REGION III MODIFICATIONS

TO

NATIONAL FUNCTIONAL GUIDELINES

FOR

ORGANIC DATA REVIEW

MULTI-MEDIA, MULTI-CONCENTRATION

(OLMO1.0-OLMO1.9)

SEPTEMBER 1994

FOREWORD

This document is a modification to the ***National Functional Guidelines for Organic Data Review*** (Draft, February, 1994). This document describes those procedures that are to be used for Region III Data Validation. It is intended for implementation for all CLP data acquired for use within Region III but it may be adapted for use with other similar methods. All comments and questions pertaining to this document should be addressed to:

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INTRODUCTION

This document is designed to offer guidance on EPA Contract Laboratory Program (CLP) analytical data evaluation and review. It has been modified for use within U.S. EPA Region III. 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 revisions through OLM01.9).

This update includes changes to instrument performance checks (formerly referred to as tuning) and calibration criteria as a result of the Response Factor Workgroup. Regional Modifications 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 usability 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. In order to facilitate communication with the data users in Region III, specific reporting formats for the data validation report are required. Each report must contain a table of the summarized data, sufficient narrative to inform the user of significant data review issues and adequate documentation to support the decisions and actions of the data reviewer. The Standard Operating Procedure for preparing the Region III data validation report is presented in Appendix B.

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 Region III SOP for Data Validation Reports. Appropriate equations are presented for easy reference and to allow the reviewer to verify calculations as needed. Contractual requirements are provided in Appendix C to facilitate comparisons with the technical requirements. Appendix D contains proposed guidance for Tentatively Identified Compounds (VOA and SV), and Appendix E contains a glossary of commonly used terms.

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 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 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.

GLOSSARY OF DATA QUALIFIER CODES (ORGANIC)

CODES RELATING TO IDENTIFICATION
(CONFIDENCE CONCERNING PRESENCE OR ABSENCE OF COMPOUNDS):

U = Not detected. The associated number indicates approximate sample concentration necessary to be detected.

(NO CODE) = Confirmed identification.

B = Not detected substantially above the level reported in laboratory or field blanks.

R = Unreliable result. Analyte may or may not be present in the sample. Supporting data necessary to confirm result.

N = Tentative identification. Consider present. Special methods may be needed to confirm its presence or absence in future sampling efforts.

CODES RELATED TO QUANTITATION
(can be used for both positive results and sample quantitation limits):

J = Analyte present. Reported value may not be accurate or precise.

K = Analyte present. Reported value may be biased high. Actual value is expected lower.

L = Analyte present. Reported value may be biased low. Actual value is expected to be higher.

UJ = Not detected, quantitation limit may be inaccurate or imprecise.

UL = Not detected, quantitation limit is probably higher.

OTHER CODES

Q = No analytical result.

NJ = Qualitative identification questionable due to poor resolution. Presumptively present at approximate quantity.

VOA

VOLATILE DATA REVIEW

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 (CCS)

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Regional Quality Assurance and Quality Control

IX. Internal Standards (CCS)

X. Target Compound Identification

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

XII. Tentatively Identified Compounds

XIII. System Performance

XIV. 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, 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. In Region III, a 14 day holding time will be applied to all non-aqueous samples. When soil holding time criteria are established and available, the procedure for qualifying soil samples will be re-evaluated.

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 are 14 days from sample collection.
>
> Water samples that have not been maintained at 4°C (± 2°C) and/or 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 circumstances, the temperature of the samples may exceed 4°C.

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

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 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).

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

   If the samples were properly preserved but the technical holding times exceeded 14 days, for aqueous and non-aqueous samples, qualify all positive results with "L" and all sample quantitation limits with "UL".

   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	None	All Compounds

   * 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 bias low and are qualified with "L".

3. Due to limited information concerning holding times for non-aqueous samples, it is recommended that a comment in the data review narrative be included to state that a holding time of 14 days was used.

Technical Holding Times

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

5. 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 may have occurred so that the field and/or shipping problem can be corrected. The reviewer may pass this information on to the Regional TPO for that laboratory, but should explain that contractually the laboratory met the requirements.

6. When there are other quality control problems in conjunction with exceeded holding times (such as suspected laboratory contamination), the reviewer should follow the hierarchy of qualifiers. In particular, if for any reason the reviewer doubts the presence of a compound, the data summary form should display only the "B" or "R" qualifier and not the "L" qualifier. This is because no net direction of bias can be inferred under these conditions. When results are reported by the laboratory as below the CRQL, the "L" qualifier is used over the "J" qualifier.

II. GC/MS Instrument Performance Check

A. Review Items: Form V VOA, 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) with each mass listing submitted to ensure the following:

   Form V VOA is present and completed for each 12-hour period during which samples were analyzed.

   The laboratory has not made transcription errors between the raw 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.

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. (See SOW for requirements).

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.

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, 174/176, 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 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 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.

III. Initial Calibration

A. Review Items: Form VI VOA, 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.

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 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).

4. The Percent Relative Standard Deviation (%RSD) from the initial calibration must be less than or equal to 30.0% for all compounds. (Contractual calibration %RSD criteria are listed in Appendix A).

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).

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.

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, 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**

NOTE: Compounds in **bold** are system monitoring compounds.

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

   a. Check and recalculate the %RSD 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 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 $\pm$ 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 the initial calibration for either $\overline{RRF}$ or %RSD, perform a more comprehensive evaluation.

E. Action

1. All volatile target compounds, including the 9 "poor performers" (see Table 2, system monitoring compounds are excluded) 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". Non-detects are not qualified. When the %RSD is grossly exceeded (i.e., > 50%) use professional judgement for qualifying non-detects as "UJ".

   b. If any initial calibration $\overline{RRF}$ is less than 0.05, qualify positive results that have acceptable mass spectral identification with "L", 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. No qualifiers are needed for volatile target compounds that were not detected. If the %RSD is grossly exceeded (i.e., >50%), professional judgement is used to qualify non-detects with "UJ".

   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 for volatile target compounds that were not detected. If the %RSD is grossly exceeded (i.e., >50%), professional judgement is used to qualify non-detects with "UJ".

   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. No qualifiers are needed for volatile target compounds that were not detected. If the %RSD is grossly exceeded (i.e., >50%), professional judgement is used to qualify non-detects with "UJ").

   NOTE: If a, b, or c options are used, a description of the process must be clearly stated in the data review narrative.

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. The potential effects on the data due to unacceptable calibration criteria should be noted in the data review narrative.

