volatile target compounds (or interfering non-target compounds) at significant concentrations above the CRQL, then this should be noted for TPO action.

2. Any volatile compound detected in the sample (other than the common volatile laboratory contaminants), that was also detected in any associated blank, is qualified if the sample concentration is less than five times (5x) the blank concentration. The quantitation limit may also be elevated. Typically, the sample CRQL is elevated to the concentration found in the sample. The reviewer should use professional judgement to determine if further elevation of the CRQL is required. For the common volatile laboratory contaminants, the results are qualified by elevating the quantitation limit to the concentration found in the sample when the sample concentration is less than 10 times (10x) the blank concentration.

   The reviewer should note that blanks may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be taken into consideration when applying the "5x" and "10x" criteria, such that a comparison of the total amount of contamination is actually made.

   Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, he/she should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. In this case, the "5x" or "10x" rules may

not apply; the target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

3. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R) due to interference. This should be noted for TPO action if the contamination is suspected of having an effect on the sample results.

4. If inordinate numbers of other target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for TPO action.

5. The same consideration given to the target compounds should also be given to Tentatively Identified Compounds (TICs), which are found in both the sample and associated blank(s). (See VOA Section XII for TIC guidance.)

6. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification(s). If instrument cross-contamination is suggested, then this should be noted for TPO action if the cross-contamination is suspected of having an effect on the sample results.

[7. If contaminants are found in the storage blanks, the following action is recommended.

a. The associated method blank data should be reviewed to determine if the contaminant(s) was also present in the method blank. If the analyte was present at a comparable level in the method blank, then the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

If the analyte was not present in the method blank, then the source of contamination may be in the storage and all associated samples should be considered for possible cross-contamination.

b. If the storage blank contains a volatile TCL compound(s) at a concentration greater than the CRQL, then all positive results for that compounds(s) should be qualified with "J". If the concentration level in the blank is significantly high, then positive sample results may require rejection and be qualified with "R". Non-detected volatile target compounds should not require qualification unless the contamination is so high that it interferes with the analysis of the non-detect compounds.]

The following are examples of applying the blank qualification guidelines. Certain circumstances may warrant deviations from these guidelines.

Example 1: Sample result is greater than the Contract Required Quantitation Limit (CRQL), but is less than the 5x or 10x multiple of the blank result.

	Rule	
	10x	5x
Blank Result	7	7
CRQL	5	5
Sample Result	60	30
Final Sample Result	60U	30U

In the example for the "10x" rule, sample results less than 70 (or 10 x 7) would be qualified as not detected. In the case of the "5x" rule, sample results less than 35 (or 5 x 7) would be qualified as not detected.

Example 2: Sample result is less than the CRQL, and is also less than the 5x or 10x multiple of the blank result.

	Rule	
	10x	5x
Blank Result	6	6
CRQL	5	5
Sample Result	4J	4J
Final Sample Result	5U	5U

Note that data are not reported as 4U, as this would be reported as a detection limit below the CRQL.

Example 3: Sample result is greater than the 5x or 10x multiple of the blank result.

	Rule	
	10x	5x
Blank Result	10	10
CRQL	5	5
Sample Result	120	60
Final Sample Result	120	60

For both the "10x" and "5x" rules, sample results exceeded the adjusted blank results of 100 (or 10x10) and 50 (or 5x10), respectively.

VI. System Monitoring Compounds
(Surrogate Spikes)

A. **Review Items:** Form II VOA *[Form II LCV]*, quantitation reports, and chromatograms.

B. **Objective**

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with system monitoring compounds (formerly referred to as surrogates) prior to sample purging. The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. **Criteria**

1. Three system monitoring compounds (1,2-dichloroethane-d4, bromofluorobenzene, and toluene-d8) are added to all samples and blanks to measure their recovery in environmental samples in sample and blank matrices.

   [For data generated through the Low Concentration Water SOW: A single surrogate, bromofluorobenzene, is added to all samples and blanks to measure the recovery in sample and blank matrices.]

2. Recoveries for system monitoring compounds *[surrogates]* in volatile samples and blanks must be within the limits specified in Appendix A *[Appendix B]* and the SOW.

D. **Evaluation**

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the System Monitoring Compound Recovery Form - Form II VOA *[Surrogate Recovery Form - Form II LCV]*. Check for any calculation or transcription errors.

2. Check that the system monitoring compound *[surrogate]* recoveries were calculated correctly. The equation can be found in Appendix A *[Appendix B]*.

3. The following should be determined from the System Monitoring Compound *[Surrogate]* Recovery form(s):

   a. If any system monitoring *[surrogate]* compound(s) in the volatile fraction is out of specification, there should be a reanalysis to confirm that the non-compliance is due to sample matrix effects rather than laboratory deficiencies.

NOTE: When there are unacceptable system monitoring compound *[surrogate]* recoveries followed by successful re-analyses, the laboratories are required to report only the successful run.

b. The laboratory failed to perform acceptably if system monitoring compounds *[surrogate]* are outside criteria with no evidence of re-analysis. Medium soils must first be re-extractracted prior to re-analysis when this occurs.

c. Verify that no blanks have system monitoring compounds *[surrogate]* outside the criteria.

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

a. System monitoring compound *[surrogate]* recovery (marginal versus gross deviation).

b. Technical holding times.

c. Comparison of the values of the target compounds reported in each sample analysis.

d. Other QC information, such as performance of internal standards.

E. **Action**

Data are qualified based on system monitoring compounds *[surrogate]* results if the recovery of any volatile system monitoring compound *[surrogate]* is out of specification. For system monitoring compound *[surrogate]* recoveries out of specification, the following approaches are suggested based on a review of all data from the package, especially considering the apparent complexity of the sample matrix.

1. If a system monitoring compound *[surrogate]* in the volatile sample has a recovery greater than the upper acceptance limit (UL):

a. Detected volatile target compounds are qualified "J.".

b. Results for non-detected volatile target compounds should not be qualified.

2. If a system monitoring compound *[surrogate]* in the volatile sample has a recovery greater than or equal to 10% but less than the lower acceptance limit (LL):

a. Detected volatile target compounds are qualified "J."

b. For non-detected volatile target compounds, the sample quantitation limit is qualified as approximated (UJ).

3. If a system monitoring compound *[surrogate]* in a volatile sample shows less than 10% recovery:

   a. Detected volatile target compounds are qualified "J".

   b. Non-detected volatile target compounds may be qualified as unusable (R).

Table 3. Qualification of Volatile Analytes Based on System Monitoring Compound *[Surrogate]* Recoveries

	SMC/Surrogate Recovery		
	> UL	10% to LL	< 10%
Detected analytes	J	J	J
Non-detected analytes	No Qualification	UJ	R

4. In the special case of a blank analysis with system monitoring compounds *[surrogate]* out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound *[surrogate]* recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for TPO action. Also note if there are potential contractual problems associated with the lack of reanalysis of samples that were out of specification.

5. Whenever possible, potential effects of the data resulting from system monitoring recoveries not meeting the advisory limits should be noted in the data review narrative.

VII. Matrix Spikes/Matrix Spike Duplicates
(Not Required for Low Concentration Water Data)

A. **Review Items:** Form III VOA-1 and VOA-2, chromatograms, and quantitation reports.

B. **Objective**

Data for matrix spike/matrix spike duplicates (MS/MSD) are generated to determine long-term precision and accuracy of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgement, this data should be used in conjunction with other available QC information.

C. **Criteria**

1. Matrix spikes (MS) and matrix spike duplicate (MSD) samples are analyzed at frequency of one MS and MSD per 20 samples of similar matrix.

2. Spike recoveries should be within the advisory limits provided on Form III VOA-1 and 2.

3. Relative percent difference (RPD) between MS and MSD recoveries must be within the advisory limits provided on Form III VOA-1 and VOA-2.

D. **Evaluation**

1. Verify that MS and MSD samples were analyzed at the required frequency and that results are provided for each sample matrix.

2. Inspect results for the MS/MSD Recovery on Form III VOA-1 and VOA-2 and verify that the results for recovery and RPD are within the advisory limits.

3. Verify transcriptions from raw data and verify calculations.

4. Check that the matrix spike recoveries and RPD were calculated correctly.

5. Compare %RSD results of non-spiked compounds between the original result, MS, and MSD.

E. **Action**

1. No action is taken on MS/MSD data alone. However, using informed professional judgment the data reviewer may use the MS and MSD results in conjunction with other QC criteria and determine the need for some qualification of the data.

2. The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated data. This determination should be made with regard to the MS/MSD sample itself as well as specific analytes for all samples associated with the MS/MSD.

3. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, then qualification should be limited to this sample alone. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

4. The reviewer must use professional judgement to determine the need for qualification of positive results of non-spiked compounds.

NOTE: If a field blank was used for the MS/MSD, a statement to that effect must be included for the TPO.

VIII. Laboratory Control Samples (Low Concentration Water)

[A. Review Items: Form III LCV-1, LCS chromatograms and quantitation reports.

B. Objective

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and on the laboratory performance.

C. Criteria

1. *A laboratory control sample (LCS) must be analyzed once per SDG and concurrently with the samples in the SDG.*

2. *The LCS contains the following volatile compounds, in addition to the required surrogate:*

Vinyl chloride	*Benzene*
1,2-Dichloroethane	*cis-1,3-Dichloropropene*
Carbon tetrachloride	*Bromoform*
1,2-Dichloropropane	*Tetrachloroethene*
Trichloroethene	*1,2-Dibromoethane*
1,1,2-Trichloroethane	*1,4-Dichlorobenzene*

3. *The percent recoveries for the LCS compounds must be within 60-140%. The LCS must meet this recovery criteria for the sample data to be accepted.*

4. *The criteria for surrogate recovery and internal standard performance also apply.*

D. Evaluation

1. *Verify that LCS samples were analyzed at the required frequency and that results are provided for each SDG.*

2. *Inspect results for the LCS Recovery on Form III LCV-1 and verify that the results for recovery are within the QC limits of 60 to 140 percent.*

3. *Verify transcriptions from raw data and verify calculations.*

4. *Check that the LCS recovery was calculated correctly by using the correct equation.*

E. Action

If the LCS criteria are not met, then the laboratory performance and method accuracy are in question. Professional judgement should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data for which the associated LCS does not meet the required criteria.

1. *Action on the LCS recovery should be based on both the number of compounds that are outside of the recovery criteria and the magnitude of the exceedance of the criteria.*

2. *If the LCS recovery criteria are not met, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution. Professional judgement should be used to*

qualify data for compounds other than those compounds that are included in the LCS. Professional judgement to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in performance of the LCS compound to the non-LCS compound.

3. *If the LCS recovery is greater than 140%, then positive sample results for the affected compound(s) should be qualified with a "J".*

4. *If the mass spectral criteria are met but the LCS recovery is less than 60%, then the associated detected target compounds should be qualified "J" and the associated non-detected target compounds should be qualified "R".*

5. *If more than half of the compounds in the LCS are not within the required recovery criteria, then all of the associated detected target compounds should be qualified "J" and all associated non-detected target compounds should be qualified "R."*

6. *Action on non-compliant surrogate recovery and internal standard performance should follow the procedures provided in VI.E and X.E, respectively. Professional judgement should be used to evaluate the impact that non-compliance for surrogate recovery and internal standard performance in the LCS has on the associated sample data.*

7. *It should be noted for TPO action if a laboratory fails to analyze an LCS with each SDG, or if a laboratory consistently fails to generate acceptable LCS recoveries.]*

IX. Regional Quality Assurance and Quality Control

A. **Review Items:** Form I VOA *[Form I LCV]*, chromatograms, and quantitation reports.

B. **Objective**

Regional Quality Assurance and Quality Control (QA/QC) refer to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. It is highly recommended that Regions adopt the use of these.

C. **Criteria**

Criteria are determined by each Region.

1. Performance evaluation sample frequency may vary.

   [For data generated through the Low Concentration Water SOW: A performance evaluation (PE) sample may be required as frequently as once per SDG.]

2. The analytes present in the PE sample must be correctly identified and quantified.

D. **Evaluation**

Evaluation procedures must follow the Region's SOP for data review. Each Region will handle the evaluation of PE samples on an individual basis. Results for PE samples should be compared to the acceptance criteria for the specific PE samples, if available.

E. **Action**

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Unacceptable results for PE samples should be noted for TPO action.

X. Internal Standards

A. **Review Items:** Form VIII VOA *[Form VIII LCV]*, quantitation reports, and chromatograms.

B. **Objective**

Internal Standards (IS) performance criteria ensures that GC/MS sensitivity and response are stable during each analysis.

C. **Criteria**

1. Internal standard area counts must not vary by more than a factor of two (-50% to +100%) from the associated calibration standard.

   [For data generated through the Low Concentration Water SOW: Internal standard area counts must not vary by more than a factor of ± 40.0% from the associated calibration standard.]

2. The retention time of the internal standard must not vary more than ±30 seconds from the retention time of the associated calibration standard.

   [For data generated through the Low Concentration Water SOW: The retention time of the internal standard must not vary more than ± 20.0 seconds from the retention time of the associated calibration standard.]

D. **Evaluation**

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary (Form VIII VOA *[Form VIII LCV]*).

2. Verify that all retention times and IS areas are within criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

   a. Magnitude and direction of the IS area shift.

   b. Magnitude and direction of the IS retention time shift.

   c. Technical holding times.

   d. Comparison of the values of the target compounds reported in each fraction.

   e. Other QC.

E. Action

1. If an IS area count for a sample or blank is outside -50% or +100% of the area for associated standard:

   a. Positive results for compounds quantitated using that IS should be qualified with "J".

   b. Non-detected compounds quantitated using an IS area count greater than 100% should not be qualified.

   c. Non-detected compounds quantitated using an IS area count less than 50% are reported as the associated sample quantitation limit and qualified with "UJ".

   d. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Non-detected target compounds should then be qualified as unusable (R).

   [If an IS area count for a sample or blank is outside ± 40.0% of the area for associated standard:

   a. Positive results for compounds quantitated using that IS should be qualified with "J".

   b. Non-detected compounds quantitated using an IS area count greater than 40% should not be qualified.

   c. Non-detected compounds quantitated using an IS area count less than 40% are reported as the associated sample quantitation limit and qualified with "UJ".

   d. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Non-detected target compounds should then be qualified as unusable (R).]

2. If an IS retention time varies by more than 30 seconds:

   [If an IS retention time varies by more than 20.0 seconds:]

   The chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Positive results should not need to be qualified as "R" if the mass spectral criteria are met.

3. If the internal standards performance criteria are grossly exceeded, then this should be noted for TPO action. Potential effects on the data resulting from unacceptable internal standard performance should be noted in the data review narrative.

XI. Target Compound Identification

A. **Review Items:** Form I VOA *[Form I LCV]*, quantitation reports, mass spectra, and chromatograms.

B. **Objective**

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand represent an absence of data and are, therefore, more difficult to assess. One example of detecting false negatives is the not reporting of a Target Compound that is reported as a TIC.

C. **Criteria**

1. The relative retention times (RRTs) must be within $\pm$0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

   a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

      [For data generated through the Low Concentration Water SOW: All ions present in the standard mass spectrum at a relative intensity greater than 25% must be present in the sample spectrum.]

   b. The relative intensities of these ions must agree within $\pm$ 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%.)

   c. Ions present at greater than 10% in the sample mass spectrum but not present in the standard spectrum must be considered and accounted for.

      [For data generated through the Low Concentration Water SOW: Ions present at greater than 25% in the sample mass spectrum but not present in the standard spectrum must be considered and accounted for.]

D. Evaluation

1. Check that the RRT of reported compounds is within ± 0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to see that it meets the specified criteria.

3. The reviewer should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carryover is a possibility and should use judgment to determine if instrument cross-contamination has affected any positive compound identification. The SOW specifies that an instrument blank must be run after samples in which a target analyte ion(s) saturates the detector.