5. When there are other quality control problems in conjunction with exceeding initial calibration criteria, the reviewer should follow the hierarchy of qualifiers. In particular, if for any reason the reviewer doubts the presence of a compound, the data summary form should display only the "B" or "R" qualifier and not the "L" or "J" qualifier.

IV. Continuing Calibration

A. Review Items: Form VII VOA, 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 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. The continuing calibration may either be a part of the initial calibration or run independently on another 12-hour analysis period.

2. The continuing calibration RRF for volatile target compounds and system monitoring compounds 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%.

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 compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that all volatile 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 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, no qualification of non-detected volatile target compounds is necessary. If the %D is grossly exceeded (>50%), professional judgement may be used to qualify non-detects with "UJ".

   c. If the continuing calibration RRF is less than 0.05, qualify positive results that have acceptable mass spectral identifications with "L".

   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. The potential effects on the data due to unacceptable calibration criteria should be noted in the data review narrative.

4. When there are other quality control problems in conjunction with exceeding continuing calibration criteria, the reviewer should follow the hierarchy of qualifiers. In particular, if for any reason the reviewer doubts the presence of a compound, the data summary form should display only the "B" or "R" qualifier and not the "L" or "J" qualifier.

V. Blanks

A. Review Items: Form I VOA, Form IV VOA, 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., methods 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.

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) 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).

E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2, 3, and 4, 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.

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. Positive sample results should be reported and qualified "B", if 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 situations where more than one blank is associated with a given sample, qualification should be based upon a comparison with the blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

For qualification purposes, consider all blanks in a case associated with all samples.

Field blanks measure contamination introduced not only in the field but also from the laboratory. In general, evaluation of the impact on specific sample results is handled the same as with laboratory blanks. The reviewer should use caution in attributing contamination to the field as opposed to laboratory sources. However, when field-introduced contamination is suspected, it is helpful for the reviewer to consult the sampling group to identify possible sources and prevent future reoccurrences. Verified field sources of contamination should be noted in the data review narrative. If a field blank has the highest concentration of a contaminant, then all samples in the associated case are qualified "B", using the 5x and 10x rule. Other field blanks associated with the case are not qualified. Specific actions are as follows:

1. If a volatile compound is found in a blank but not found in the sample, no action is taken.

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 "B", when the sample concentration is less than five times (5x) the blank concentration. For common volatile laboratory contaminants, the results are qualified "B", when the sample concentration is less than 10 times (10x) the blank concentration.

3. 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 it 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.

VI. System Monitoring Compounds (Surrogate Spikes)

A: Review Items: Form II VOA 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 and blank matrices.

2. Recoveries for system monitoring compounds in volatile samples and blanks must be within the limits specified in Appendix A 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. Check for any calculation or transcription errors.

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

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

   a. If any system monitoring 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 recoveries followed by successful analyses, the laboratories are required to report only the successful run.

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

c. Verify that no blanks have system monitoring compounds 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 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 results if the recovery of any volatile system monitoring compound is out of specification. For system monitoring compound 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. (Also, see Table 3.)

1. If a system monitoring compound in the volatile sample has a recovery greater than the upper acceptance limit:

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

b. Results for non-detected volatile target compounds should be qualified "UJ".

2. If a system monitoring compound in the volatile sample has a recovery greater than or equal to 10% but less than the lower acceptance limit:

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 in a volatile sample shows less than 10% recovery:

a. Detected volatile compounds are qualified "L".

b. Non-detected volatile target compounds are qualified as unusable, "R".

4. 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.

5. 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 in the report narrative.

6. 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 XIII for TIC guidance.)

7. 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. Sample results which are possible artifacts of carry-over should be flagged as unusable "R".

8. When there is convincing evidence that contamination is restricted to a particular instrument, matrix, or concentration level, the 5x/10x rule will only be applied to compare contaminated blanks to certain associated samples (as opposed to all samples in the case). Some examples are as follows:

   Column bleed (siloxanes) may be localized to a particular instrument.

   Methanol extractions in the medium soil volatile analysis protocol can give rise to contaminants that are not seen in the low-level aqueous analyses.

   Common laboratory contaminants, such as methylene chloride, are generally too unpredicatable to safely assume contamination is restricted to a particular instrument, matrix, or concentration level.

9. For benzene and/or toluene, the reviewer may identify that the observed laboratory contamination is attributable to a specific, regular, and predictable process (such as trap bleed), which results in a constant 1 or 2 ppb instrument level concentration in all runs (both samples and blanks). In this situation, the reviewer may want to consider flaging certain results as tentatively identified, "N", as opposed to "B", if the sample instrument level is clearly greater than the consistent level of contamination detected in blanks and other samples. (This particular situation supercedes the 5x/10x rule.)

10. The following are examples of applying the blank qualification guidelines. Certain circumstances may warrant deviations from these guidelines. Any deviations must be clearly stated in the data review narrative.

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	60B	30B

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

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	4B	4B

Note that data are reported as 4B, indicating that the qualitative presence is not confirmed.

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	12O	60
Final Sample Result	12O	60

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

4. If two or three system monitoring compounds in the volatile sample have recoveries outside acceptance limits, refer to Table 3.

Table 3. Qualification of Volatile Analytes Based on System Monitoring Compound Recoveries

	1 or more < 10%	1 High/Low	2 or 3 High/Low	2 or 3 All Low	2 or 3 All High
Detected Analytes	L	J	J	L	K
Non-Detected Analytes	R	UJ	UJ	UL	None

5. In the special case of a blank analysis with system monitoring compounds 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 recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence.

6. 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.

7. Positive results for compounds already flagged for blank contamination, "B", will not need a separate flag for system monitoring compound recoveries. However, these situations should be addressed in the data review narrative and the support documentation.

8. When dilutions are performed which prevent detection of system monitoring compounds, the data review narrative and support documentation should indicate that extraction efficiency/method accuracy cannot be verified.

9. When both the initial analysis and the reanalysis have system monitoring compound recoveries outside of criteria, the data summary form should normally contain the highest concentration obtained for each compound detected, provided that system monitoring compound recoveries in the analysis being reported do not suggest a high bias. However, if a demonstrated laboratory contaminant is detected in one analysis but not in the other, the negative result may be more appropriate to report.

When the reanalysis of a sample is within the system monitoring compound recovery criteria, the laboratory is required to provide only data for the acceptable analysis. If both sets of data are provided, and if a compound was detected in the initial analysis but not in the reanalysis, then the positive result should be reported (provided the compound is not a demonstrated laboratory contaminant). The reported result should be flagged as estimated "J", due to possible sample inhomogeneity.