[The reviewer should be aware of situations when sample carryover is a possibility and should use judgment to determine if instrument cross-contamination has affected any positive compound identification. The SOW specifies that an instrument blank must be run after samples which contain target compounds at levels exceeding the initial calibration range (25 ug/L for non-ketones, 125 ug/L for ketones) or non-target compounds at concentrations greater than 100 ug/L or saturated ions from a compound (excluding the compound peaks in the solvent front).]

4. Check the chromatogram to verify that peaks are accounted for, i.e., major peaks are either identified as target compounds, TICs, system monitoring compounds *[surrogate]*, or internal standards.

E. Action

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

2. Professional judgement must be used to qualify the data if it is determined that cross-contamination has occurred.

3. Any changes made to the reported compounds or concerns regarding target compound identifications should be clearly indicated in the data review narrative. The necessity for numerous or significant changes should be noted for TPO action.

XII. Compound Quantitation and Reported CRQLs

A. **Review Items:** Form I VOA *[Form I LCV]*, sample preparation sheets, SDG narrative, quantitation reports, and chromatograms.

B. **Objective**

The objective is to ensure that the reported quantitation results and Contract Required Quantitation Limits (CRQLs) are accurate.

C. **Criteria**

1. Compound quantitation, as well as the adjustment of the CRQLs, must be calculated according to the correct equation.

2. Compound RRFs must be calculated based on the internal standard (IS) associated with that compound, as listed in Appendix A *[Appendix B]* (also as specified in the Statement of Work) for packed column analyses. For analyses performed by capillary column method (EPA Method 524.2), the target compounds will not necessarily be associated with the same internal standard as in the packed column, depending on the compound elution order. Quantitation must be based on the quantitation ion (m/z) specified in the SOW for both the IS and target analytes. The compound quantitation must be based on the RRF from the appropriate daily standard.

D. **Evaluation**

1. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and quantitation limits. Check the reported values.

2. Verify that the correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout, in both the calibration as well as the quantitation process. For analyses performed by capillary column, the reviewer should use professional judgement to determine that the laboratory has selected the appropriate internal standard.

3. Verify that the CRQLs have been adjusted to reflect all sample dilutions and dry weight factors that are not accounted for by the method.

E. **Action**

1. If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgement to decide which value is the best value. Under these circumstances, the reviewer may determine

qualification of data is warranted. A description of the reasons for data qualification and the qualification that is applied to the data should be documented in the data review narrative.

2. Numerous or significant failures to accurately quantify the target compound or to properly evaluate and adjust CRQLs should be noted for TPO action.

XIII. Tentatively Identified Compounds

A. **Review Items:** Form I VOA-TIC *[Form I LCV-TIC]*, chromatograms, and library search printout and spectra for three TIC candidates.

B. **Objective**

Chromatographic peaks in volatile fraction analyses that are not target analytes, system monitoring compounds *[surrogate]*, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified by a National Institute of Standards and Technology (NIST) mass spectral library search and the identifications assessed by the data reviewer.

C. **Criteria**

For each sample, the laboratory must conduct a mass spectral search of the NIST library and report the possible identity for the 10 largest volatile fraction peaks which are not system monitoring compound, internal standard, or target compounds, but which have area or height greater than 10 percent of the area or height of the nearest internal standard. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I VOA-TIC).

[For data generated through the Low Concentration Water SOW: For each sample, the laboratory must conduct a mass spectral search of the NIST library and report the possible identity for the 10 largest volatile fraction peaks which are not surrogate, internal standard, or TCL compounds, but which have area greater than or equal to 40 percent of the area of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the TCL compounds, using total ion areas for the TIC and the internal standard, and assuming a relative response factor of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I LCV-TIC).]

NOTE: Since the SOW revision of October 1986, the CLP does not allow the laboratory to report as tentatively identified compounds any target compound which is properly reported in another fraction. For example, late eluting volatile target compounds should not be reported as semivolatile TICs.

D. **Evaluation**

1. Guidelines for tentative identification are as follows:

   a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.

      [Major ions (greater than 25% relative intensity) in the reference spectrum should be present in the sample spectrum.]

   b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.

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

d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compounds.

e. When the above criteria are not met, but in the technical judgement of the data reviewer or mass spectral interpretation specialist the identification is correct, the data reviewer may report the identification.

f. If in the data reviewer's judgement the identification is uncertain or there are extenuating factors affecting compound identifications, the TIC result may be reported as "unknown".

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10 percent of the internal standard height, but present in the blank chromatogram at similar relative retention time.

[Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level non-TCL compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 40 percent of the internal standard area but present in the blank chromatogram at similar relative retention time.]

4. All mass spectra for every sample and blank must be examined.

5. Since TIC library searches often yield several candidate compounds having a close matching score, all reasonable choices must be considered.

6. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

Examples:

a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 ug/L or 4000 ug/Kg.

b. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.

8. Target compounds could be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

9. Library searches should not be performed on internal standards or system monitoring compounds.

10. TIC concentration should be estimated assuming a RRF of 1.0.

E. **Action**

1. All TIC results should be qualified "NJ", tentatively identified, with approximated concentrations.

2. General actions related to the review of TIC results are as follows:

   a. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.

   b. If all contractually required peaks were not library searched and quantitated, the designated representative could request these data from the laboratory.

3. TIC results which are not sufficiently above 10x the level in the blank should not be reported. (Dilutions and sample size must be taken into account when comparing the amounts present in blanks and samples.)

4. When a compound is not found in any blanks, but is a suspected artifact of common laboratory contaminant, the result may be qualified as unusable (R).

5. In deciding whether a library search result for a TIC represents a reasonable identification, professional judgment must be exercised. If there is more than one possible match, the result may be reported as "either compound X or compound Y." If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to substituted aromatic compound).

6. The reviewer may elect to report all similar compounds as a total. (e.g., All alkanes may be summarized and reported as total hydrocarbons.)

7. Other case factors may influence TIC judgements. If a sample TIC match is poor but other samples have a TIC with a good library match, similar relative retention time, and the same ions, identification information may be inferred from the other sample TIC results.

8. Physical constants, such as boiling point, may be factored into professional judgement of TIC results.

9. Any changes made to the reported data or any concerns regarding TIC identifications should be indicated in the data review narrative.

10. Failure to properly evaluate and report TICs should be noted for TPO action.

XIV. System Performance

A. **Review Items:** Form VIII VOA *[Form VIII LCV]*, Form III VOA-1 and VOA-2 *[Form III LCV-1]*, and chromatograms.

B. **Objective**

During the period following Instrument Performance QC checks (e.g. blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. **Criteria**

There are no specific criteria for system performance. Professional judgement should be applied to assess the system performance.

D. **Evaluation**

1. Abrupt, discrete shifts in the reconstructed ion chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High RIC background levels or shifts in absolute retention times of internal standards.

   b. Excessive baseline rise at elevated temperature.

   c. Extraneous peaks.

   d. Loss of resolution.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

[3. A drift in instrument sensitivity may occur during the 12-hour time period. This could be discerned by examination of the IS area on Form VIII LCV for trends such as a continuous or near-continuous increase or decrease in the IS area over time.

4. The results of the LCS analysis (Form III LCSV) may also be used to assess instrument performance.]

E. Action

Professional judgement must be used to qualify the data if it is determined that system performance has degraded during sample analyses. Any degradation of system performance which significantly affected the data should be documented for TPO action.

XV. Overall Assessment of Data

A. **Review Items:** Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPjP), and Sampling and Analysis Plan (SAP).

B. **Objective**

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the useability of the data.

C. **Criteria**

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. **Evaluation**

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the useability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPjP (specifically the Data Quality Objectives), SAP, and communication with data user that concerns the intended use and desired quality of these data.

E. **Action**

1. Use professional judgement to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Any inconsistency of the data with the SDG narrative should be noted for TPO action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his/her assessment of the useability of the data within the given context.

SEMIVOLATILE DATA REVIEW

**** Data review guidelines that are unique to data generated through the Low Concentration Water SOW are contained within brackets ([ ]) and written in italics. ****

The semivolatile data requirements to be checked are listed below:

I. Technical Holding Times (CCS - Contractual holding times only)

II. GC/MS Instrument Performance Check (CCS)

III. Initial Calibration (CCS)

IV. Continuing Calibration (CCS)

V. Blanks (CCS)

VI. Surrogate Spikes (CCS)

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Laboratory Control Samples (CCS)

IX. Regional Quality Assurance and Quality Control

X. Internal Standards (CCS)

XI. Target Compound Identification

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XIII. Tentatively Identified Compounds

XIV. System Performance (CCS)

XV. Overall Assessment of Data

NOTE: "CCS" indicates that the contractual requirements for these items will also be checked by CCS; CCS requirements are not always the same as the data review criteria.

I. Technical Holding Times

A. **Review Items:** Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]*, EPA Sample Traffic Report and/or chain-of-custody, raw data, and sample extraction sheets.

B. **Objective**

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of sample extraction and analysis.

C. **Criteria**

Technical requirements for sample holding times have only been established for water matrices. The holding times for soils (and other non-aqueous matrices such as sediments, oily wastes, and sludge) are currently under investigation. When the results are available they will be incorporated into the data evaluation process. Additionally, results of holding time studies will be incorporated into the data review criteria as the studies are conducted and approved.

The holding time criteria for water samples, as stated in the current 40 CFR Part 136 (Clean Water Act) is as follows:

> For semivolatile compounds in cooled (@ 4°C) water samples the maximum holding time is 7 days from sample collection to extraction and 40 days from sample extraction to analysis.

It is recommended that semivolatile compounds in non-aqueous samples be extracted within 14 days of sample collection.

The contractual holding times, which differ from the technical holding times, state that water samples are to be extracted within 5 days from the validated time of sample receipt (VTSR) at the laboratory, and soil samples are to be extracted within 10 days from the VTSR. Also, contractually both water and soil sample extracts must be analyzed within 40 days of sample extraction. However, the contractual delivery due date is 35 days from the VTSR.

[For data generated through the Low Concentration SOW: The contractual delivery due date is 14 days from the VTSR.]

D. **Evaluation**

Technical holding times for sample extraction are established by comparing the sampling date on the EPA Sample Traffic Report with the dates of extraction on Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]* and the sample extraction sheets. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]*.

Verify that the traffic report indicates that the samples were received intact and iced. If the samples were not iced or there were any problems with the samples upon receipt, then discrepancies in the sample condition could effect the data.

E. Action

1. If technical holding times are exceeded, flag all positive results as estimated "J" and sample quantitation limits as estimated "UJ" and document that holding times were exceeded.

2. If technical holding times are grossly exceeded, either on the first analysis or upon re-analysis, the reviewer must use professional judgement to determine the reliability of the data and the effects of additional storage on the sample results. The reviewer may determine that positive results or the associated quantitation limits are approximates and should be qualified with "J" or "UJ", respectively. The reviewer may determine that non-detect data are unusable (R).

3. Due to limited information concerning holding times for soil samples, it is left to the discretion of the data reviewer to apply water holding time criteria to soil samples. Professional judgement is required to evaluate holding times for soil samples.

4. Whenever possible, the reviewer should comment on the effect of the holding time exceedance on the resulting data in the data review narrative.

5. When contractual and/or technical holding times are exceeded, this should be noted as an action item for the TPO.

6. The reviewer should also be aware of the scenario in which the laboratory has exceeded the technical holding times, but met contractual holding times. In this case, the data reviewer should notify the Regional TPO (where samples were collected) and/or RSCC that shipment delays have occurred so that the field problem can be corrected. The reviewer may pass this information on to the laboratory's TPO, but should explain that contractually the laboratory met the requirements.

II. GC/MS Instrument Performance Check

A. **Review Items:** Form V SV *[Form V LCSV]*, and DFTPP mass spectra and mass listing.

B. **Objective**

Gas chromatograph/mass spectrometer (GC/MS) instrument performance checks (formerly referred to as tuning) are performed to ensure mass resolution, identification and, to some degree, sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. **Criteria**

The analysis of the instrument performance check solution must be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, decafluorotriphenylphosphine (DFTPP) for volatile analysis, must meet the ion abundance criteria given below.

Decafluorotriphenylphosphine (DFTPP)

m/z	ION ABUNDANCE CRITERIA
51	30.0 - 80.0% of m/z 198
68	Less than 2.0% of m/z 69
69	Present
70	Less than 2.0% of m/z 69
127	25.0 - 75.0% of m/z 198
197	Less than 1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0 - 9.0% of m/z 198
275	10.0 - 30.0% of m/z 198
365	Greater than 0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0 - 110.0% of m/z 198
443	15.0 - 24.0% of m/z 442

NOTE: All ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

D. **Evaluation**

1. Compare the data presented on each GC/MS Instrument Performance Check (Form V SV *[Form V LCSV]*) with each mass listing submitted and ensure the following:

   a. Form V SV *[Form V LCSV]* is present and completed for each 12-hour period during which samples were analyzed.

b. The laboratory has not made any transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.

c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.

d. The laboratory has not made any calculation errors.

2. Verify from the raw data (mass spectral listing) that the mass assignment is correct and that the mass is normalized to m/z 198.

3. Verify that the ion abundance criteria was met. The criteria for m/z 68, 70, 441, and 443 are calculated by normalizing to the specified m/z.

4. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the DFTPP spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged and background subtraction must be accomplished using a single scan prior to the elution of DFTPP.

NOTE: All instrument conditions must be identical to those used in the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the quality assurance objectives and are therefore unacceptable.

E. Action

1. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, then the reviewer must use professional judgement to assess the data. The laboratory's TPO should be notified.

3. If mass assignment is in error (such as m/z 199 is indicated as the base peak rather than m/z 198), classify all associated data as unusable (R).

4. If ion abundance criteria are not met, professional judgement may be applied to determine to what extent the data may be utilized. Guidelines to aid in the application of professional judgement in evaluating ion abundance criteria are discussed as follows:

a. Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment and are very important. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile.

b. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 40% relative abundance (criteria: 10.0-30.0%) and other criteria are met, then the deficiency is minor.

c. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.

5. Decisions to use analytical data associated with DFTPP instrument performance checks not meeting contract requirements should be clearly noted in the data review narrative.

6. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those specified in the SOW and ILD.4 above, additional information on the DFTPP instrument performance checks should be obtained. If the techniques employed are found to be at variance with contract requirements, the procedures of the laboratory may merit evaluation. Concerns or questions regarding laboratory performance should be noted for TPO action. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the DFTPP peak), then this should be noted for TPO action.

III. Initial Calibration

A. **Review Items:** Form VI SV-1 and SV-2 *[Form VI LCSV-1 and LCSV-2]*, quantitation reports, and chromatograms.

B. **Objective**

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the semivolatile Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.

C. **Criteria**

1. Initial calibration standards containing both semivolatile target compounds and surrogates are analyzed at concentrations of 20, 50, 80, 120, and 160 ug/L at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.

   [For data generated through the Low Concentration SOW: Initial calibration standards containing both semivolatile TCL compounds and surrogates are analyzed at concentrations of 5, 10, 20, 50, and 80 ug/L at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated DFTPP tuning check. The following nine compounds require initial calibration at 20, 50, 80, 100, and 120 ug/L: 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, pentachlorophenol, and 2,4,6-tribromophenol (surrogate).]

2. Minimum Relative Response Factor (RRF) criteria must be greater than or equal to 0.05. Contractual RRF criteria are listed in Appendix A *[Appendix B]*.

3. The Percent Relative Standard Deviations (%RSD) for the RRFs in the initial calibration must be less than or equal to 30%.

D. **Evaluation**

1. Verify that the correct concentration of standards were used for the initial calibration (i.e., 20, 50, 80, 120, and 160 ug/L). For the eight compounds with higher CRQLs, only a four-point initial calibration is required (i.e., 50, 80, 120, and 160 ug/L).

   [Verify that the correct concentration of standards were used for the initial calibration (i.e., 5, 10, 20, 50, and 80 ug/L). For the nine compounds listed in III.C.1. with higher CRQLs, verify that a five point initial calibration at 20, 50, 80, 100, and 120 ug/L was performed.]