VII. Matrix Spike/Matrix Spike Duplicate

A. Review Items: Form III VOA-I 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 spike (MS) and matrix spike duplicate (MSD) samples are analyzed at a 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 VOA-2 and SOW.

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 and SOW.

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 RPDs 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 judgement, the data reviewer may use the MS and MSD results in conjunction with other QC criteria to 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.

5. When non-spiked compounds are present in either the MS or MSD results, a table in the data review narrative is constructed showing original (unspiked) sample results for non-spiked compounds, non-spiked compounds present in the MS and MSD and the calculated %RSD.

VIII. Regional Quality Assurance and Quality Control

A. Review Items: Form I VOA, chromatograms, and quantitation reports, and QAPjP.

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.

C. Criteria

Criteria are dependent on the type of QC sample. Frequency may vary.

1. The analytes present in the PE sample must be correctly identified and quantitated.

D. Evaluation

1. Evaluation of Performance Evaluation (PE) Samples are not to be presented as part of the data review. All Form Is associated with the Performance Evaluation Samples are to be sent (with a cover memo stating the case number and laboratory information) directly to the Quality Assurance Branch in Region III.

   U.S. Environmental Protection Agency
   Region III, Central Regional Laboratory
   Quality Assurance Branch
   201 Defense Highway, Suite 200
   Annapolis, MD 21401

   Attn: Program Support Section

2. Percent difference between target compounds present in the field duplicate samples shall be determined. Evaluation of the percent difference compared to those specified in the site QAPjP may be presented in the data review narrative.

E. Action

1. Field duplicate results are to be presented in a table format in the data review narrative. If target compounds were not present in either of the field duplicate samples, then a table is not required. The percent difference is to be calculated and presented in the table. (If one of the field duplicates was also used as a matrix spike/matrix spike duplicate sample, then the table should include any non-spiked compounds detected, along with the relative standard deviation.)

   No action is taken based on percent difference of field duplicate sample data alone. However using informed professional judgement the data reviewer may use the field duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data.

2. Other types of Regional QC Samples

Professional judgement is needed for evaluating other types of QC samples that may be associated with a particular case of samples. This information may be used in conjunction with other QC criteria to determine the need for qualification of data.

IX. Internal Standards

A. Review Items: Form VII VOA, 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.

2. The retention time of the internal standard must not vary more than ±30 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).

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, then:

   a. Positive results for compounds quantitated using that IS should be qualified as estimated, "J".

   b. Non-detected compounds quantitated using an IS area count greater than +100% or less that 50% should be qualified "UJ".

c. 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:

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.

X. Target Compound Identification

A. Review Items: Form I VOA, 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).

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.

   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.

D. Evaluation

1. Check that the RRT of reported compounds is within $\pm$ 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 carry-over is a possibility and should use professional judgement 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.

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, 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". The data review narrative and support documentation would verify that the misidentified peak was library searched as a TIC, if appropriate.

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

3. If the presence of a target compound is strongly suggested by raw data, but its mass spectrum contains minor inadequacies, the compound may be added to the data summary form and qualified as a tentative identification, "N". The reviewer should address corroborating evidence in the narrative, such as the presence of the compound in closely related compounds in the same sample.

4. If the laboratory did not report a compound of acceptable matching quality, the reviewer should add this compound to the sample data summary form. The narrative and the support documentation should indicate this action. The reviewer should request the laboratory to reexamine and resubmit the result, particularly if the value is greater than the CRQL.

5. Any changes made to the reported compounds or concerns regarding target compound identifications should be clearly indicated in the data review narrative. .

XI. Compound Quantitation and Reported CRQLs

A. Review Items: Form I VOA, 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 (also as specified in the SOW) 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 through out, 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 and in the document support.

2. Calculation errors can sometimes be revealed by abnormally high system monitoring compound recoveries, matrix spike recoveries, or inappropriately high results for certain compounds.

3. The reviewer must assure that any results in error by more than 10 percent are identified and corrected on the sample data summary. If laboratory resubmission is not performed, the reviewer should document his/her changes to the data in the narrative and support documentation.

4. If a sample concentration is above the highest standard and contract required dilutions were not performed, the chromatogram and mass spectrum should be examined for signs of a saturated signal. If the ion used for quantitation was saturated, then the result should be flagged as biased low, "L". If the ion used for quantitation was not saturated, the result should be flagged as estimated, "J".

XII. Tentatively Identified Compounds

A. Review Items: Form I VOA-TIC chromatograms, and library search printout and spectra for three tentatively identified compounds (TIC) candidates.

B. Objective

Chromatographic peaks in volatile fraction analyses that are not target analytes, system monitoring compounds 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 compounds, internal standards, or target compounds, but which have an 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).

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.

   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 a 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 fluorotrichloromethane), 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.

11. See Appendix B for additional guidance.

E. Action

1. All TIC results should be qualified "J", estimated concentration, on the laboratory Form I-TICs.

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. Blank Results

   Form I-TIC which contain sample results that are questioned by laboratory results, should be flagged "B" and a line drawn through these data for emphasis (initialed and dated), on the Form I-TIC that is included in the validation report.

   To be considered questionable, a sample TIC concentration must be within 10 times the concentration of one of the blank results. If different volumes/weights are used, the total amount of compound in the extract must be compared for sample versus blank. For VOA data, an instrument level comparison is used unless the contamination is proven to originate during sample storage (before preparation/analysis). In general, blanks analyzed within the same case, by the same lab, may be cross-applied to either soil or water samples extracted or analyzed on other days.

   To question a sample result, only presumptive evidence for the presence of the compound in the blank is necessary. The presence of the TIC in the blank is suggested in any of the following situations:

   a. Relative retention times (RRTs) match for sample versus blank, and the sample library search result matches the same compound or compound class as the library search result for the blank.

   b. RRTs match, but library search results do not list the same compound or class for sample versus blank. However, some of the largest ions in the sample are also in the blank, and a direct comparison of sample versus blank spectra suggests that the TIC in the sample is quite possibly the same compound as that in the blank.

c. A peak at the same RRT as the sample TIC is present in the chromatogram of the blank, but no library search was performed or included in the data. (The labs do not have to library search peaks less than 10% of the height of the nearest internal standard, although these peaks may still be important to identify low-level blank contaminants that can question sample results at levels above 10% of the nearest internal standard height.)

All blank results must be attached in the support documentation section of the data review.