2. If any sample results were calculated using an initial calibration, verify that the correct standard (i.e., the 50 ppb standard) was used for calculating sample results and that the samples were analyzed within 12 hours of the associated instrument performance check.

[If any sample results were calculated using an initial calibration, verify that the correct standard (i.e., the 20 ug/L standard or 80 ug/L for the compounds listed in III.C.1.) was used for calculating sample results and that the samples were analyzed within 12 hours of the associated DFTPP tuning check.]

3. Evaluate the RRFs for all semivolatile target compounds and surrogates:

   a. Check and recalculate the RRF and $\overline{RRF}$ for at least one semivolatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that all semivolatile target compounds and surrogates have RRFs that are greater than or equal to 0.05.

NOTE: Because historical performance data indicate poor response and/or erratic behavior, the semivolatile compounds in Table 4 have no contractual maximum %RSD criteria. Contractually they must meet a minimum RRF criteria of 0.01, however, for data review purposes, the "greater than or equal to 0.05" criterion is applied to all semivolatile compounds.

Table 4. Semivolatile Target Compounds Exhibiting Poor Response

2,2'-oxybis(1-Chloropropane)	Diethylphthalate
4-Chloroaniline	4-Nitroaniline
Hexachlorobutadiene	4,6-Dinitro-2-methylphenol
Hexachlorocyclopentadiene	N-Nitrosodiphenylamine
2-Nitroaniline	Di-n-butylphthalate
Dimethylphthalate	Butylbenzylphthalate
3-Nitroaniline	3-3'-Dichlorobenzidine
2,4-Dinitrophenol	bis(2-Ethylhexyl)phthalate
4-Nitrophenol	Di-n-octylphthalate
Carbazole†	*2,4,6-Tribromophenol (surr)‡*
Nitrobenzene-d_5 (surr)‡	

† **Multi-media, Multi-concentration only**
‡ *Low Concentration Water only*

4. Evaluate the %RSD for all semivolatile target compounds and surrogates.

   a. Check and recalculate the %RSD for one or more semivolatile target compound(s); verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. Verify that all semivolatile target compounds have a %RSD of less than 30%. The contractual criteria for an acceptable initial calibration specifies that up to any 4 semivolatile target compounds may fail to meet minimum RRF or maximum %RSD as long as they have RRFs that are greater than or equal to 0.010, and %RSD of less than or equal to 40.0%. For data review purposes, however, all compounds must be considered for qualification when the %RSD exceeds the ± 30.0% criterion.

c. If the %RSD is greater than 30.0%, then the reviewer should use professional judgement to determine the need to check the points on the curve for the cause of the non-linearity. This is checked by eliminating either the high point or the low point and recalculating the %RSD.

5. If errors are detected in the calculations of either the $\overline{RRF}$ or the %RSD, perform a more comprehensive recalculation.

E. **Action**

1. All semivolatile target compounds, including the 19 "poor performers" will be qualified using the following criteria:

   a. If the %RSD is greater than or equal to 30.0% and the RRF is greater than 0.05, qualify positive results with "J", and non-detected semivolatile target compounds using professional judgement.

   b. If the RRF is less than 0.05, qualify positive results that have acceptable mass spectral identification with "J" using professional judgement, and non-detects as unusable (R).

2. At the reviewer's discretion, a more in-depth review to minimize the qualification of data can be accomplished by considering the following:

   a. If any of the required semivolatile compounds have a %RSD greater than 30.0%, and if eliminating either the high or the low point of the curve does not restore the %RSD to less than or equal to 30.0%:

      i. Qualify positive results for that compound(s) with "J".

      ii. Qualify non-detected semivolatile target compounds based on professional judgement.

   b. If the high point of the curve is outside of the linearity criteria (e.g. due to saturation):

      i. No qualifiers are required for positive results in the linear portion of the curve.

      ii. Qualify positive results outside of the linear portion of the curve with "J".

iii. No qualifiers are needed for non-detected target compounds.

c. If the low end of the curve is outside of the linearity criteria:

i. No qualifiers are required for positive results in the linear portion of the curve.

ii. Qualify low level positive results in the area of non-linearity with "J".

iii. Qualify non-detected semivolatile target compounds using professional judgement.

3. If the laboratory has failed to provide adequate calibration information, the designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgement to assess the data.

4. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the data review narrative.

5. If calibration criteria are grossly exceeded, this should be noted for TPO action.

IV. Continuing Calibration

A. **Review Items:** Form VII SV-1 and SV-2 *[Form VII LCSV-1 and LCSV-2]*, quantitation reports, and chromatograms.

B. **Objective**

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for semivolatile target compounds. Continuing calibration establishes the 12-hour relative response factors on which the quantitations are based and checks satisfactory performance of the instrument on a day-to-day basis.

C. **Criteria**

1. Continuing calibration standards containing both target compounds and surrogates are analyzed at the beginning of each 12-hour analysis period following the analysis of the instrument performance check and prior to the analysis of blanks and samples.

2. The minimum Relative Response Factors (RRF) for semivolatile target compounds and surrogates must be greater than or equal to 0.05.

3. The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF must be within $\pm$ 25.0% for all target compounds.

D. **Evaluation**

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for all semivolatile target compounds and surrogates.

   a. Check and recalculate the continuing calibration RRF for at least one semivolatile target compound for each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that all semivolatile target compounds and surrogates have RRFs within specifications.

NOTE: Because historical performance data indicate poor response and/or erratic behavior, the compounds in Table 4 (Section IILD.3) have no contractual maximum %D criteria. Contractually they must meet a minimum RRF criterion of 0.01, however, for data review purposes, the "greater than or equal to 0.05" criterion is applied to all semivolatile compounds.

3. Evaluate the %D between initial calibration $\overline{RRF}$ and continuing calibration RRF for one or more semivolatile compounds.

   a. Check and recalculate the %D for at least one semivolatile target compound for each internal standard; verify that the recalculated value agrees with the laboratory reported value(s).

   b. Verify that the %D is within the $\pm$ 25.0% criterion, for all semivolatile target compounds and surrogates. Note those compounds which have a %D outside the $\pm$ 25.0% criterion. The contractual criteria for an acceptable continuing calibration specifies that up to any 4 semivolatile target compounds may fail to meet minimum RRF or maximum %D as long as they have RRFs that are greater than or equal to 0.010, and %D of less than or equal to 40.0%. For data review purposes, however, all compounds must be considered for qualification when the %D exceeds the $\pm$ 25.0% criterion.

4. If errors are detected in the calculations of either the continuing calibration RRF or the %D, perform a more comprehensive recalculation.

E. Action

1. The reviewer should use professional judgement to determine if it is necessary to qualify the data for any semivolatile target compound. If qualification of data is required, it should be performed using the following guidelines:

   a. If the %D is outside the $\pm$ 25.0% criterion and the continuing calibration RRF is greater than or equal to 0.05, qualify positive results "J".

   b. If the %D is outside the $\pm$ 25.0% criterion and the continuing calibration RRF is greater than or equal to 0.05, qualify non-detected semivolatile target compounds "UJ".

   c. If the continuing calibration RRF is less than 0.05, qualify positive results that have acceptable mass spectral identification with "J" or use professional judgement.

   d. If the continuing calibration RRF is less than 0.05, qualify non-detected semivolatile target compounds as unusable (R).

2. If the laboratory has failed to provide adequate calibration information, the designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgement to assess the data.

3. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the data review narrative.

4. If calibration criteria are grossly exceeded, this should be noted for TPO action.

V. Blanks

A. **Review Items:** Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]*, Form IV SV *[Form IV LCSV]*, chromatograms, and quantitation reports.

B. **Objective**

The purpose of laboratory (or field) blank analyses is to determine the existence and magnitude of contamination problems resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, trip blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. **Criteria**

1. No contaminants should be found in the blanks.

2. The method blank must be analyzed on each GC/MS system used to analyze that specific group or set of samples.

D. **Evaluation**

1. Review the results of all associated blank, Form I SV-1 and SV-2, and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that a method blank analysis has been reported per matrix, per concentration level, for each extraction batch and for each GC/MS system used to analyze semivolatile samples. The reviewer can use the Method Blank Summary (Form IV SV) to assist in identifying samples associated with each method blank.

E. **Action**

If the appropriate blanks were not analyzed with the frequency described above, then the data reviewer should use professional judgement to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should be noted for TPO action.

Action in the case of unsuitable blank results depends on the circumstances and origin of the blank. Positive sample results should be reported unless the concentration of the compound in the sample is less than or equal to 10 times (10x) the amount in any blank for the common phthalate contaminants, or 5 times the amount for other compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

Specific actions are as follows:

1. If a semivolatile compound is found in a blank but not found in the sample, no action is taken. If the contaminants found are volatile target compounds (or interfering non-target compounds) at significant concentrations above the CRQL, then this should be noted for TPO action.

2. Any semivolatile compound detected in the sample (other than the common phthalate contaminants), that was also detected in any associated blank, is qualified if the sample concentration is less than five times (5x) the blank concentration. The quantitation limit may also be elevated. Typically, the sample CRQL is elevated to the concentration found in the sample. The reviewer should use professional judgement to determine if further elevation of the CRQL is required. For phthalate contaminants, the results are qualified "U" by elevating the sample quantitation limit to the sample concentration when the sample result is less than 10x the blank concentration.

   The reviewer should note that blanks may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be taken into consideration when applying the "5x" and "10x" criteria, such that a comparison of the total amount of contamination is actually made.

   Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, he/she should qualify the data. In this case, the "5x" or "10x" rules may not apply; the sample value should be reported as a non-detect. An explanation of the rationale used for this determination should be provided in the narrative accompanying the Regional Data Assessment Summary.

3. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted for TPO action if the contamination is suspected of having an effect on the sample results.

4. If inordinate amounts of other target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for TPO action.

5. The same consideration given to the target compounds should also be given to Tentatively Identified Compounds (TICs) which are found in both the sample and associated blank(s). (See SV Section XII for TIC guidance.)

6. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgement should be used to determine if instrument cross-contamination has affected any positive compound

identification(s). If instrument cross-contamination is suggested, then this should be noted for TPO action if the cross-contamination is suspected of having an effect on the sample results.

The following are examples of applying the blank qualification guidelines. Certain circumstances may warrant deviations from these guidelines.

Example 1: Sample result is greater than the Contract Required Quantitation Limit (CRQL), but is less than the 5x or 10x multiple of the blank result.

	Rule	
	10x	5x
Blank Result	7	7
CRQL	5	5
Sample Result	60	30
Qualified Sample Result	60U	30U

In the example for the "10x" rule, sample results less than 70 (or 10 x 7) would be qualified as non-detects. In the case of the "5x" rule, sample results less than 35 (or 5 x 7) would be qualified as non-detects.

Example 2: Sample result is less than CRQL, and is also less than the 5x or 10x multiple of the blank result.

	Rule	
	10x	5x
Blank Result	6	6
CRQL	5	5
Sample Result	4J	4J
Qualified Sample Result	5U	5U

Note that data are not reported as 4U, as this would be reported as a detection limit below the CRQL.

Example 3: Sample result is greater than the 5x or 10x multiple of the blank result.

	Rule	
	10x	5x
Blank Result	10	10
CRQL	5	5
Sample Result	120	60
Qualified Sample Result	120	60

For both the "10x" and "5x" rules, sample results exceeded the adjusted blank results of 100 (or 10x10) and 50 (or 5x10), respectively.

VI. Surrogate Spikes

A. **Review Items:** Form II SV-1 and SV-2 *[Form II LCSV]*, chromatograms, and quantitation reports.

B. **Objective**

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample preparation. The evaluation of the results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. **Criteria**

1. Surrogate spikes, 4 acid compounds (3 required and 1 advisory) and 4 base/neutral compounds (3 required and 1 advisory) are added to all samples and blanks to measure their recovery in sample and blank matrices.

   [For data generated through the Low Concentration SOW: Surrogate spikes, 3 acid compounds and 3 base/neutral compounds, are added to all samples and blanks to measure their recovery in sample and blank matrices.]

2. Surrogate spike recoveries for semivolatile samples and blanks must be within the limits specified on in Appendix A and on Form II SV-1 and SV-2.

   [For data generated through the Low Concentration SOW: Surrogate spike recoveries for semivolatile samples and blanks must be within the limits specified in Appendix B and on Form II LCSV.]

D. **Evaluation**

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the surrogate spike recoveries on the Surrogate Recovery Form II SV-1 and SV-2 *[Form II LCSV]*. Check for any transcription or calculation errors.

2. Check that the surrogate spike recoveries were calculated correctly. The equation can be found in Appendix A *[Appendix B]*.

3. The following should be determined from the Surrogate Recovery form(s):

   a. If any two base/neutral or acid surrogates are out of specification, or if any one base/neutral or acid extractable surrogate has a recovery of less than 10%, then there should be a reanalysis to confirm that the non-compliance is due to sample matrix effects rather than laboratory deficiencies.

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

b. The laboratory has failed to perform satisfactorily if surrogate recoveries are out of specification and there is no evidence of reinjection of the extract, or reextraction and reanalysis (if reinjection fails to resolve the problem).

c. Verify that no blanks have surrogates recoveries outside the criteria.

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

a. Surrogate recovery (marginal versus gross deviation).

b. Technical holding times.

c. Comparison of the values of the target compounds reported in each fraction.

d. Other QC information, such as performance of internal standards.

E. **Action**

Data are not qualified with respect to surrogate recovery unless two or more semivolatile surrogates, within the same fraction (base/neutral or acid fraction), are out of specification. For surrogate spike recoveries out of specification, the following approaches are suggested based on a review of all data from the case, especially considering the apparent complexity of the sample matrix.

1. If two or more surrogates in either semivolatile fraction (base/neutral or acid fraction) have a recovery greater than the upper acceptance limit (UL):

a. Specify the fraction that is being qualified, i.e. acid, base/neutral, or both.

b. Detected semivolatile target compounds are qualified "J."

c. Results for non-detected semivolatile target compounds should not be qualified.

2. If two or more surrogates in either semivolatile fraction have a recovery greater than or equal to 10% but less than the lower acceptance limit (LL):

a. Specify the fraction that is being qualified, i.e. acid, base/neutral, or both.

b. Detected semivolatile target compounds are qualified "J."

c. For non-detected semivolatile target compounds, the sample quantitation limit is qualified as approximated (UJ).

3. If any surrogate in either semivolatile fraction show less than 10% recovery:

   a. Specify the fraction that is being qualified, i.e. acid, base/neutral, or both.

   b. Detected semivolatile target compounds are qualified "J".

   c. Non-detected semivolatile target compounds may be qualified as unusable (R).

Table 5. Qualification of Semivolatile Analytes Based on Surrogate Recoveries

	Surrogate Recovery		
	> UL	10% to LL	< 10%
Detected analytes	J	J	J
Non-detected analytes	No Qualification	UJ	R

4. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgement allows some use of the affected data, analytical problems should be noted for TPO action. Also note if there are potential contractual problems associated with the lack of re-analysis of samples that were out of specification.

5. Whenever possible, the potential effects of the data resulting from system monitoring recoveries not meeting the advisory limits should be noted in the data review narrative.

VII. Matrix Spikes/Matrix Spike Duplicates
(Not Required for Low Concentration Water Data)

A. **Review Items:** Form III SV-1 and SV-2, chromatograms, and quantitation reports.

B. **Objective**

Data for matrix spikes/matrix spike duplicates (MS/MSD) are generated to determine long-term precision and accuracy of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgement, this data should be used in conjunction with other available QC information.

C. **Criteria**

1. Matrix spikes and matrix spike duplicate samples are analyzed at frequency of one MS and MSD per 20 samples of similar matrix.

2. Matrix spike and matrix spike duplicate recoveries should be within the advisory limits established on Form III SV-1 and SV-2.

3. The Relative Percent Differences (RPDs) between matrix spike and matrix spike duplicate recoveries should be within the advisory limits listed on Form III SV-1 and SV-2.

D. **Evaluation**

1. Verify that MS and MSD samples were analyzed at the required frequency and that results are provided for each sample matrix.