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", and a line drawn through the result (initialed and dated) on a copy of the Form I-TIC that is included in the validation report.

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). These changes may be made directly on a copy of the Form I-TIC, as long as changes are initialed and dated.

6. 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 result.

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

8. Any changes made to the reported data or any concerns regarding TIC identifications should be indicated in the data review narrative. Any changes made regarding TIC identifications or qualifications are to be made on copies of the laboratory generated Form I-TIC and not the originals.

XIII. System Performance

A. Review Items: Form VIII VOA, Form III VOA-1 and VOA-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 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.

E. Action

Professional judgement must be used to qualify the data if it is determined that system performance has degraded during sample analyses.

XIV. 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 where necessary, 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. 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

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. Regional Quality Assurance and Quality Control

IX. Internal Standards (CCS)

X. Target Compound Identification

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

XII. Tentatively Identified Compounds

XIII. System Performance (CCS)

XIV. 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, 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 further required that semivolatile compounds in properly preserved non-aqueous samples be extracted within 7 days from sample collection and the extracts analyzed within 40 days from sample extraction.

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.

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 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.

Technical Holding Times SV

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. a. 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. However, please note that some extractable compounds are extremely persistent in the environment (e.g., PAHs) in non-aqueous matrices and would not be expected to degrade significantly during sample storage. The reviewer must use professional judgement in the application of data qualifiers to those compounds in non-aqueous matrices.

   b. If in the professional judgement of the data reviewer a loss of semivolatile compound(s) is evident due to exceeding the holding time criteria, the affected positive results or the associated quantitation limits may be qualified as biased low, "L" or "UL" respectively. The narrative must contain the reviewer's justification for qualification of the compound results as biased low.

2. If technical holding times are grossly exceeded (greater than 2 times the required technical holding time), 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. Because of limited information concerning holding times for non-aqueous samples, it is recommended that a comment in the data review narrative be included to state that aqueous holding times were applied.

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

5. 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 may have occurred so that the field problem can be corrected.

6. When there are other quality control problems in conjunction with exceeded holding times (such as suspected laboratory contamination), the reviewer should follow the hierarchy of qualifiers. In particular, if for any reason the reviewer doubts the presence of a compound, the data summary should display only the "B" or "R" qualifier, and not the "L" qualifier. This is because no net direction of bias can be inferred under these conditions.

II. GC/MS Instrument Performance Check

A. Review Items: Form V SV, 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 semivolatile 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) with each mass listing submitted and ensure the following:

   a. Form V SV 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.

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 II.D.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. 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 in the report narrative.

III. Initial Calibration

A. Review Items: Form VI SV-1 and SV-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.

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

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). (See Appendix A for list).

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.

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. If problems are suspected with low response factor or compound identification, also check elution order.

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	

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 or equal to 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 $\pm$ 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.

Initial Calibration **SV**

E. Action

1. All semivolatile target compounds, including the 19 "poor performers" (see Table 4) will be qualified using the following criteria:

   a. If the %RSD is greater than 30.0% and the $\overline{RRF}$ is greater than or equal to 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 resulting from a failure to meet calibration criteria should be noted in the data review narrative.

5. When it is suspected that relative response factors were incorrectly generated from misidentified peaks or incorrect area measurements, the laboratory should be contacted to requantitate these RRFs and associated sample results. The report narrative should identify affected results and document the cause of the reviewer's suspicions. In addition, a CLP telephone log must be completed.

6. Positive results for compounds flagged for blank contamination "B" will not need a separate flag "J" in the data summary form for minimum RRF, %RSD, or %D outside criteria. However, these situations should be addressed in the data review narrative.

IV. Continuing Calibration SV

A. Review Items: Form VII SV-1 and SV-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 III.D.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 based on professional judgement.

   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 resulting from a failure to meet calibration criteria should be noted in the data review narrative.

Continuing Calibration SV

4. When it is suspected that relative response factors were incorrectly generated from misidentified peaks or incorrect area measurements, the laboratory should be contacted to requantitate these RRFs and associated sample results. The report narrative should identify affected results and document the cause of the reviewer's suspicions. In addition, a CLP telephone log must be completed.

5. Positive results for compounds flagged for blank contamination "B" will not need a separate flag "J" in the data summary form for minimum RRF, %RSD, or %D outside criteria. However, these situations should be addressed in the data review narrative.

V. Blanks

A. Review Items: Form I SV-1 and SV-2, Form IV SV, 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.

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 comparison with the associated blank* having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

Field blanks measure contamination introduced not only in the field but also from the laboratory. In general, evaluation of the impact on specific sample results is handled as with laboratory blanks. The reviewer should use caution in attributing contamination to the field as opposed to laboratory sources. However, when field-introduced contamination is suspected, it is helpful for the reviewer to consult the sampling group to identify possible sources and prevent future reoccurrences. Verified field sources of contamination should be noted in the data review narrative. If a field blank has a highest concentration of a contaminant, then all samples in the associated case are qualified "B", using the 5x and 10x rule. Other field blanks associated with the case are not qualified.

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 in the report narrative.

2. Any semivolatile compound detected in the sample (other than the common phthalate contaminants), that was also detected in any associated blank, is qualified "B" if the sample concentration is less than five times (5x) the blank concentration. For phthalate contaminants, the results are qualified "B" when the sample result is less than 10x the blank concentration.

   In using the 5x/10x rule to compare blank results to sample results which were calculated using different weights, volumes, or dilution factors, the reviewer must choose between comparing the levels detected with the instrument, the total amount of compound (ug of contamination) present in the extracts, or the final concentration of the contaminant in the sample aliquots. Often, more than one approach will be acceptable and will yield the equivalent flagging of sample results.

   a. Comparisons involving sample dry weight correction factors, but with all other calculation factors the same for sample versus blank:

      o In this case, the reviewer can compare the wet weight concentrations, instrument levels, or the total amount of compound (ug of contaminant) in the extracts. All of these approaches will be acceptable and will yield equivalent flagging of sample results.

   b. When the sample has a smaller initial aliquot size than the blank (purge or extraction weight/volume), but all other calculation factors beyond this analytical step are identical (i.e.,

* For qualification purposes, to determine the highest concentration of a contaminant, consider all blanks in a case associated with all samples.

same final extract volumes, injection volumes, and extract dilution factors for sample versus blank):

- o In this case, it is acceptable and equivalent to compare either instrument levels, the total amount of compound (ug of contaminant) in the extracts, or the concentration of contaminant in the extracts.