2. Inspect results for the MS/MSD Recovery on Form III SV-1 and SV-2 and verify that the results for recovery and RPD are within the advisory limits.

3. Verify transcriptions from raw data and verify calculations.

4. Check that the recoveries and RPD were calculated correctly.

5. Compare results (%RSD) of non-spiked compounds between the original result, MS, and MSD.

E. **Action**

1. No action is taken on MS/MSD data alone. However, using informed professional judgment the data reviewer may use the matrix spike and matrix spike duplicate results in conjunction with other QC criteria and determine the need for some qualification of the data.

2. The data reviewer should first try to determine to what extent the results of the MS/MSD effect the associated data. This determination should be made with regard to the

MS/MSD sample itself as well as specific analytes for all samples associated with the MS/MSD.

3. In those instances where it can be determined that the results of the MS/MSD effect only the sample spiked, then qualification should be limited to this sample alone. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

4. The reviewer must use professional judgement to determine the need for qualification of positive results of non-spiked compounds.

NOTE: If a field blank was used for the MS/MSD, a statement to that effect must be included for TPO action.

VIII. Laboratory Control Samples
(Low Concentration Water)

[A. Review Items: Form III LCSV, LCS chromatograms and quantitation reports.

B. Objective

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance.

C. Criteria

1. *Laboratory control samples are analyzed at frequency of once per 20 samples per SDG. The LCS must be prepared and analyzed concurrently with the samples in the SDG.*

2. *LCS percent recoveries must be within the QC limits provided on Form III LCSV. The LCS must meet the recovery criteria for the sample data to be accepted.*

3. *The LCS contains the following semivolatile target compounds, in addition to the required surrogates:*

Phenol	*1,2,4-Trichlorobenzene*
2-Chlorophenol	*Naphthalene*
4-Chloroaniline	*2,4-Dinitrotoluene*
2,4,6-Trichlorophenol	*Diethylphthalate*
bis(2-Chloroethyl)ether	*N-Nitrosodiphenylamine*
N-Nitroso-di-n-propylamine	*Hexachlorobenzene*
Hexachloroethane	*Benzo(a)pyrene*
Isophorone	

4. *The criteria for surrogate recovery and internal standard performance also apply.*

D. Evaluation

1. *Verify that LCS samples were analyzed at the required frequency.*

2. *Inspect the results for LCS Recovery on Form III LCSV and verify that the results for recovery are within the advisory limits.*

3. *Verify transcriptions from raw data and verify calculations.*

4. *Check that the recoveries were calculated correctly.*

E. Action

If the LCS criteria are not met, then the laboratory performance and method accuracy are in question. Professional judgement should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data for which the associated LCS does not meet the required criteria.

1. *Action on the LCS recovery should be based on both the number of compounds that are outside of the recovery criteria and the magnitude of the exceedance of the criteria.*

2. *If the LCS recovery criteria are not met, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution. Professional judgement should be used to*

qualify data for compounds other than those compounds that are included in the LCS. Professional judgement to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in performance of the LCS compound to the non-LCS compound.

3. *If the LCS recovery is greater than 140%, then positive sample results for the affected compound(s) should be qualified with a "J".*

4. *If the mass spectral criteria are met but the LCS recovery is less than 60%, then the associated detected target compounds should be qualified "J" and the associated non-detected target compounds should be qualified "R".*

5. *If more than half of the compounds in the LCS are not within the required recovery criteria, then all of the associated detected target compounds should be qualified "J" and all associated non-detected target compounds should be qualified "R."*

6. *Action on non-compliant surrogate recovery and internal standard performance should follow the procedures provided in VI.E and X.E, respectively. Professional judgement should be used to evaluate the impact that non-compliance for surrogate recovery and internal standard performance in the LCS has on the associated sample data.*

7. *It should be noted for TPO action if a laboratory fails to analyze an LCS with each SDG, or if a laboratory consistently fails to generate acceptable LCS recoveries.]*

IX. Regional Quality Assurance and Quality Control

A. **Review Items:** Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]*, chromatograms, quantitation report, traffic report and raw data for Regional QC samples.

B. **Objective**

Regional Quality Assurance and Quality Control (QA/QC) refer to any QA and/or QC initiated by the Region, including field duplicates, Regional Performance Evaluation (PE) samples, blind spikes, and blind blanks. It is highly recommended that Regions adopt the use of these.

C. **Criteria**

Criteria are determined by each Region.

1. Performance evaluation sample frequency may vary.

   [For data generated through the Low Concentration SOW: A performance evaluation (PE) sample may be required as frequently as once per SDG.]

2. The analytes present in the PE sample must be correctly identified and quantified.

D. **Evaluation**

Evaluation procedures must follow the Region's SOP for data review. Each Region will handle the evaluation of PE samples on an individual basis. Results for PE samples should be compared to the acceptance criteria for the specific PE samples, if available.

E. **Action**

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Unacceptable results for PE samples should be noted for TPO action.

X. Internal Standards

A. **Review Items:** Form VIII SV-1 and SV-2 *[Form VIII LCSV-1 and LCSV-2]*, quantitation reports, and chromatograms.

B. **Objective**

Internal Standards (IS) performance criteria ensure that GC/MS sensitivity and response are stable during every analytical run.

C. **Criteria**

1. Internal standard area counts for samples and blanks must not vary by more than a factor of two (- 50% to + 100%) from the associated calibration standard.

   [For data generated through the Low Concentration Water SOW: Internal standard area counts must not vary by more than a factor of ± 40.0% from the associated calibration standard.]

2. The retention time of the internal standards in samples and blanks must not vary by more than ± 30 seconds from the retention time of the associated calibration standard.

   [For data generated through the Low Concentration SOW: The retention time of the internal standards in samples and blanks must not vary by more than ±20.0 seconds from the retention time of the associated calibration standard.]

D. **Evaluation**

1. Check raw data (e.g., chromatograms and quantitation lists) for samples and blanks to verify the internal standard retention times and areas reported on the Internal Standard Area Summary (Forms VIII SV-1, VIII SV-2 *[Form VIII LCSV-1 and LCSV-2]*).

2. Verify that all retention times and IS areas are within the required criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

   a. Magnitude and direction of the IS area shift.

   b. Magnitude and direction of the IS retention time shift.

   c. Technical holding times.

   d. Comparison of the values of the target compounds reported in each fraction.

E. **Action**

1. If an IS area count for a sample or blank is outside - 50% or + 100% of the area for the associated standard:

a. Positive results for compounds quantitated using that IS should be qualified with "J".

b. Non-detected compounds quantitated using an IS area count greater than 100% should not be qualified.

c. Non-detected compounds quantitated using an IS area count less than 50% are reported as the associated sample quantitation limit and qualified with "UJ".

d. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Non-detected target compounds should then be qualified as unusable (R).

[If an IS area count for a sample or blank is outside ± 40.0% of the area for associated standard:

a. Positive results for compounds quantitated using that IS should be qualified with "J".

b. Non-detected compounds quantitated using an IS area count greater than 40% should not be qualified.

c. Non-detected compounds quantitated using an IS area count less than 40% are reported as the associated sample quantitation limit and qualified with "UJ".

d. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Non-detected target compounds should then be qualified as unusable (R).]

2. If an IS retention time varies by more than 30 seconds:

[If an IS retention time varies by more than 20.0 seconds:]

The chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection (R) of the data for that sample fraction. Positive results should not need to be qualified with "R" if the mass spectral criteria are met.

3. If the internal standards performance criteria are grossly exceeded, then this should be noted for TPO action. Potential effects on the data resulting from unacceptable internal standard performance should be noted in the data review narrative.

XI. Target Compound Identification

A. **Review Items:** Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]*, quantitation reports, mass spectra, and chromatograms.

B. **Objective**

Qualitative criteria for compound identification have been established to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied much more easily in detecting false positives than false negatives. More information is available due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand represent an absence of data and are, therefore, much more difficult to assess. One example of detecting false negatives is the reporting of a Target Compound as a TIC.

C. **Criteria**

1. Compound must be within ± 0.06 relative retention time (RRT) units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard must match according to the following criteria:

   a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum

      [For data generated through the Low Concentration SOW: All ions present in the standard mass spectrum at a relative intensity greater than 25% must be present in the sample spectrum.]

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

   c. Ions present at greater than 10% in the sample mass spectrum but not present in the standard spectrum must be considered and accounted for.

      [For data generated through the Low Concentration SOW: Ions present at greater than 25% in the sample mass spectrum but not present in the standard mass spectrum must be considered and accounted for.]

D. **Evaluation**

1. Check that the RRT of reported compounds is within ± 0.06 RRT units of the standard relative retention time.

2. Check that the sample compound spectra against the laboratory standard spectra to verify that its meets the specified criteria.

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

4. Check the chromatogram to verify that peaks are accounted for, i.e., major peaks are either identified as target compounds, TICs, surrogates, or internal standards.

E. Action

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

2. Professional judgement must be used to qualify the data if it is determined that cross-contamination has occurred.

3. Any changes made to the reported compounds or concerns regarding target compound identifications should be clearly indicated in the data review narrative. The necessity for numerous or significant changes should be noted for TPO action.

XII. Compound Quantitation and Reported CRQLS

A. **Review Items:** Form I SV-1 and SV-2 *[Form I LCSV-1 and LCSV-2]*, sample preparation sheets, case narrative, sample clean-up sheets, quantitation reports, and chromatograms.

B. **Objective**

The objective is to ensure that the reported quantitation results and Contract Required Quantitation Limits (CRQLs) for semivolatile target compounds are accurate.

C. **Criteria**

1. Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the correct equation.

2. Compound area responses must be calculated based on the internal standard (IS) associated with that compound, as listed in Appendix A *[Appendix B]* (also as specified in the Statement of Work). Quantitation must be based on the quantitation ion (m/z) specified in the SOW for both the IS and target analytes. The compound quantitation must be based on the RRF from the appropriate daily calibration standard.

D. **Evaluation**

1. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists, chromatograms, and sample preparation log sheets should be compared to the reported positive sample results and quantitation limits. Check the reported values.

2. Verify that the correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout the calibration and quantitation processes.

3. Verify that the CRQLs have been adjusted to reflect all sample dilutions, concentrations, splits, clean-up activities, and dry weight factors that are not accounted for by the method.

E. **Action**

1. If there are any discrepancies found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgement to decide which value is the best value. Under these circumstances, the reviewer may determine qualification of data is warranted. Decisions made on data quality should be included in the data review narrative. A description of the reasons for data qualification and the qualification that is applied to the data should be documented in the data review narrative.

2. Numerous or significant failures to accurately quantify the target compound or to properly evaluate and adjust CRQLs should be noted for TPO action.

XIII. Tentatively Identified Compounds

A. **Review Items:** Form I SV-TIC *[Form I LCSV-TIC]*, chromatograms, and library search printout with spectra for three TIC candidates.

B. **Objective**

Chromatographic peaks in semivolatile fraction analyses that are not target analytes, surrogates, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified by a National Institute of Standards and Technology (NIST) mass spectral library search and the identifications assessed by the data reviewer.

C. **Criteria**

For each sample, the laboratory must conduct a mass spectral search of the NIST library and report the possible identity for the 20 largest semivolatile fraction peaks which are not surrogate, internal standard, or target compounds, but which have area or height greater than 10 percent of the area or height of the nearest internal standard. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I SV-TIC).

[For data generated through the Low Concentration SOW: For each sample, the laboratory must conduct a mass spectral search of the NIST library and report the possible identity for the 20 largest semivolatile fraction peaks which are not surrogates, internal standards, or TCL compounds, but which have an area greater than 50 percent of the area of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the TCL compounds, using total ion areas for the TIC and the internal standard, and assuming a relative response factor of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I LCSV-TIC).]

NOTE: Since the SOW revision of October 1986, the CLP does not allow the laboratory to report as tentatively identified compounds any target compound which is properly reported in another fraction. For example, late eluting volatile target compounds should not be reported as semivolatile TICs.

D. **Evaluation**

1. Guidelines for tentative identification are as follows:

   a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.

      [Major ions (greater than 25% relative intensity) in the reference spectrum should be present in the sample spectrum.]

   b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.

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

d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compounds.

e. When the above criteria are not met, but in the technical judgment of the data reviewer or mass spectral interpretation specialist the identification is correct, the data reviewer may report the identification.

f. If in the data reviewer's judgment the identification is uncertain or there are extenuating factors affecting compound identifications, the TIC result may be reported as "unknown".

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

[Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks with areas greater than or equal to 50 percent of the area of the nearest internal standard.]

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10 percent of the internal standard height, but present in the blank chromatogram at a similar relative retention time.

[Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level non-TCL compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which have areas less than 50 percent of the internal standard area, but present in the blank chromatogram at a similar relative retention time.]

4. All mass spectra for each sample and blank must be examined.

5. Since TIC library searches often yield several candidate compounds having a close matching score, all reasonable choices should be considered.

6. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

Examples:

a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 ug/L or 4000 ug/Kg.

b. Solvent preservatives, such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

c. Aldol reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. Occasionally, a target compound may be identified as a TIC in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.

8. Target compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

9. Library searches should not be performed on internal standards or surrogates.

10. TIC concentration should be estimated assuming a RRF of 1.0.

E. Action

1. All TIC results should be qualified "NJ", tentatively identified, with approximated concentrations.

2. General actions related to the review of TIC results are as follows:

   a. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.

   b. If all contractually required peaks were not library searched and quantitated, the designated representative could request these data from the laboratory.

3. TIC results which are not sufficiently above the level in the blank should not be reported. (Dilutions and sample size must be taken into account when comparing the amounts present in blanks and samples.)

4. When a compound is not found in any blanks, but is a suspected artifact of common laboratory contamination, the result may be qualified as unusable (R).

5. In deciding whether a library search result for a TIC represents a reasonable identification, professional judgment must be exercised. If there is more than one possible match, the result may be reported as "either compound X or compound Y." If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to substituted aromatic compound).

6. The reviewer may elect to report all similar isomers as a total. (All alkanes may be summarized and reported as total hydrocarbons.)

7. Other case factors may influence TIC judgments. If a sample TIC match is poor but other samples have a TIC with a good library match, similar relative retention time, and the same ions, identification information may be inferred from the other sample TIC results.

8. Physical constants, such as boiling point, may be factored into professional judgment of TIC results.

9. Any changes made to the reported data or any concerns regarding TIC identifications should be indicated in the data review narrative.

10. Failure to properly evaluate and report TICs should be noted for TPO action.

XIV. System Performance

A. **Review Items:** Form III SV-1 and SV-2 *[Form III LCSV]*, Form VIII SV-1 and SV-2 *[Form VIII LCSV-1 and LCSV-2]*, and chromatograms.

B. **Objective**

During the period following Instrument Performance QC checks (e.g. blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a through review of the ongoing data acquisition can yield indicators of instrument performance.

C. **Criteria**

There are no specific criteria for system performance. Professional judgement should be used to assess the system performance.

D. **Evaluation**

1. Abrupt, discrete shifts in the reconstructed ion chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline shift could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds at or near the detection limit to be non-detects. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High RIC background levels or shifts in absolute retention times of internal standards.

   b. Excessive baseline rise at elevated temperature.

   c. Extraneous peaks.

   d. Loss of resolution as suggested between by factors such as non-resolution of 2,4- and 2,5- dinitrotoluene.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

[3. A drift in instrument sensitivity may occur during the 12-hour time period. This could be discerned by examination of the IS area on Form VIII LCSV-1 and LCSV-2 for trends such as a continuous or near-continuous increase or decrease in the IS area over time.

4. The results of the LCS analysis (Form III LCSV) may also be used to assess instrument performance.]

E. Action

Professional judgement must be used to qualify the data if it is determined that system performance has degraded during sample analyses. Any degradation of system performance which significantly affected the data should be documented for TPO action.

XV. Overall Assessment of Data

A. **Review Items:** Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPjP), and Sampling and Analysis Plan (SAP).

B. **Objective**

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the useability of the data.

C. **Criteria**

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. **Evaluation**

1. Evaluate any technical problems which have not been previously addressed.

2. Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

3. If appropriate information is available, the reviewer may assess the useability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPjP (specifically the Data Quality Objectives), SAP, and communication with data user that concerns the intended use and desired quality of the data.

E. **Action**

1. Use professional judgement to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Any inconsistency of that data with the SDG Narrative should be noted for TPO action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his/her assessment of the useability of the data within the given context.

APPENDIX A

CONTRACTUAL REQUIREMENTS AND EQUATIONS

MULTI-MEDIA, MULTI-CONCENTRATION - MM/MC (OLM01.0)

APPENDIX A

MULTI-MEDIA, MULTI-CONCENTRATION CONTRACTUAL REQUIREMENTS AND EQUATIONS FOR VOLATILE DATA REVIEW

II. GC/MS Instrument Performance Check

Use equation II.1 to verify that the laboratory has not made errors the calculation of the percent relative abundance.

$$\% \ Relative \ Abundance = \frac{abundance \ of \ X}{abundance \ of \ Y} \times 100\% \qquad (II.1)$$

For example, the percent relative abundance of m/z 96 (X) relative to m/z 95 (Y) is calculated as follows:

$$\% \ Relative \ Abundance = \frac{abundance \ of \ m/z \ 96}{abundance \ of \ m/z \ 95} \times 100\%$$

III. Initial Calibration

Data Review Criteria: All volatile target compounds and system monitoring compounds must have a Relative Response Factor (RRF) of greater than or equal to 0.05 and a percent relative standard deviation (%RSD) of less than or equal to 30%.

Contractual Criteria: The maximum %RSD for volatile compounds is 20.5% and the minimum RRF criteria vary as specified in the Table A.1 (The volatile compounds listed separately in Table 2 on page 13 are not contractually required to meet a maximum %RSD but do have to meet a contractual minimum RRF of 0.010). The contractual criteria for an acceptable initial calibration specifies that up to any 2 volatile target compounds may fail to meet minimum RRF or maximum %RSD as long as they have RRFs that are greater than or equal to 0.010, and %RSD of less than or equal to 40.0%.

Table A.1 Minimum RRF Criteria for Volatile Target Compunds

Volatile Compound	Minimum RRF
Bromomethane	0.100
Vinyl chloride	0.100
1,1-Dichloroethene	0.100
1,1-Dichloroethane	0.200
Chloroform	0.200
1,2-Dichloroethane	0.100
1,1,1-Trichloroethane	0.100
Carbon tetrachloride	0.100
Bromodichloromethane	0.200
cis-1,3-Dichloropropene	0.200

Table A.1 Minimum RRF Criteria for Volatile Target Compunds (continued)

Volatile Compound	Minimum RRF
Trichloroethene	0.300
Dibromochloromethane	0.100
1,1,2-Trichloroethane	0.100
Benzene	0.500
trans-1,3-Dichloropropene	0.100
Bromoform	0.100
Tetrachloroethene	0.200
1,1,2,2-Tetrachloroethane	0.500
Toluene	0.400
Chlorobenzene	0.500
Ethylbenzene	0.100
Styrene	0.300
Xylenes (total)	0.300
Bromofluorobenzene	0.200

Initial calibration RRFs and $\overline{RRF}$ are calculated using equations III.1 and III.2.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{(III.1)}$$

$$\overline{RRF} = \frac{\sum_{i=1}^{5} RRF_i}{5} \qquad \text{(III.2)}$$

where:

RRF_i = "i"th Relative Response Factor
A = Area of the characteristic ion (EICP) measured
C = Concentration
is = Internal standard
x = Analyte of interest

The %RSD is calculated using equations III.3 and III.4.

$$\sigma = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}} \qquad \text{(III.3)}$$

$$\%RSD = \frac{\sigma}{\bar{x}} \times 100 \qquad \text{(III.4)}$$

where:

σ = Standard deviation of 5 relative response factors
$\bar{x}$ = Mean of 5 relative response factors

IV. Continuing Calibration

Data Review Criteria: All compounds must be considered for qualification when the %D exceeds the ± 25.0% criterion.

Contratual Criteria: The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF is ± 25% for all compounds listed in Table A.1. The contractual criteria for an acceptable continuing calibration specifies that up to any 2 volatile target compounds may fail to meet minimum RRF or maximum %D as long as they have RRFs that are greater than or equal to 0.010, and %D of less than or equal to 40.0%.

Check the continuing calibration RRF calculations for volatile target compounds using equation III.1. The %D between initial calibration $\overline{RRF}$ and continuing calibration RRF is calculated using equation IV.1.

$$\%\ D = \frac{\overline{RRF_I} - RRF_C}{\overline{RRF_I}} \times 100\% \qquad \text{(IV.1)}$$

where:

$\overline{RRF_I}$ = average relative response factor from initial calibration.
RRF_C = relative response factor from continuing calibration standard.

VI. System Monitoring Compounds

The volatile system monitoring compounds (surrogates) and their contractual recovery limits are listed in Table A.2.

Table A.2 System Monitoring Compound Contractual Requirements

System Monitoring Compound	%Recovery Limits	
	Water Samples	Soil Samples
SMC1 Toluene-d_8	88 - 110	84 - 138
SMC2 Bromofluorobenzene	86 - 115	59 - 113
SMC3 1,2-Dichloroethane-d_4	76 - 114	70 - 121

Use equation VI.1 to check that the system monitoring compound recoveries were calculated correctly:

$$\% \ Recovery = \frac{Concentration/amount\ found}{Concentration/amount\ spiked} \times 100\% \qquad (VI.1)$$

VII. Matrix Spikes/Matrix Spike Duplicates

The matrix spike/matrix spike duplicate contractual requirements are listed in Table A.3.

Table A.3 MS/MSD Contractual Requirements

Compound	%R - Water	%R - Soil	RPD - Water	RPD - Soil
1,1-Dichloroethene	61 - 145	59 - 172	≤14	≤22
Trichloroethene	71 - 120	62 - 137	≤14	≤24
Benzene	76 - 127	66 - 142	≤11	≤21
Toluene	76 - 125	59 - 139	≤13	≤21
Chlorobenzene	75 - 130	60 - 133	≤13	≤21

Verify that the matrix spike recoveries and RPD were calculated correctly using equations VII.1 and VII.2.

$$\% \ Recovery = \frac{SSR - SR}{SA} \times 100\% \qquad (VII.1)$$

where:

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

$$RPD = \frac{|MSR - MSDR|}{1/2\ (MSR + MSDR)} \times 100\% \qquad (VII.2)$$

where:

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

IX. Internal Standards

Table A.4 contains the volatile internal standards and their corresponding target compounds. These criteria have been established for packed columns only. Specific criteria for capillary columns have not been included in the SOW at this time.

Table A.4 Internal Standards and Their Corresponding Target Compounds

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	1,1,1-Trichloroethane	2-Hexanone
Bromomethane	Carbon Tetrachloride	4-Methyl-2-Pentanone
Vinyl Chloride	Bromodichloromethane	Tetrachloroethene
Chloroethane	Bromoform	1,1,2,2-Tetrachloroethane
Methylene Chloride	1,2-Dichloropropane	Toluene
Acetone	trans-1,3-Dichloropropene	Chlorobenzene
Carbon Disulfide	Trichloroethene	Ethylbenzene
1,1-Dichloroethene	Dibromochloromethane	Styrene
1,1-Dichloroethane	1,1,2-Trichloroethane	Total Xylenes
1,2-Dichloroethene(total)	Benzene	Bromofluorobenzene (SMC)
Chloroform	cis-1,3-Dichloropropene	Toluene-d_8 (SMC)
1,2-Dichloroethane	Bromoform	
2-Butanone		
1,2-Dichloroethane-d_4 (SMC)		

SMC = System Monitoring Compound

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

Check the reported positive sample results and quantitation limits with the quantitation lists and chromatograms using equations XI.1, XI.2, or XI.3. Characteristic ions for the volatile target compounds are contained in Table A.5. Characteristic ions for System Monitoring Compounds and Internal Standards are contained in Table A.6.

Concentration for waters:

$$ug/L = \frac{A_x \times I_s \times Df}{A_{is} \times RRF \times V_o} \qquad \text{(XI.1)}$$

Concentration for low level soils:
(Dry weight basis)

$$ug/Kg = \frac{A_x \times I_s}{A_{is} \times RRF \times W_s \times D} \quad \text{(XI.2)}$$

Concentration for medium level soils:
(Dry weight basis)

$$ug/Kg = \frac{A_x \times I_s \times V_t \times 1000 \times Df}{A_{is} \times RRF \times V_a \times W_s \times D} \quad \text{(XI.3)}$$

where:

Ax = area of characteristic ion (EICP) for compound being measured
A_{is} = area of characteristic ion (EICP) for the internal standard
I_s = amount of internal standard added (ng)
RRF = daily response factor for compound being measured
V_o = volume of water purged (mL)
W_s = weight of sample (g)
D = (100 - % moisture)/100% - conversion to dry weight
V_t = volume of methanol (mL)†
V_i = volume of extract added (uL) for purging
Df = dilution factor‡
V_a = volume of the aliquot of the methanol extract (uL) added to reagent water for purging

† This volume is typically 10.0 mL, even though only 1.0 mL is transferred to the vial. See the SOW for more details.

‡ The dilution factor for analysis of soil/sediment samples for volatiles by the medium level method is defined as the ratio of the number of microliters (uL) of methanol added to the reagent water for purging (V_a) to the number of microliters of the methanol extract of the sample contained in volume V_a. If no dilution is performed, then the dilution factor equals 1.0.

The CRQL for a diluted sample should be calculated as follows:

Adjusted CRQL = Non-adjusted CRQL x Sample Dilution Factor (XI.4)

For example, the adjusted CRQL for a water sample with a 10U non-diluted CRQL and a 1 to 100 dilution (100.0 dilution factor) would be 1000U, according to the following calculation:

$$1000U = 10U \times 100$$

The CRQL adjustment for dry weight for a soil sample should be calculated as follows:

$$\textit{Dry Weight CRQL} = \frac{\textit{Non-adjusted CRQL}}{\left(\frac{100 - \textit{\%moisture}}{100}\right)} \qquad \text{(XI.5)}$$

For example, the dry weight CRQL for a soil sample with a 10U non-adjusted CRQL and a 10% moisture would be 11U, according to the following calculation:

$$11U = \frac{10U}{\left(\frac{100 - 10}{100}\right)}$$

Table A.5 Characteristic Ions for Volatile Target Compounds

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

Table A.5 Characteristic Ions for Volatile Target Compounds (Continued)

Analyte	Primary Ion*	Secondary Ion(s)
Tetrachloroethene	164	129, 131, 166
Toluene	92	92
Chlorobenzene	112	114
Ethyl benzene	106	91
Styrene	104	78, 103
Total Xylenes	106	91

** While m/z 43 is used for quantitation of 2-Butanone, m/z 72 must be present for positive identification.

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

Table A.6 Characteristic Ions for System Monitoring Compounds and Internal Standards for Volatile Organic Compounds

Compound	Primary Ion	Secondary Ion(s)
SYSTEM MONITORING COMPOUNDS		
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane-d_4	65	102
Toluene-d_8	98	70, 100
INTERNAL STANDARDS		
Bromochloromethane	128	49, 130, 51
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

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CONTRACTUAL REQUIREMENTS AND EQUATIONS FOR SEMIVOLATILE DATA REVIEW

II. GC/MS Instrument Performance Check

Use equation II.1 to verify that the laboratory has not made errors in the calculation of the percent relative abundance.

For example, the percent relative abundance of m/z 443 (X) relative to m/z 442 (Y) is calculated as follows:

$$\% \text{ Relative Abundance} = \frac{\text{abundance of m/z 443}}{\text{abundance of m/z 442}} \times 100\%$$

III. Initial Calibration

Data Review Criteria: All semivolatile target compounds and surrogates must have a Relative Response Factor (RRF) of greater than or equal to 0.05 and a percent relative standard deviation (%RSD) of less than or equal to 30%.

Contractual Criteria: The maximum %RSD for most semivolatile compounds is 20.5% and the minimum RRF criteria vary as specified in Table A.7 (The semivolatile compounds listed separately in Table 4 on page 52 are not contractually required to meet a maximum %RSD but do have to meet a contractual minimum RRF of 0.010). The contractual criteria for an acceptable initial calibration specifies that up to any 4 semivolatile target compounds may fail to meet minimum RRF or maximum %RSD as long as they have RRFs that are greater than or equal to 0.010, and %RSD of less than or equal to 40.0%.

Table A.7 Minimum RRF Criteria for Semivolatile Target Compounds

Semivolatile Compounds	Minimum RRF
Phenol	0.800
bis(-2-Chloroethyl)ether	0.700
2-Chlorophenol	0.800
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
2-Methylphenol	0.700
4-Methylphenol	0.600
N-Nitroso-di-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
bis(-2-Chloroethoxy)methane	0.300

Table A.7 Minimum RRF Criteria for Semivolatile Target Compounds (Continued)

Semivolatile Compounds	Minimum RRF
2,4-Dichlorophenol	0.200
1,2,4-Trichlorobenzene	0.200
Naphthalene	0.700
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
2-Chloronaphthalene	0.800
Acenaphthylene	1.300
2,6-Dinitrotoluene	0.200
Acenaphthene	0.800
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
4-Chlorophenyl-phenylether	0.400
Fluorene	0.900
4-Bromophenyl-phenylether	0.100
Hexachlorobenzene	0.100
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Fluoranthene	0.600
Pyrene	0.600
Benzo(a)anthracene	0.800
Chrysene	0.700
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
Nitrobenzene-d_5	0.200
2-Fluorobiphenyl	0.700
Terphenyl-d_{14}	0.500
Phenol-d_5	0.800
2-Fluorophenol	0.600
2-Chlorophenol-d_4	0.800
1,2-Dichlorobenzene-d_4	0.400

Initial calibration RRF and $\overline{RRF}$ are calculated using equations III.1 and III.2; %RSD is calculated using equations III.3 and III.4.

IV. Continuing Calibration

Data Review Criteria: All semivolatile target compounds should meet a %D criterion of ± 25%.

Contractual Criteria: The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF is ± 25.0% for the compounds listed in Table A.4. The contractual criteria for an acceptable continuing calibration specifies that up to any 4 semivolatile target compounds may fail to meet minimum RRF or maximum %D as long as they have RRFs that are greater than or equal to 0.010, and %D of less than or equal to 40.0%.

Check the continuing calibration RRF calculations for semivolatile target compounds using equation III.1, and evaluate the %D between initial calibration $\overline{RRF}$ and continuing calibration RRF using equation IV.1.

VI. Surrogate Spikes

The semivolatile surrogate compounds and their contractual recovery limits are listed in Table A.8.

Table A.8 Semivolatile Surrogate Requirements

Surrogate	%Recovery Limits	
	Water Samples	Soil Samples
S1 Nitrobenzene-d_5	35 - 114	23 - 120
S2 2-Fluorobiphenyl	43 - 116	30 - 115
S3 Terphenyl-d_{14}	33 - 141	18 - 137
S4 Phenol-d_5	10 - 110	24 - 113
S5 2-Fluorophenol	21 - 110	25 - 121
S6 2,4,6-Tribromophenol	10 - 123	19 - 122
S7 2-Chlorophenol-d_4	33 - 110*	20 - 130*
S8 1,,2-Dichlorobenzene-d_4	16 - 110*	20 - 130*

* Advisory limits

Use equation VI.1 to verify that the surrogate recoveries were calculated correctly.

VII. Matrix Spikes/Matrix Spike Duplicates

The matrix spike/matrix spike duplicate contractual requirements are listed in Table A.9.

Verify that the matrix spike recoveries and RPD were calculated correctly using equations VII.1 and VII.2.

IX. Internal Standards

Table A.10 contains the semivolatile internal standards and their corresponding target compounds.