- o Final concentrations of sample versus blank should not be compared.

c. When the sample has a larger final extract volume or a greater dilution factor than the blank:

- o If the laboratory contaminant may have been introduced after or during the sample dilution step, then a direct comparison of instrument levels is appropriate. For example, comparing the instrument level result for a water sample that was diluted 1:100 prior to injection would take into account possible laboratory contamination of the syringe, instrument, or dilution solvent.

- o On the other hand, if it is highly probable that the contamination originated before the dilution step, then it is more appropriate to calculate and compare the total amount of compound (ug of contaminant) present in the undiluted extract of the sample versus the blank. For example, a BNA extract diluted 1:100 prior to injection may only be subject to phthalate contamination prior to the dilution step (i.e., during extraction/concentration).

- o If the results of a dilution run are to be flagged "B" because of blank contamination, the reviewer should attempt to determine whether an undiluted run was also performed. If so, the undiluted run may be used to verify the presence of a compound detected at levels too high to be questioned or, conversely, to prove that a compound was actually not present at levels multiplied by a dilution factor.

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. 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.

7. Blanks or samples run after a matrix spike or standard should be carefully examined to determine the occurrence of instrument or syringe carry-over. Since the efficiency of sample transfer can vary dramatically according to apparatus and operator techniques, professional judgment should be used in each case to determine whether sample or blank results are attributable to carry-over. Some common examples are as follows:

   o Zero to one percent syringe carry-over occasionally in BNA runs.

   o Higher percentages of carry-over following BNA runs that are saturated.

   Sample results which are possible artifacts of carry-over should be flagged as unusable,"R".

8. When there is convincing evidence that contamination is restricted to a particular instrument, matrix, or concentration level, the 5X/10X rule will only be applied to compare contaminated blanks to certain associated samples (as opposed to all samples in the case). Some examples are as follows:

   o Column bleed (siloxanes) may be localized to a particular instrument.

   o Common laboratory contaminants, such as methylene chloride and phthalates, are generally too unpredictable to safely assume contamination is restricted to a particular instrument, matrix, or concentration level.

Blanks **SV**

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	Rule 5x
Blank Result	7	7
CRQL	5	5
Sample Result	60	30
Qualified Sample Result	60B	30B

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

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

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

Note that data are reported as 4B, indicating that the qualitative presence is not confirmed.

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

	Rule 10x	Rule 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, 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 because of 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.

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

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. 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.

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 because of 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 re-injection of the extract, or re-extraction and reanalysis (if re-injection 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.

5. When both the initial analysis and the reanalysis have surrogate recoveries outside of criteria, the data summary should normally contain the highest concentration obtained for each compound detected, provided that surrogate recoveries in the analysis being reported do not suggest a high bias. However, if a demonstrated laboratory contaminant is detected in one analysis but not the other, the negative result may be more appropriate to report.

When the reanalysis of a fraction is within surrogate recovery criteria, the laboratory is required to provide only data for the acceptable analysis. If both sets of data are provided, and if a compound was detected in the initial analysis but not the reanalysis, then the positive result should be reported (provided the compound is not a demonstrated laboratory contaminant). The reported result should be flagged as estimated "J", due to possible sample inhomogeneity.

6 If advisory surrogates are outside established criteria, professional judgement will be used in qualifying the sample results. If the results are outside the criteria, then qualification would only affect similar target compounds.

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.

Note: These actions apply to all surrogates, except for "advisory" surrogates. Professional judgement should be used in qualifying sample results based on advisory surrogate recoveries. Qualification based on advisory surrogate recoveries should be applied to similar compounds in the sample only. Specify in the narrative any actions taken based on advisory surrogate recovery.

Surrogate Spikes SV

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 biased high, "K".

   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 biased low, "L".

   c. For non-detected semivolatile target compounds, the sample quantitation limit is qualified as biased low, "UL".

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 biased low, "L".

   c. Non-detected semivolatile target compounds may be qualified as unusable "R". (If advisory surrogate limits are not met, use professional judgement to qualify non-detected compounds).

Table 5. Qualification of Semivolatile Analytes Based on Surrogate Recoveries

SURROGATE RECOVERY

	2 or 3 all high	2 or 3 all low	2 or 3 mixed high/low	1 or more < 10% rec.
Detected analytes	K	L	J	L
Non-detected analytes	none	UL	UJ	R

4. If two or more surrogate recoveries in either semivolatile fraction (base/neutral or acid fraction) are outside surrogate recovery limits, and one of the recoveries is below the lower limit (but > 10%) and the other recovery is above the upper limit:

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

b. Detected semivolatile target compounds are qualified as estimated, "J".

c. Non-detected semivolatile target compounds are qualified as estimated, "UJ".

5. 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.

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

7. Positive results for compounds already flagged for blank contamination will not need a separate flag for surrogate recoveries. However, these situations should be addressed in the narrative or the support documentation.

8. When dilutions are performed which prevent detection of BNA surrogate compounds, the narrative or support documentation should indicate that extraction efficiency/method accuracy cannot be verified.

9. Although semivolatile surrogate recoveries cannot usually be correlated with specific analytes, in the following cases specific action will be allowed based upon a particular surrogate:

   a. When a semivolatile surrogate is the deuterated analog of a TCL analyte (for example, d_5-phenol and phenol), a low recovery for the surrogate can be used to flag positive results and quantitation limits as biased low for the undeuterated analog. (This applies even if no other surrogates are outside criteria or if other surrogates are biased high instead of low.)

   b. When d_{12}-terphenyl is biased low, positive results and quantitation limits for the heavier polyaromatic hydrocarbons (those which elute starting with fluorathene) can be considered as biased low. (This applies even if no other surrogates are outside criteria or if other surrogates are biased high instead of low.)

   c. When 2,4,6-tribromophenol is biased low,positive results and quantitation limits for trichlorophenols and pentachlorophenol can be considered as biased low. (this applies even if no other surrogates are outside criteria or if other surrogates are biased high instead of low.)

VII. Matrix Spikes/Matrix Spike Duplicates

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 spike 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 and in the SOW.

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 and in the SOW.

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 RPDs 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.

Matrix Spikes/Matrix Spike Duplicates SV

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.

5. When extremely low % recoveries are noted, qualify data for all affected compounds using professional judgement.

6. When non-spiked compounds are present in either the MS or MSD results, a table in the data review narrative is constructed showing original (unspiked) sample results for non-spiked compounds, non-spiked compounds present in the MS and MSD and the calculated %RSD.