Table A.9 Semivolatile MS/MSD Contractual Requirements

Compound	%R - Water	%R - Soil	RPD - Water	RPD - Soil
Phenol	12 - 110	26 - 90	≤ 42	≤ 35
2-Chlorophenol	27 - 123	25 - 102	≤ 40	≤ 50
1,4-Dichlorobenzene	36 - 97	28 - 104	≤ 28	≤ 27
N-Nitroso-di-n-propylamine	41 - 116	41 - 126	≤ 38	≤ 38
1,2,4-Trichlorobenzene	39 - 98	38 - 107	≤ 28	≤ 23
4-Chloro-3-methylphenol	23 - 97	26 - 103	≤ 42	≤ 33
Acenaphthene	46 - 118	31 - 137	≤ 31	≤ 19
4-Nitrophenol	10 - 80	11 - 114	≤ 50	≤ 50
2,4-Dinitrotoluene	24 - 96	28 - 89	≤ 38	≤ 47
Pentachlorophenol	9 - 103	17 - 109	≤ 50	≤ 47
Pyrene	26 - 127	35 - 142	≤ 31	≤ 36

Table A.10 Semivolatile Internal Standards and Their Corresponding Target Compounds

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Phenol	Nitrobenzene	Hexachlorocyclopentadiene
bis(2-Chloroethyl)ether	Isophorone	2,4,6-Trichlorophenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol
1,3-Dichlorobenzene	2,4-Dimethylphenol	2-Chloronaphthalene
1,4-Dichlorobenzene	bis(2-Chloroethoxy)methane	2-Nitroaniline
1,2-Dichlorobenzene	2,4-Dichlorophenol	Dimethyl phthalate
2-Methylphenol	1,2,4-Trichlorobenzene	Acenaphthylene
2,2'-oxybis-(1-Chloropropane)	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloroaniline	Acenaphthene
N-Nitroso-Di-n-propylamine	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
2-Fluorophenol (surr)	2-Methylnaphthalene	Dibenzofuran
Phenol-d_5 (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene
2-Chlorobenzene-d_4 (surr)		2,6-Dinitrotoluene
1,2-Dichlorobenzene-d_4 (surr)		Diethyl phthalate
		4-Chlorophenyl-phenyl ether
		Fluorene
		4-Nitroaniline
		2-Fluorobiphenyl (surr)
		2,4,6-Tribromophenol (surr)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Butylbenzyl phthalate	Benzo(b)fluoranthene
4-Bromophenyl phenyl ether	3,3'-Dichlorobenzidine	Benzo(k)fluoranthene
Hexachlorobenzene	Benzo(a)anthracene	Benzo(a)pyrene
Pentachlorophenol	bis(2-Ethylhexyl)phthalate	Indeno(1,2,3-cd)pyrene
Phenanthrene	Chrysene	Dibenz(a,h)anthracene
Carbazole	Terphenyl-d_{14} (surr)	Benzo(g,h,i)perylene
Anthracene		
Di-n-butyl phthalate		
Fluoranthene		

surr = surrogate compound

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

Check the reported positive sample results and quantitation limits with the quantitation lists and chromatograms using equations XI.6, XI.7, or XI.8. Equation XI.4 should be used to adjust the CRQL for a diluted sample, and equation XI.5 should be used to adjust the CRQL for a soil sample. Characteristic ions for semivolatile target compounds are contained in Table A.11. Characteristic ions for semivolatile surrogates and internal standards are contained in Table A.12. Characteristic ions for pesticides and Aroclors are contained in Table A.13.

Concentration for waters:

$$ug/L = \frac{A_x \times I_s \times V_t \times Df}{A_{is} \times RRF \times V_o \times V_i} \qquad \text{(XI.6)}$$

Concentration for soils/sediments:
(Dry weight basis)

$$ug/Kg = \frac{A_x \times I_s \times V_t \times Df}{A_{is} \times RRF \times V_i \times W_s \times D} \qquad \text{(XI.7)}$$

where:

Ax = area of characteristic ion (EICP) for compound being measured
A_{is} = area of characteristic ion (EICP) for the internal standard
I_s = amount of internal standard added (ng)
RRF = daily relative response factor for compound being measured
V_o = volume of water extracted (mL)
V_i = volume of extract injected (uL)
V_t = volume of concentrated extract (uL)
Df = dilution factor†
D = (100 - % moisture)/100% - conversion to dry weight
W_s = weight of sample (g)

† The dilution factor for analysis of water samples for semivolatiles by the method specified in SOW OLM01.0 is calculated using equation XI.8. If no dilution is performed, then the dilution factor equals 1.0.

$$Df = \frac{uL \text{ of the most concentated extract used} + uL \text{ of clean solvent}}{uL \text{ of the most concentrated extract used}} \qquad \text{(XI.8)}$$

Table A.11 Characteristic Ions for Semivolatile Target Compounds

Analyte	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
2,2'-oxybis(1-Chloropropane)	45	77, 79
4-Methylphenol	108	107
N-Nitroso-di-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127

Table A.11 Characteristic Ions for Semivolatile Target Compounds (Continued)

Parameter	Primary Ion	Secondary Ion(s)
2-Nitroaniline	65	92, 138
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126

Table A.11 Characteristic ions for Semivolatile Target Compounds (Continued)

Analyte	Primary Ion	Secondary Ion(s)
Benz(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	---
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277

Table A.12 Characteristic Ions for Semivolatile Surrogates and Internal Standards

Analyte	Primary Ion	Secondary Ion(s)
SURROGATES		
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d_5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
2-Chlorophenol-d_4	132	68, 134
1,2-Dichlorobenzene-d_4	152	115, 150
INTERNAL STANDARDS		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenapthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

Table A.13 Characteristic Ions for Pesticides/Aroclors

Analyte	Primary Ion	Secondary Ion(s)
alpha-BHC	183	181, 109
beta-BHC	181	183, 109
delta-BHC	183	181, 109
gamma-BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Aldrin	66	263, 220
Heptachlor epoxide	353	355, 351
Endosulfan I	195	339, 341
Dieldrin	79	263, 279
4,4'-DDE	246	248, 176
Endrin	263	82, 81
Endrin ketone	317	67, 319
Endrin aldehyde	67	250, 345
Endosulfan II	337	339, 341
4,4'-DDD	235	237, 165
Endosulfan sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane (alpha and/or gamma)	373	375, 377
Toxaphene	159	231, 233
Arochlor-1016	222	260, 292
Arochlor-1221	190	222, 260
Arochlor-1232	190	222, 260
Arochlor-1242	222	256, 292
Arochlor-1248	292	362, 326
Arochlor-1254	292	362, 326
Arochlor-1260	360	362, 394

APPENDIX B

CONTRACTUAL REQUIREMENTS AND EQUATIONS

LOW CONCENTRATION WATER - LCW
(OLC01.0)

DRAFT 12/90
Revised 6/91

LOW CONCENTRATION WATER
CONTRACTUAL REQUIREMENTS AND EQUATIONS FOR VOLATILE DATA REVIEW

II. GC/MS Instrument Performance Check

Use equation II.1 to verify that the laboratory has not made errors the calculation of the percent relative abundance.

$$\%\ Relative\ Abundance = \frac{abundance\ of\ X}{abundance\ of\ Y} \times 100\% \qquad (II.1)$$

For example, the percent relative abundance of m/z 96 (X) relative to m/z 95 (Y) is calculated as follows:

$$\%\ Relative\ Abundance = \frac{abundance\ of\ m/z\ 96}{abundance\ of\ m/z\ 95} \times 100\%$$

III. Initial Calibration

Data Review Criteria: All volatile target compounds and system monitoring compounds must have a Relative Response Factor (RRF) of greater than or equal to 0.05 and a percent relative standard deviation (%RSD) of less than or equal to 30%.

Contractual Criteria: The maximum %RSD for most volatile compounds is 20.5% and the minimum RRF criteria vary as specified in the following table (The volatile compounds listed separately in Table 2 on page 13 are not contractually required to meet a maximum %RSD but do have to meet a contractual minimum RRF of 0.010). The contractual criteria for an acceptable initial calibration specifies that up to any 2 volatile target compounds may fail to meet minimum RRF or maximum %RSD as long as they have RRFs that are greater than or equal to 0.010, and %RSD of less than or equal to 40.0%.

Initial calibration RRFs and $\overline{RRF}$ are calculated using equations III.1 and III.2.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad (III.1)$$

$$\overline{RRF} = \frac{\sum_{i=1}^{5} RRF_i}{5} \qquad (III.2)$$

where:

RRF_i = "i"th Relative Response Factor
A = Area of the characteristic ion (EICP) measured
C = Concentration
is = Internal standard
x = Analyte of interest

Table B.1. Technical Acceptance Criteria for Initial and Continuing Calibration for Volatile Organic Compounds

Target Volatile Compound	Minimum RRF	Maximum %RSD	%D
Benzene	0.500	30.0	±30.0
Bromochloromethane	0.100	30.0	±30.0
Bromodichloromethane	0.200	30.0	±30.0
Bromoform	0.100	30.0	±30.0
Bromomethane	0.100	30.0	±30.0
Carbon tetrachloride	0.100	30.0	±30.0
Chlorobenzene	0.500	30.0	±30.0
Chloroform	0.200	30.0	±30.0
Dibromochloromethane	0.100	30.0	±30.0
1,2-Dibromoethane	0.100	30.0	±30.0
1,2-Dichlorobenzene	0.400	30.0	±30.0
1,3-Dichlorobenzene	0.600	30.0	±30.0
1,4-Dichlorobenzene	0.500	30.0	±30.0
1,1-Dichloroethane	0.200	30.0	±30.0
1,2-Dichloroethane	0.100	30.0	±30.0
1,1-Dichloroethene	0.100	30.0	±30.0
cis-1,3-Dichloropropene	0.200	30.0	±30.0
trans-1,3-Dichloropropene	0.100	30.0	±30.0
Ethylbenzene	0.100	30.0	±30.0
Styrene	0.300	30.0	±30.0
1,1,2,2-Tetrachloroethane	0.500	30.0	±30.0
Tetrachloroethene	0.200	30.0	±30.0
Toluene	0.400	30.0	±30.0
1,1,1-Trichloroethane	0.100	30.0	±30.0
1,1,2-Trichloroethane	0.100	30.0	±30.0
Trichloroethene	0.300	30.0	±30.0
Vinyl Chloride	0.100	30.0	±30.0
Xylenes (total)	0.300	30.0	±30.0
4-Bromofluorobenzene	0.200	30.0	±30.0

The %RSD is calculated using equations III.3 and III.4.

$$\sigma = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}} \quad \text{(III.3)}$$

$$\%RSD = \frac{\sigma}{\bar{x}} \times 100 \quad \text{(III.4)}$$

where:

σ = Standard deviation of 5 relative response factors

$\bar{x}$ = Mean of 5 relative response factors

IV. Continuing Calibration

Data Review Criteria: All volatile target compounds should meet a %D criterion of ± 30%.

Contractual Criteria: The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF is ± 30% for all compounds listed in Table B.1 (Page B-2). The contractual criteria for an acceptable continuing calibration specifies that up to any 2 volatile target compounds may fail to meet minimum RRF or maximum %D as long as they have RRFs that are greater than or equal to 0.010, and %D of less than or equal to 40.0%.

Check the RRF calculations for volatile target compounds using equation III.1 (Page B-1). The %D between initial calibration $\overline{RRF}$ and continuing calibration RRF is calculated using equation IV.1.

$$\%\ D = \frac{\overline{RRF_I} - RRF_C}{\overline{RRF_I}} \times 100\% \quad \text{(IV.1)}$$

where:

$\overline{RRF_i}$ = average relative response factor from initial calibration.

RRF_c = relative response factor from continuing calibration standard.

VI. Surrogate Spikes

The volatile surrogate compound and the contractual recovery limits are listed below.

Surrogate Spike	%Recovery Limits
BFB Bromofluorobenzene	80 - 120

Use equation VI.2 to check that the surrogate percent recovery was calculated correctly:

$$\% \ Recovery = \frac{Q_D}{Q_A} \times 100\% \qquad \text{(VI.2)}$$

where:

Q_D = Quantity determined by analysis.
Q_A = Quantity added to samples/blanks.

VII. Laboratory Control Samples (LCS)

Laboratory Control Sample compounds are listed in Table B.2. The contractual percent recovery limits are from **60 to 140 percent**. However, these limits may eventually be expanded by the Agency during the period of performance if the limits are found to be too restrictive.

Table B.2 Volatile Laboratory Control Sample Compounds

Vinyl Chloride
1,2-Dichloroethane
Carbon Tetrachloride
1,2-Dichloropropane
Trichloroethene
1,1,2-Trichloroethane
Benzene
cis-1,3-Dichloropropene
Bromoform
Tetrachloroethene
1,2-Dibromoethane
1,4-Dichlorobenzene

Check that the LCS recovery was calculated correctly by using equation VI.2.

IX. Internal Standards

Table B.3 contains the volatile internal standards and their corresponding target compounds.

Table B.3. Volatile Internal Standards and Their Corresponding Target Compounds

1,4-Difluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene d_4
Chloromethane	1,1,1-Trichloroethane	Bromoform
Bromomethane	Carbon tetrachloride	1,2-Dibromo-3-chloropropane*
Vinyl Chloride	Bromodichloromethane	1,2-Dichlorobenzene*
Chloroethane	1,2-Dichloropropane	1,3-Dichlorobenzene*
Bromochloromethane*	cis-1,3-Dichloropropene	1,4-Dichlorobenzene*
Methylene Chloride	Trichloroethene	
Acetone	Dibromochloromethane	
Carbon disulfide	1,1,2-Trichloroethane	
1,1-Dichloroethene	Benzene	
1,1-Dichloroethane	trans-1,3-Dichloropropene	
cis-1,2-Dichloroethene**	4-Methyl-2-Pentanone	
trans-1,2-Dichloroethene**	2-Hexanone	
Chloroform	Tetrachloroethene	
1,2-Dichloroethane	1,1,2,2-Tetrachloroethane	
2-Butanone	1,2-Dibromoethane*	
4-Bromofluorobenzene (surr)	Toluene	
	Chlorobenzene	
	Ethylbenzene	
	Styrene	
	Total Xylenes	

* compounds not on Multi-media, Multi-concentration TCL
** on Multi-media, Multi-concentration TCL as total 1,2-Dichloroethene

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

Check the reported positive sample results and quantitation limits with the quantitation lists and chromatograms using equation XI.1. Primary and secondary Quantitation ions are listed in Table B.4 (Page B-7).

$$ug/L = \frac{A_x \times I_s \times D_f}{A_{is} \times RRF \times V_o} \qquad \text{(XI.1)}$$

where:

Ax = area of characteristic ion (EICP) for compound being measured
A_{is} = area of characteristic ion for the internal standard
I_s = amount of internal standard added (ng)
RRF = relative response factor for compound being measured
V_o = volume of water purged (mL)
Df = dilution factor

The CRQL for a diluted sample should be calculated as follows:

$$\text{Adjusted CRQL} = \text{Non-adjusted CRQL} \times \text{Sample Dilution Factor} \quad \text{(XI.4)}$$

For example, the adjusted CRQL for a water sample with a 10U non-diluted CRQL and a 1 to 100 dilution (100.0 dilution factor) would be 1000U, according to the following calculation:

$$1000U = 10U \times 100$$

TABLE B.4 Volatile Quantitation Ions

Volatile Target Compounds	Primary Quantitation Ion	Secondary Ions
Acetone	43	58
Benzene	78	---
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
2-Butanone	43	72*
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
Dibromochloromethane	129	127
1,2-Dibromo-3-chloropropane	75	155, 157
1,2-Dibromoethane	107	109, 188
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
cis-1,3-Dichloropropene	75	77

* Quantitation of this analyte is based on m/z 43 but m/z 72 must be present in the spectrum.