VIII. Regional Quality Assurance and Quality Control

A. Review Items: Form I SV, 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.

C. Criteria

Criteria are dependent on the type of QC sample. Frequency may vary.

1. The analytes present in the PE sample must be correctly identified and quantitated.

D. Evaluation

1. Evaluation of Performance Evaluation (PE) Samples are not to be presented as part of the data review. All forms associated with the Performance Evaluation Samples are to be sent (with a cover memo stating the case number and laboratory information) directly to the Quality Assurance Branch in Region III.

   U.S. Environmental Protection Agency
   Region III, Central Regional Laboratory
   Quality Assurance Branch
   201 Defense Highway, Suite 200
   Annapolis, MD 21401

   Attn: Program Support Section

2. Percent difference between target compounds present in the field duplicate samples shall be determined. Evaluation of the percent difference compared to those specified in the site Quality Assurance Project Plan may be presented in the data review narrative.

E. Action

1. Field duplicate results are to be presented in a table form in the data review narrative. If target compounds were not present in either of the field duplicate samples, then a table is not required. The percent difference is to be calculated and presented in the table. (if one of the field duplicates was also used as a matrix spike/matrix spike duplicate sample, then the table should include any non-spiked compounds detected, along with the % relative standard deviation.)

No action is taken based on percent difference of field duplicate sample data alone. However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria and determine the need for some qualification of the data.

2. Other types of Regional QC Samples

Professional judgement is needed for evaluating other types of QC samples that may be associated with a particular case of samples. This information may be used in conjunction with other QC criteria to determine the need for qualification of data.

IX. Internal Standards

A. Review Items: Form VIII SV-1 and SV-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.

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.

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).

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% or less than 50% should be qualified with "UJ".

c. 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:

   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.

X. Target Compound Identification

A. Review Items: Form I SV-1 and SV-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 $\pm$ 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.

   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.

D. Evaluation

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

2. Check 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.

4. If it is determined that incorrect identifications were made, all such data should be reported as not-detected, and the narrative and the support documentation should indicate this action. In addition, the reviewer should verify that the misidentified peak was library searched as a TIC, if appropriate.

5. If the presence of a target compound is strongly suggested by raw data, but its mass spectrum contains minor inadequacies, the compound may be added to the data summary and qualified as a tentative identification "N". The reviewer should address corroborating evidence in the narrative, such as the presence of the compound in closely related compounds in the same sample.

6. If the laboratory did not report a compound of acceptable matching quality, the reviewer should add this compound to the sample data summary. The narrative and the support documentation should indicate this action, as well as the ORDA. The reviewer should request the laboratory to re-examine and resubmit the result, particularly if the value is greater than the CRQL.

XI. Compound Quantitation and Reported CRQLS

A. Review Items: Form I SV-1 and SV-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 (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. Calculation errors can sometimes be revealed by abnormally high surrogate recoveries, matrix spike recoveries, or inappropriately high results for certain compounds.

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.

Compound Quantitation and Reported CRQLS SV

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

3. The reviewer must assure that any results in error by more than 10 percent are identified and corrected on the sample data summary. If laboratory resubmission is not performed, the reviewer should document his/her changes to the data in the narrative or support documentation. Calculation errors should also be noted on the ORDA.

4. If a sample concentration is above the highest standard and contract required dilutions were not performed, the TPO should be informed on the ORDA. The chromatogram and mass spectrum should be examined for signs of a saturated signal. If the ion used for quantitation was saturated, then the result should be flagged as biased low, "L". If the ion used for quantitation was not saturated, the result should be flagged as estimated, "J".

5. When sample results were quantitated using RRFs from the wrong calibration standard, the laboratory should resubmit these results. The ORDA should identify affected results and document the error. In addition, a CLP telephone log must be completed.

XII. Tentatively Identified Compounds

A. Review Items: Form I SV-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).

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.

   b. The relative intensities of the major ions should agree within $\pm$ 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.

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.

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 fluorotrichloromethane), 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 "J", estimated concentration on the Laboratory Form I-TICs.

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. Blank Results

   Form I-TIC which contain sample results that are questioned by blank results, should be flagged "B" and a line drawn through these data for emphasis (initialed and dated).

   To be considered questionable, a sample TIC concentration must be within 10 times the concentration of one of the blank results. If different volumes/weights are used, the total amount of compound in the extract must be compared for sample versus blank. In general, blanks analyzed within the same case, by the same lab, may be cross-applied to either soil or water samples extracted or analyzed on other days.

   To question a sample result, only presumptive evidence for the presence of the compound in the blank is necessary. The presence of the TIC in the blank is suggested in any of the following situations:

   a. Relative retention times (RRTs) match for sample versus blank, and the sample library search result matches the same compound or compound class as the library search result for the blank.

   b. RRTs match, but library search results do not list the same compound or class for sample versus blank. However, some of the largest ions in the sample are also in the blank, and a direct comparison of sample versus blank spectra suggests that the TIC in the sample is quite possibly the same compound as that in the blank.

   c. A peak at the same RRT as the sample TIC is present in the chromatogram of the blank, but no library search was performed or included in the data. (The labs do not have to library

search peaks less than 10% of the height of the nearest internal standard, although these peaks may still be important to identify low-level blank contaminants that can question sample results at levels above 10% of the nearest internal standard height.)

All blank results must be attached in the support documentation section of the data review.

4. When a compound is not found in any blanks, but is a suspected artifact of common laboratory contamination, the reviewer should cross off the reported TIC result on the copy of the Form I-TIC and note the reason(s) in the narrative.

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). These changes may be made directly on a copy of the Form I-TIC, as long as changes are initialed and dated.

6. 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.

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

8. Any changes made to the reported data or any concerns regarding TIC identifications should be indicated in the data review narrative. Any changes made regarding TIC identifications or qualifications are to be made on copies of the laboratory generated Form I-TIC and not the originals.

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

XIII. System Performance

A. Review Items: Form III SV-1 and SV-2, Form VIII SV-1 and SV-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 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.

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.

XIV. 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.

PESTICIDE/AROCLOR DATA REVIEW

The pesticide/Aroclor data requirements to be checked are listed below.

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

II. GC/ECD Instrument Performance Check

III. Initial Calibration (CSS)

IV. Continuing Calibration (CCS)

V. Blanks

VI. Surrogate Spikes (CCS)

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Regional Quality Assurance and Quality Control

IX. Pesticide Cleanup Checks

X. Target Compound Identification

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

XII. Overall Assessment of Data

Note: "CCS" indicated 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 PEST, EPA Sample Traffic Report, and/or chain-of-custody, raw data, SDG Narrative, 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 sediment, 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 pesticides and Aroclors in cooled (@ 4°C) water samples, the technical holding time is 7 days from sample collection to extraction and 40 days from sample extraction to analysis.

It is recommended that pesticides and Aroclors in soil samples in properly preserved non-aqueous samples be extracted within 7 days of sample collection and extracts analyzed within 40 days from sample extraction.

The contractual holding times, which differ from the technical holding times, state that extraction of water samples by separatory funnel must be completed within 5 days of validated time of sample receipt (VTSR), extraction of water samples by continuous liquid-liquid extraction procedures must be started within 5 days of VTSR, and soil/sediment samples are to be extracted within 10 days of 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 either 14 days or 35 days after receipt in the laboratory of the last sample in the SDG, depending on the contract.

D. Evaluation

Technical holding times for sample extraction are established by comparing the sample collection date on the EPA Sample Traffic Report with the dates of extraction on Form I PEST 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 PEST.

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, the discrepancies in the sample condition could affect the data.

E. Action

1. If technical holding times are exceeded, qualify all detected compound results as estimated "J" and sample quantitation limits as estimated "UJ", and document in the data review narrative that holding times were exceeded. However, please note that some extractable compounds are extremely persistent in the environment (e.g., PCBs) in non-aqueous matrices and would not be expected to degrade significantly during sample storage. The reviewer must use professional judgement in the application of data qualifiers to those compounds in non-aqueous matrices.

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 effect of additional storage on the sample results. The reviewer may determine that detected compound results or the associated quantitation limits are approximates and should be qualified with "J" or "UJ", respectively. The reviewer may determine that non-detected target compound data are unusable (R).

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

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

5. 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 indicating that shipment delays have occurred so that the field and/or shipping problems 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.

6. When there are other quality control problems in conjunction with exceeded holding times (such as suspected laboratory contamination), the reviewer should follow the hierarchy of qualifiers. In particular, if for any reason the reviewer doubts the presence of a compound, the data summary should display only the "B" or "R" qualifier, and not the "J" qualifier.

II. GC/ECD Instrument Performance Check

A. Review Items: Form VI PEST-4, Form VII PEST-1, Form VIII PEST, chromatograms, and data system printouts.

B. Objective

Performance checks on the gas chromatograph with electron capture detector (GC/ECD) system are performed to ensure adequate resolution and instrument sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. Criteria

1. Resolution Check Mixture

   a. The Resolution Check Mixture must be analyzed at the beginning of every initial calibration sequence, on each GC column and instrument used for analysis. The Resolution Check Mixture contains the following pesticides and surrogates:

gamma-Chlordane	Endrin ketone
Endosulfan I	Methoxychlor
4,4'-DDE	Tetrachloro-m-xylene
Dieldrin	Decachlorobiphenyl
Endosulfan sulfate	

   b. The depth of the valley between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0 percent of the height of the shorter peak.

2. Performance Evaluation Mixture

   a. The Performance Evaluation Mixture (PEM) must be analyzed at the beginning (following the resolution check mixture) and at the end of the initial calibration sequence. The PEM must also be analyzed at the beginning of every other 12-hour analytical period. The PEM contains the following pesticides and surrogates:

gamma-BHC	Endrin
alpha-BHC	Methoxychlor
4,4'-DDT	Tetrachloro-m-xylene
beta-BHC	Decachlorobiphenyl

   b. The resolution of adjacent peaks for the PEM injections in each calibration (initial and continuing) must be 100 percent for both GC columns.

c. The absolute retention times of each of the single component pesticides and surrogates in all PEM analyses must be within the specific retention time windows centered around the mean retention times determined from the three-point initial calibrations using the Individual Standard Mixtures. A list of the retention time windows is included in Appendix A.

For example, for a given pesticide the mean retention time is first determined from the initial calibration and found to be 12.69 minutes. The retention time window for this pesticide is ± 0.05 minutes. Therefore, the calculated retention time window would range from 12.64 to 12.74

d. The relative percent difference (RPD) between the calculated amount and the true amount for each of the single component pesticides and surrogates in the PEM analyses must be less than or equal to 25.0 percent.

e. The percent breakdown is the amount of decomposition that 4,4'-DDT and Endrin undergo when analyzed on the GC column. For Endrin, the percent breakdown is determined by the presence of Endrin aldehyde and/or Endrin ketone in the GC chromatogram. For 4,4'-DDT, the percent breakdown is determined from the presence of 4,4'-DDD and/or 4,4'-DDE in the GC chromatogram. The equations used to verify these calculations are provided in Appendix A.

i. The individual percent breakdown for both 4,4'-DDT and Endrin in each PEM must be less than or equal to 20.0 percent for both GC columns.

ii. The combined percent breakdown for 4,4'-DDT and Endrin in each PEM must be less than or equal to 30.0 percent for both GC columns.

D. Evaluation

1. Resolution Check Mixture

a. Verify from the Form VIII PEST that the resolution check mixture was analyzed at the beginning of the initial calibration sequence on each GC column and instrument used for analysis.

b. Check the resolution check mixture data and Form VI PEST-4 to verify that the resolution criterion between two adjacent peaks for the required compounds is less than or equal to 60%. The resolution criteria requires that the depth of the valley between two adjacent peaks in the resolution check mixture must be greater than or equal to 60% of the height of the shorter peak.

2. Performance Evaluation Mixture

a. Verify from the Form VIII PEST that the Performance Evaluation Mixture (PEM) was analyzed at the proper frequency and position sequence.

b. Check the PEM data from the initial and continuing calibrations to verify that the resolution between adjacent peaks is 100 percent on both GC columns.

c. Check the PEM data from the initial and continuing calibrations and Form VII PEST-1 to verify that the absolute retention times for the pesticides in each analysis are within the calculated retention time windows based on the mean RT from the three-point initial calibration using equations and examples found in Appendix A.

d. Verify that the relative percent difference (RPD) between the calculated amount and the true amount for each of the pesticides and surrogates is less than or equal to 25.0 percent.

e. Verify that the individual breakdown on each GC column for 4,4'-DDT and Endrin is less than or equal to 20.0 percent, and that the combined breakdown is less than or equal to 30.0 percent.

E. Action

1. Resolution Check Mixture: If resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Detected target compounds that were not adequately resolved should be qualified with "J". Qualitative identifications may also be questionable if coelution exists. Non-detects with retention times in the region of coelution may not be valid, depending on the extent of the problem. Professional judgement should be used to determine the need to qualify data as unusable (R).