TABLE B.4 Volatile Quantitation Ions (Continued)

Volatile Target Compounds	Primary Quantitation Ion	Secondary Ions
trans-1,3-Dichloropropene	75	77
Ethylbenzene	91	106
2-Hexanone	43	58, 57, 100
Methylene chloride	84	86, 49
4-Methyl-2-pentanone	43	58, 100
Styrene	104	78
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	166	168, 129
Toluene	91	92
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Trichloroethene	95	130, 132
Vinyl chloride	62	64
Xylenes (total)	106	91
SURROGATE COMPOUND AND INTERNAL STANDARDS:		
4-Bromofluorobenzene	95	174, 176
Chlorobenzene-d_5	117	82, 119
1,4-Dichlorobenzene-d_4	150	115, 152
1,4-Difluorobenzene	114	63, 88

LOW CONCENTRATION WATER
CONTRACTUAL REQUIREMENTS AND EQUATIONS FOR SEMIVOLATILE DATA REVIEW

II. GC/MS Instrument Performance Check

Use equation II.1 (Page B-1) to verify that the laboratory has not made errors the calculation of the percent relative abundance.

For example, the percent relative abundance of m/z 443 (X) relative to m/z 442 (Y) is calculated as follows:

$$\% \text{ Relative Abundance} = \frac{\text{abundance of m/z 443}}{\text{abundance of m/z 442}} \times 100\%$$

III. Initial Calibration

Data Review Criteria: All semivolatile target compounds and surrogates must have a Relative Response Factor (RRF) of greater than or equal to 0.05 and a percent relative standard deviation (%RSD) of less than or equal to 30%.

Contractual Criteria: The maximum %RSD for most semivolatile compounds is 20.5% and the minimum RRF criteria vary as specified in the following table (The semivolatile compounds listed separately in table 4 on page 52 are not contractually required to meet a maximum %RSD but do have to meet a contractual minimum RRF of 0.010). The contractual criteria for an acceptable initial calibration specifies that up to any 4 semivolatile target compounds may fail to meet minimum RRF or maximum %RSD as long as they have RRFs that are greater than or equal to 0.010, and %RSD of less than or equal to 40.0%.

Initial calibration RRFs and $\overline{RRF}$ are calculated using equations III.1 and III.2 (Page B-1); %RSD is calculated using equations III.3 and III.4 (Page B-3).

IV. Continuing Calibration

Data Review Criteria: All semivolatile target compounds should meet a %D criterion of $\pm$ 25%.

Contractual Criteria: The percent difference (%D) between the initial calibration $\overline{RRF}$ and the continuing calibration RRF is $\pm$ 25.0% for the compounds listed in Table B.5. The contractual criteria for an acceptable continuing calibration specifies that up to any 4 semivolatile target compounds may fail to meet minimum RRF or maximum %D as long as they have RRFs that are greater than or equal to 0.010, and %D of less than or equal to 40.0%.

Check the RRF calculations for semivolatile target compounds using equation III.1 (Page B-1), and evaluate the %D between initial calibration $\overline{RRF}$ and continuing calibration RRF using equation IV.1 (Page B-3).

Table B.5. Acceptance Criteria for Initial and Continuing Calibration for Semivolatile Organic Compounds

Semivolatile Compounds	Minimum RRF	Maximum %RSD	%D
Phenol	0.800	20.5	±25.0
bis(-2-Chloroethyl)ether	0.700	20.5	±25.0
2-Chlorophenol	0.700	20.5	±25.0
2-Methylphenol	0.700	20.5	±25.0
4-Methylphenol	0.600	20.5	±25.0
N-Nitroso-di-n-propylamine	0.500	20.5	±25.0
Hexachloroethane	0.300	20.5	±25.0
Nitrobenzene	0.200	20.5	±25.0
Isophorone	0.400	20.5	±25.0
2-Nitrophenol	0.100	30.0	±30.0
2,4-Dimethylphenol	0.200	30.0	±30.0
bis(2-Chloroethoxy)methane	0.300	20.5	±25.0
2,4-Dichlorophenol	0.200	20.5	±25.0
1,2,4-Trichlorobenzene	0.200	20.5	±25.0
Naphthalene	0.700	20.5	±25.0
4-Chloro-3-methylphenol	0.200	20.5	±25.0
2-Methylnaphthalene	0.400	20.5	±25.0
2,4,6-Trichlorophenol	0.200	20.5	±25.0
2,4,5-Trichlorophenol	0.200	20.5	±25.0
2-Chloronaphthalene	0.800	20.5	±25.0
Acenaphthylene	1.300	20.5	±25.0
Acenaphthene	0.800	20.5	±25.0
Dibenzofuran	0.800	20.5	±25.0
2,4-Dinitrotoluene	0.200	30.0	±30.0
2,6-Dinitrotoluene	0.200	20.5	±25.0
4-Chlorophenyl-phenylether	0.400	20.5	±25.0
Fluorene	0.900	20.5	±25.0
4-Bromophenyl-phenylether	0.100	20.5	±25.0
Hexachlorobenzene	0.100	20.5	±25.0
Pentachlorophenol	0.050	20.5	±25.0
Phenanthrene	0.700	20.5	±25.0
Anthracene	0.700	20.5	±25.0
Fluoranthene	0.600	20.5	±25.0

Table B.5. Acceptance Criteria for Initial and Continuing Calibration for Semivolatile Organic Compounds (continued)

Semivolatile Compounds	Minimum RRF	Maximum %RSD	%D
Pyrene	0.600	20.5	±25.0
Benz(a)anthracene	0.800	20.5	±25.0
Chrysene	0.700	20.5	±25.0
Benzo(b)fluoranthene	0.700	20.5	±25.0
Benzo(k)fluoranthene	0.700	20.5	±25.0
Benzo(a)pyrene	0.700	20.5	±25.0
Indeno(1,2,3-cd)pyrene	0.500	20.5	±25.0
Dibenz(a,h)anthracene	0.400	20.5	±25.0
Benzo(g,h,i)perylene	0.500	20.5	±25.0
Phenol-d_5 (surr)	0.800	20.5	±25.0
2-Fluorophenol (surr)	0.600	20.5	±25.0
Terphenyl-d_{14} (surr)	0.500	20.5	±25.0
2-Fluorobiphenyl (surr)	0.700	20.5	±25.0

VI. Surrogate Spikes

Surrogate spike recoveries for semivolatile samples and blanks must be within the limits specified in Table B.6.

Table B.6 Semivolatile Surrogate Recovery Requirements

Surrogate Compound	% Recovery
Nitrobenzene-d_5	40 - 112
2-Fluorobiphenyl	42 - 110
p-Terphenyl-d_{14}	24 - 140
Phenol-d_5	17 - 113
2-Fluorophenol	16 - 110
2,4,6-Tribromophenol	18 - 126

Use equation VI.2 to verify that the surrogate recoveries were calculated correctly.

VII. Laboratory Control Samples (LCS)

The percent recovery for each of the compounds in the LCS spiking solution must be within the recovery limits listed in Table B.7. However, these limits may eventually be expanded by the Agency during the period of performance if the limits are found to be too restrictive.

Table B.7 Semivolatile Laboratory Control Sample Compounds and Recevery Limits

Compound	%Recovery
Phenol	44 - 120
2-Chlorophenol	58 - 110
4-Chloroaniline	35 - 98
2,4,6-Trichlorophenol	65 - 110
bis(2-Chloroethyl)ether	64 - 110
N-Nitroso-di-n-propylamine	34 - 102
Hexachloroethane	32 - 77
Isophorone	49 -110
1,2,4-Trichlorobenzene	44 - 96
Naphthalene	56 - 160
2,4-Dinitrotoluene	61 - 140
Diethylphthalate	76 - 104
N-Nitrosodiphenylamine	35 - 120
Hexachlorobenzene	30 - 95
Benzo(a)pyrene	55 - 92

Check that the recoveries were calculated correctly by using equation VI.2 (Page B-4).

IX. Internal Standards

Table B.8 (Page B-14) contains the semivolatile internal standards and their corresponding target compounds.

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

Check the reported positive sample results and quantitation limits with the quantitation lists and chromatograms using equation XI.6. Equation XI.4 (Page B-6) should be used to adjust the CRQL for a diluted sample. Table B.9 (Page B-15,16,17) contains the semivolatile primary and secondary Quantitation ions.

$$ug/L = \frac{A_x \times I_s \times V_t \times Df}{A_{is} \times RRF \times V_o \times V_i} \qquad \text{(XI.6)}$$

where:

Ax = area of characteristic ion (EICP) for compound being measured
A_{is} = area of characteristic ion (EICP) for the internal standard
I_s = amount of internal standard added (ng)
RRF = daily relative response factor for compound being measured
V_o = volume of water extracted (mL)
V_i = volume of extract injected (uL)
V_t = volume of concentrated extract (uL)
Df = dilution factor

Table B.8. Semivolatile Internal Standards and Their Corresponding Target Compounds

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Phenol	Nitrobenzene	Hexachlorocyclopentadiene
bis(2-Chloroethyl)ether	Isophorone	2,4,6-Trichlorophenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol
2-Methylphenol	2,4-Dimethylphenol	2-Chloronaphthalene
2,2'-oxybis-(1-Chloropropane)	bis(2-Chloroethoxy)methane	2-Nitroaniline
4-Methylphenol	2,4-Dichlorophenol	Dimethyl phthalate
N-Nitroso-di-n-propylamine	1,2,4-Trichlorobenzene	Acenaphthylene
2-Fluorophenol (surr)	Naphthalene	3-Nitroaniline
Phenol-d_5 (surr)	4-Chloroaniline	Acenaphthene
	Hexachlorobutadiene	2,4-Dinitrophenol
	4-Chloro-3-methylphenol	4-Nitrophenol
	2-Methylnaphthalene	Dibenzofuran
	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene
		2,6-Dinitrotoluene
		Diethyl phthalate
		4-Chlorophenyl-phenyl ether
		Fluorene
		4-Nitroaniline
		2-Fluorobiphenyl (surr)
		2,4,6-Tribromophenol (surr)

surr = surrogate compound

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Butylbenzyl phthalate	Benzo(b)fluoranthene
4-Bromophenyl phenyl ether	3,3'-Dichlorobenzidine	Benzo(k)fluoranthene
Hexachlorobenzene	Benzo(a)anthracene	Benzo(a)pyrene
Pentachlorophenol	bis(2-Ethylhexyl)phthalate	Indeno(1,2,3-cd)pyrene
Phenanthrene	Chrysene	Dibenz(a,h)anthracene
Anthracene	Terphenyl-d_{14} (surr)	Benzo(g,h,i) perylene
Di-n-butyl phthalate		
Fluoranthene		

surr = surrogate compound

Table B.9 Semivolatile Quantitation Ions

Analyte	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
2,2'-oxybis(1-Chloropropane)	45	77, 79
4,-Methylphenol	108	107
N-nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
bis(-2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138

Table B.9 Semivolatile Quantitation Ions (Continued)

Analyte	Primary Ion	Secondary Ion(s)
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl phthalate	149	---

Table B.9 Semivolatile Quantitation Ions (Continued)

Analyte	Primary Ion	Secondary Ion(s)
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
Surrogates		
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
d-5 Nitrobenzene	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

APPENDIX C

CONTRACTUAL REQUIREMENT COMPARISON TABLES

Table C.1. Comparison of Requirements for Volatile Data Review

REQUIREMENT	MULTI-MEDIA, MULTI-CONCENTRATION	LOW CONCENTRATION WATERS
Target Compound List	33 Target Compounds	40 Target Compounds
Data Turnaround	35 days	14 days
Technical Holding Time	7 days if not preserved 14 days if preserved	7 days if not preserved 14 days if preserved
Initial Calibration	5 levels: 10 - 200 ug/L	5 levels: 1 - 25 ug/L (5 - 125 for Ketones)
Continuing Calibration	mid-level: 50 ug/L	mid-level: 5 ug/L (25 for Ketones)
Blanks	Method Blanks Instrument Blanks	Method Blanks Instrument Blanks Storage Blanks
SMC/Surrogates	SMC: 1,2-Dichloroethane-d_4 Bromofluorobenzene Toluene-d_8	Surrogate: Bromofluorobenzene
MS/MSD	Frequency: 1 per 20 samples, per matrix	N/A
LCS	N/A	1 per SDG
Regional QA/QC	PEs - variable	PEs - 1 per SDG
Internal Standards	IS Area: - 50% to + 100% IS RT Shift: $\pm$ 30 sec. 3 compounds: Chlorobenzene-d_5 1,4-Difluorobenzene Bromochloromethane	IS Area: $\pm$ 40% IS RT Shift: $\pm$ 20 sec. 3 compounds: Chlorobenzene-d_5 1,4-Difluorobenzene 1,4-Dichlorobenzene
CRQL	10 ppb (water/low soil) 1200 ppb (med soil)	1 - 5 ug/L
TICs	largest 10 $\geq$10% of nearest IS	largest 10 $\geq$40% of nearest IS

Table C.2. Comparison of Requirements for Semivolatile Data Review

REQUIREMENT	MULTI-MEDIA, MULTI-CONCENTRATION	LOW CONCENTRATION WATERS
Target Compound List	64 Target Compounds	60 Target Compounds
Data Turnaround	35 days	14 days
Technical Holding Time	Extraction - 5 days Analysis - 40 days after extraction	Extraction - 5 days Analysis - 40 days after extraction
Initial Calibration	5 levels: 20 - 160 ug/L	5 levels: varies
Continuing Calibration	mid-level: 50 ug/L	mid-level: varies
Blanks	Method Blanks Instrument Blanks	Method Blanks Instrument Blanks Storage Blanks
Surrogates	8 compounds	6 compounds
MS/MSD	Frequency: 1 per 20 samples, per matrix	N/A
LCS	N/A	1 per SDG
Regional QA/QC	PEs - variable	PEs - 1 per SDG
Internal Standards	IS Area: - 50% to + 100% IS RT Shift: $\pm$ 30 sec.	IS Area: - 50% to 100% IS RT Shift: $\pm$ 20 sec.
CRQLs	10 - 50 ppb (water) 330 - 1700 ppb (low soil) 10,000 - 50,000 (med soil)	5 - 20 ug/L
TICs	largest 20 $\geq$10% of nearest IS	largest 20 $\geq$50% of nearest IS

APPENDIX D

PROPOSED GUIDANCE FOR TENTATIVELY IDENTIFIED COMPOUNDS (VOA AND SV)

Proposed Guidance for Tentatively Identified Compounds (VOA)

A. **Review Items:** Form I VOA-TIC, chromatograms, library search printout and spectra for three TIC candidates, and GC retention time data.

B. **Objective**

Chromatographic peaks in volatile analyses that are not TCL compounds, system monitoring compounds, or internal standards are potential tentatively identified compounds (TICs) or library search compounds (LSCs). TICs must be qualitatively identified by a library search of the National Institute of Standards and Technology (NIST) mass spectral library, and the identifications assessed by the data reviewer.

C. **Criteria**

For each sample, the laboratory must conduct a library search of the NIST mass spectral library and report the possible identity for the 10 largest volatile fraction peaks which are not surrogates, internal standards, or TCL compounds, but which have a peak area greater than 40 percent of the peak area of the nearest internal standard. TIC results are reported for each sample on the Organic Analysis Data Sheet (Form I VOA-TIC).

Note: Since the SOW revision of October 1986, the CLP does not allow the laboratory to report as tentatively identified compounds any TCL compound which is properly reported in another fraction. (For example, late eluting volatile TCL compounds must not be reported as semivolatile TICs.)

D. **Evaluation**

1. Guidelines for Tentative Identification are as follows:

   The interpretation of library search compounds (LSCs) is one of the aspects of data review which calls for the fullest exercise of professional judgement. The reviewer must be thoroughly familiar with the principles and practice of mass spectral interpretation and of gas chromatography. Because the interpretation process is labor-intensive, it is important to document the process involved in arriving at a tentative identification.

   Worksheets for "Tentative Identification of Library Search Compounds" are provided in Appendix B for the volatile GC/MS fractions to assist in generating the information needed to make a reasonable tentative identification of the LSCs.

   The process involved in tentatively identifying a library search compound may be summarized as follows:

   a. Identify all samples in the related group (Case, SAS or SDG) in which the unknown compound occurs. Calculation of relative retention times (RRT) and comparison of RRT and mass spectral data across samples is extremely helpful in identifying unknowns that occur repeatedly in related samples. Use one worksheet per unknown for all samples in which it occurs.

   b. Inspect the library search spectrum retrieved for each unknown, to determine if detailed mass spectral interpretation is necessary. Often, it is obvious that the

correct match is among the spectra retrieved for the unknown from the several samples in which it is found. It may only be necessary to check the unknown's RRT versus a reference list of VOA (generated under similar conditions and after accounting for bias in the sample) to arrive at a satisfactory tentative identification. Some references are provided. If a reference RRT is not available, then a comparison of the unknown's RRT or boiling point to the RRT or boiling point of a closely related compound may also provide a satisfactory tentative identification. Within a compound class, retention time increases with increasing boiling point.

c. In the event that serious ambiguity still exists after examining the library spectra and RRT data, a full mass spectral interpretation can narrow down the possibilities. While a full discussion of manual mass spectral interpretation is beyond the scope of this document, several key points may be mentioned as important objects:

- o Determine a likely molecular weight. Depending on the unknown, the MW may or may not be apparent due to the extent of fragmentation. The MW of the retrieved library spectra, interpreted in light of the RRT, may be helpful if the molecular ion is not present.

- o Determine the isotope ratios (M+1)/M, (M+2)/M, (M+4)/M, etc. (where M is the molecular ion) and determine a short list of possible molecular formulas. Isotope ratios will also reveal the presence of S, Cl, and Br.

- o Calculate the total number of rings-plus-double-bonds in the unknown by applying the following equation to the likely molecular formulas, to determine the degree of unsaturation.

  Number of rings-plus-double bonds (r+db):

  $$(r+db) = C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

  where: C = no. of carbons
  H = no. of hydrogens
  X = no. of halogens
  N = no. of nitrogens

  Note: oxygen and sulfur do not need to be accounted for. An aromatic ring counts as four rings and double bonds.

- o Calculate the mass losses represented by major peaks in the unknown spectrum, and relate these to the fragmentation of neutral moieties from the molecular ion or other daughter ions.

- o Using the information gathered on molecular weight, molecular formula, degree of unsaturation, and mass losses in the unknown spectrum, combined with the RRT data, give as precise a description of the unknown as possible, including an exact identification if it is justified.

d. In the event that the unknown spectrum is not that of a pure compound, mass spectral interpretation may not be possible. However, in some instances, a mixed spectrum may be recognized as two compounds having very similar relative retention times. Target compounds, surrogates and internal standards may also be responsible for extra ions in an unknown spectrum.

2. Check the raw data to verify that the laboratory has generated a library search spectrum for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level non-TCL compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 40 percent of the internal standard peak area or height, but present in the blank chromatogram at similar relative retention time.

4. All mass spectra for every sample and blank must be examined.

5. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

Examples:

a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 ug/L or 4000 ug/Kg.

b. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

6. Occasionally, a TCL compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.

7. TCL compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

8. Library searches should not be performed on internal standards or surrogates.

9. TIC concentration should be estimated assuming a RRF of 1.0.

E. Action

1. All TIC results should be qualified as tentatively identified (N) with estimated concentrations (J) or (NJ).

2. General actions related to the review of TIC results are as follows:

   a. A non-TCL compound is not considered to be "tentatively identified" until the mass spectrum and retention time data have been reviewed according to the evaluation guidelines in XIII.D. The review should be documented on the Tentative Identification of Library Search Compound worksheet. The worksheet will be useful if a better library match for the unknown is retrieved in another Case, SAS, or SDG. It may also be used in writing a Special Analytical Service Statement of Work to identify the unknown, or if the sample is sent to an EPA research laboratc ·LSC identification by multiple spectral techniques.

   b. If all contractually required peaks were not library searched, the desig... representative could request these data from the laboratory.

3. TIC results which are not sufficiently above the level in the blank should not be reported. (Dilutions and sample size must be taken into account when comparing the amounts present in blanks and samples.)

4. When a compound is not found in any blanks, but is a suspected artifact or common laboratory contaminant, the result may be qualified as unusable (R).

5. The reviewer may elect to report all similar isomers as a total. (All alkanes may be summarized and reported as total hydrocarbons.)

6. The data reviewer should state the degree of confidence (high, medium, low) in the tentative identification after completing the review process.

7. The complete "Tentative Identification of Library Search Compound" worksheet should be attached to the final data review report.

APPENDIX

Equation 1:

$$RI = 100 \quad \frac{RTunk - RTz}{RTz+1 - RTz} + 100Z$$

where: RTunk is the retention time of the unknown
RTz is the retention time of the preceeding retention index standard
RTz+1 is the retention time of the following retention index standard
Z = number of rings in the retention index standard
RI = Lee Retention Index

Retention Index Standards

naphthalene	z=2	RI=200.00
phenanthrene	z=3	RI=300.00
chrysene	z=4	RI=400.00
Benzo(g,h,i) perylene	z=5	RI=500.00

Note: when these compounds are not dound in the sample of interest, RT data for the deuterated internal standards or most recent calibration may be used. Retention time shifts and bias must be accounted for.

Equation 2

Number of rings-plus-double bonds (r+db):

$$(r+db) = C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

where: C = no. of carbons
H = no. of hydrogens
X = no. of halogens
N = no. of nitrogens

Note: oxygen and sulfur do not need to be accounted for. An aromatic ring counts as four rings and double bonds.

REFERENCES

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3. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., Spectrometric Identification of Organic Compounds 4th ed., Wiley, New York, 1981.

4. Vassilaros, D.M., Kong, R.C., Later, D.W. and Lee, M.L., "Linear Retention Index System for polycyclic Aromatic Compounds. Critical Evaluation and Additional Indices". J. of Chromatography, 252 (1982) pp. 1-20.

Proposed Guidance for Tentatively Identified Compounds (SV)

A. **Review Items:** Form I SV-TIC, chromatograms, library search printout and spectra for three TIC candidates, and GC retention time data.

B. **Objective**

Chromatographic peaks in semivolatile analyses that are not TCL compounds, surrogates, or internal standards are potential tentatively identified compounds (TICs) or library search compounds (LSCs). TICs must be qualitatively identified by a library search of the National Institute of Standards and Technology (NIST) mass spectral library, and the identifications assessed by the data reviewer.

C. **Criteria**

For each sample, the laboratory must conduct a library search of the NIST mass spectral library and report the possible identity for the 20 largest semivolatile fraction peaks which are not surrogates, internal standards, or TCL compounds, but which have a peak area greater than 50 percent of the peak area of the nearest internal standard. TIC results are reported for each sample on the Organic Analysis Data Sheet (Form I SV-TIC).

Note: Since the SOW revision of October 1986, the CLP does not allow the laboratory to report as tentatively identified compounds any TCL compound which is properly reported in another fraction. (For example, late eluting volatile TCL compounds must not be reported as semivolatile TICs.)

D. **Evaluation**

1. Guidelines for Tentative Identification are as follows:

   The interpretation of library search compounds (LSCs) is one of the aspects of data review which calls for the fullest exercise of professional judgement. The reviewer must be thoroughly familiar with the principles and practice of mass spectral interpretation and of gas chromatography. Because the interpretation process is labor-intensive, it is important to document the process involved in arriving at a tentative identification.

   Worksheets for "Tentative Identification of Library Search Compounds" are provided in Appendix B for the semivolatile GC/MS fractions to assist in generating the information needed to make a reasonable identification of the TICs.

   The process involved in tentatively identifying a library search compound may be summarized as follows:

   a) Identify all samples in the related group (Case, SAS or SDG) in which the unknown compound occurs. Calculation of retention indices (RI) and comparison of RI and mass spectra across samples is extremely helpful in identifying unknowns that occur repeatedly in related samples. Use one worksheet per unknown for all samples in which it occurs. Retention indices are calculated according to the following example:

$$RI = 100 \quad \frac{RTunk - RTz}{RTz+1 - RTz} + 100Z$$

where: RTunk is the retention time of the unknown
RTz is the retention time of the preceeding retention index standard
RTz+1 is the retention time of the following retention index standard
Z = number of rings in the retention index standard
RI = Lee Retention Index

Retention Index Standards

naphthalene	z=2	RI=200.00
phenanthrene	z=3	RI=300.00
chrysene	z=4	RI=400.00
Benzo(g,h,i) perylene	z=5	RI=500.00

Note: when these compounds are not dound in the sample of interest, RT data for the deuterated internal standards or most recent calibration may be used. Retention time shifts and bias must be accounted for.

b) Inspect the library search spectrum retrieved for each unknown, to determine if detailed mass spectral interpretation is necessary. Often, it is obvious that the correct match is among the spectra retrieved for the unknown from the several samples in which it is found. It may only be necessary to check the unknown's RI versus a reference list of SV (generated under similar conditions and after accounting for bias in the sample) to arrive at a satisfactory tentative identification. Some references are provided. If a reference RI is not available, then a comparison of the unknown's RI or boiling point to the RI or boiling point of a closely related compound may also provide a satisfactory tentative identification. Within a compound class, retention time increases with increasing boiling point.

c) In the event that serious ambiguity still exists after examining the library spectra and RI data, a full mass spectral interpretation can narrow down the possibilities. While a full discussion of manual mass spectral interpretation is beyond the scope of this document, several key points may be mentioned as important objects:

- o Determine a likely molecular weight. Depending on the unknown, the MW may or may not be apparent due to the extent of fragmentation. The MW of the retrieved library spectra, interpreted in light of the RI, may be helpful if the molecular ion is not present.

- o Determine the isotope ratios (M+1)/M, (M+2)/M, (M+4)/M, etc. (where M is the molecular ion) and determine a short list of possible molecular formulas. Isotope ratios will also reveal the presence of S, Cl, and Br.

- o Calculate the total number of rings-plus-double-bonds in the unknown by applying the follwing equation to the likely molecular formulas, to determine the degree of unsaturation.

  Number of rings-plus-double bonds (r+db):

  $$(r+db) = C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

  where: C = no. of carbons
  H = no. of hydrogens
  X = no. of halogens
  N = no. of nitrogens

  Note: oxygen and sulfur do not need to be accounted for. An aromatic ring counts as four rings and double bonds.

- o Calculate the mass losses represented by major peaks in the unknown spectrum, and relate these to the fragmentation of neutral moieties from the molecular ion or other daughter ions.

- o Using the information gathered on molecular weight, molecular formula, degree of unsaturation, and mass losses in the unknown spectrum, combined with the RI data, give as precise a description of the unknown as possible, including an exact identification if it is justified.

d) In the event that the unknown spectrum is not that of a pure compound, mass spectral interpretation may not be possible. However, in some instances, a mixed spectrum may be recognized as two compounds having very similar retention indices (for example, ortho-terphenyl, RI=317.43 and nonadecane, RI=317.20). This particular coelution would result in an unknown spectrum having a polycyclic aromatic pattern at m/z 230, the MW of terphenyl, with an hydrocarbon type pattern at m/z 43,57,71, etc. Target compounds, surrogates and internal standards may also be responsible for extra ions in an unknown spectrum, and may be treated similarly.

2. Check the raw data to verify that the laboratory has generated a library search spectrum for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level non-TCL compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10 percent of the internal standard peak area or height, but present in the blank chromatogram at similar relative retention time.

4. All mass spectra for every sample and blank must be examined.

5. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   Examples:

   a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 ug/L or 4000 ug/Kg.

   b. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

   c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

6. Occasionally, a TCL compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.

7. TCL compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

8. Library searches should not be performed on internal standards or surrogates.

9. TIC concentration should be estimated assuming a RRF of 1.0.

E. Action

1. All TIC results should be qualified as tentatively identified (N) with estimated concentrations (J) or (NJ).

2. General actions related to the review of TIC results are as follows:

   a. A non-TCL compound is not considered to be "tentatively identified" until the mass spectrum and retention time data have been reviewed as per section XIII D. The review should be documented on the Tentative Identification of Library Search Compound worksheet. The worksheet will be useful if a better library match for the unknown is retrieved in another Case, SAS, or SDG. It may also be used in writing a Special Analytical Service Statement of Work to identify the unknown, or if the sample is sent to an EPA research laboratory for LSC identification by multiple spectral techniques.

b. If all contractually required peaks were not library searched, the designated representative could request these data from the laboratory.

3. TIC results which are not sufficiently above the level in the blank should not be reported. (Dilutions and sample size must be taken into account when comparing the amounts present in blanks and samples.)

4. When a compound is not found in any blanks, but is a suspected artifact or common laboratory contaminant, the result may be qualified as unusable (R).

5. The reviewer may elect to report all similar isomers as a total. (All alkanes may be summarized and reported as total hydrocarbons.)

6. The data reviewer should state the degree of confidence (high, medium, low) in the tentative identification after completing the review process.

7. The complete "Tentative Identification of Library Search Compound" worksheet should be attached to the final data review report.

APPENDIX E

GLOSSARY OF TERMS

APPENDIX I

GLOSSARY OF TERMS

APO	Administrative Project Officer
BFB	Bromofluorobenzene - volatile instrument performance check compound
BNA	Base/Neutral/Acid Compounds - compounds analyzed by semivolatile technique
Case	A finite, usually predetermined number of samples collected over a given time period for a particular site. A Case consists of one or more Sample Delivery Group(s).
CCS	Contract Compliance Screening - process in which SMO inspects analytical data for contractual compliance and provides results to the Regions, laboratories and EMSL/LV.
CF	Calibration Factor
CRQL	Contract Required Quantitation Limit
CSF	Complete SDG File
DFTPP	Decafluorotriphenylphosphine - semivolatile instrument performance check compound
DPO	Deputy Project Officer
EICP	Extracted Ion Current Profile
GC/EC	Gas Chromatography/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GPC	Gel Permeation Chromatography - A sample clean-up technique that separates compounds by size and molecular weight. Generally used to remove oily materials from sample extracts.
IS	Internal Standards - Compounds added to every VOA and BNA standard, blank, matrix spike duplicate, and sample extract at a known concentration, prior to instrumental analysis. Internal standards are used as the basis for quantitation of the target compounds.
LCS	Laboratory Control Sample
MS/MSD	Matrix Spike/Matrix Spike Duplicate
m/z	The ratio of mass (m) to charge (z) of ions measured by GC/MS
OADS	Organic Analysis Data Sheet (Form I)
ORDA	Organic Regional Data Assessment - from earlier version of the Functional Guidelines
NIST	National Institute of Standards and Technology

PCB	Polychlorinated biphenyl (Arochlor is a trademark)
PE	Sample Performance Evaluation Sample
QA	Quality Assurance - Total program for assuring the reliability of data.
QC	Quality Control - Routine application of procedures for controlling the monitoring process
RIC	Reconstructed Ion Chromatogram
RPD	Relative Percent Difference (between matrix spike and matrix spike duplicate)
RRF	Relative Response Factor
$\overline{RRF}$	Average Relative Response Factor
RRT	Relative Retention Time (with relation to internal standard)
RSD	Relative Standard Deviation
RT	Retention Time
SDG	Sample Delivery Group - Defined by one of the following, whichever occurs first: • Case of field samples • Each 20 field samples within a Case • Each 14-day calendar period during which field samples in a Case are received, beginning with receipt of the first sample in the SDG. (For VOA contracts, the calendar period is 7-day.)
SMC	System Monitoring Compound - formerly surrogates for volatile analysis.
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
SV	Semivolatile analysis - Method based on analysis by GC/MS for BNA organic compounds.
TCL	Target Compound List
TIC	Tentatively Identified Compound - A compound tentatively identified from search of the NIST mass spectral library that is not on the TCL.
TPO	Technical Project Officer

VOA	Volatile Organic Analysis - Method based on the purge and trap technique for organic compound analysis.
VTSR	Validated Time of Sample Receipt - Time of sample receipt at the laboratory as recorded on the shipper's delivery receipt and Sample Traffic Report.