2. Performance Evaluation Mixture Retention Times: Retention time windows are used in qualitative identification. If the retention times of the pesticides in the PEM do not fall within the retention time windows, the associated sample results should be carefully evaluated. All samples injected after the last in-control standard are potentially affected.

   a. For the affected samples, check to see if the sample chromatograms contain any peaks that are close to the expected retention time window of the pesticide of interest. If no peaks are present either within or close to the retention time window of the deviant target pesticide compound, then there is usually no affect on the data (i.e., non-detected values can be considered valid). Sample data that are potentially affected by standards not meeting the retention time windows should be noted in the data review narrative.

   b. If the affected sample chromatograms contain peaks which may be of concern (i.e., above the CRQL and either close to or within the expected retention time window of the analyte of interest), then the reviewer should determine the extent of the effect on the data and may choose to qualify detected target compound "NJ" and non-detected target compounds "R". In some cases, additional effort by the reviewer may be necessary to determine if sample peaks represent the compounds of interest, for example:

i. The reviewer can examine the data package for the presence of three or more standards containing the pesticide of interest that were run within a 72-hour period during which the sample was analyzed.

ii. If three or more such standards are present, the mean and standard deviation of the retention time window can be re-evaluated.

iii. If all standards and matrix spikes fall within the revised window, the valid positive or negative sample results can be determined using this window.

iv. The narrative should identify the additional efforts taken by the reviewer and the resultant impact on data usability. In addition, the support documentation should contain all calculations and comparisons generated by the reviewer.

c. If the reviewer can not resolve the problem of concern with the available data, all positive results and quantitation limits should be qualified "R".

3. If PEM resolution criteria are not met, quantitative results for compounds in the region where the criteria is not met may not be accurate due to inadequate resolution. Positive sample results for compounds that were not adequately resolved should be qualified "J". If in the professional judgement of the reviewer, qualitative identifications are questionable due to poor resolution, positive sample results should be qualified "NJ". Non-detected target compounds that would elute in the region of coelution may not be valid depending on the extent of the coelution problem. Professional judgement should be used to qualify detection limits unusable "R".

4. If RPD criteria are not met, qualify all associated positive results generated during the analytical sequence with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

5. 4,4'-DDT/Endrin Breakdown:

a. If 4,4'-DDT breakdown is greater than 20.0 percent:

i. Qualify all positive results for DDT with "L" (biased low). If DDT was not detected, but DDD and DDE are detected, then qualify the quantitation limit for DDT as unusable (R).

ii. Qualify positive results for DDD and/or DDE as presumptively present at an approximated quantity (NJ).

b. If Endrin breakdown is greater than 20.0 percent:

i. Qualify all positive results for Endrin with "L" biased low. If Endrin was not detected, but Endrin aldehyde and Endrin ketone are detected, then qualify the quantitation limit for Endrin as unusable (R).

ii. Qualify positive results for Endrin ketone and Endrin aldehyde as presumptively present at an approximated quantity (NJ).

c. If the combined 4,4'-DDT and Endrin breakdown is greater than 30.0 percent:

i. Qualify all positive results for DDT and Endrin, "J" estimated. If Endrin was not detected, but Endrin aldehyde and Endrin ketone are detected, then qualify the quantitation limit for Endrin as unusable (R). If DDT was not detected, but DDD and DDE are detected, then qualify the quantitation limit for DDT as unusable (R).
ii. Qualify positive results for Endrin ketone and Endrin aldehyde as presumptively present at an approximated quantity (NJ). Qualify positive results for DDD and/or DDE as presumptively present at an approximated quantity (NJ).

6. Potential effects on the sample data resulting from the initial calibration problems should be noted in the data review narrative.

III. Initial Calibration

A. Review Items: Form VI PEST-1,2,3, and 4, Form VII PEST-1, Form VIII PEST, chromatograms, and data system printouts.

B. Objective

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide and Aroclor target compounds. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence and of producing a linear calibration curve.

C. Criteria

1. Individual Standard Mixtures

   a. Individual Standard Mixtures A and B (containing all of the single component pesticides and surrogates) must be analyzed at low, midpoint, and high levels during the initial calibration, on each GC column and instrument used for analysis.

   b. The resolution between any two adjacent peaks in the midpoint concentration of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent on both columns.

   c. The absolute retention times of each of the single component pesticides and surrogates are determined from three-point initial calibration using the Individual Standard Mixtures. A list of the retention time windows and an example for calculating retention time windows is given in section III in Appendix A.

   d. At least one chromatogram from each of the Individual Standard Mixtures A and B must yield peaks that give recorder deflections between 50 to 100 percent of full scale.

   e. The concentrations of the low, medium, and high level standards containing all of the single component pesticides and surrogates (Individual Standard Mixtures A and B) must meet the following criteria on both GC columns.

      The low point corresponds to the CRQL for each analyte. The midpoint concentration must be 4 times the low point. The high point must be at least 16 times the low point, but a higher concentration may be chosen.

   f. The Percent Relative Standard Deviation (%RSD) of the calibration factors for each of the single component pesticides and surrogates in the initial calibration on both columns for Individual Standard Mixtures A and B must be less than or equal to 20.0 percent, except as noted below. For the two surrogates, the %RSD must be less than or equal to 30.0 percent.

Up to two single component target pesticides (other than the surrogates) per column may exceed the 20.0 percent limit but the %RSD must be less than or equal to 30.0 percent.

Note: Either peak area or peak height may be used to calculate the calibration factors that are, in turn, used to calculate %RSD. However, the type of peak measurement used to calculate each calibration factor for a given compound must be consistent. For example, if peak area is used to calculate the low point calibration factor for endrin, then the mid and high point calibration factors for endrin must also be calculated using peak area.

2. Multi-component Target Compounds

a. The multi-component target compounds (the 7 Aroclors and Toxaphene) must each be analyzed separately at a single concentration level during the initial calibration sequence. The analysis of the multi-component target compounds must also contain the pesticide surrogates.

b. For each multi-component analyte, the retention times are determined for three to five peaks. A retention time window of $\pm$ 0.07 minutes is used to determine retention time windows for all multi-component analyte peaks.

c. Calibration factor data must be determined for each peak selected from the multi-component analytes.

D. Evaluation

1. Individual Standard Mixtures

a. Verify from the Form VIII PEST that the Individual Standard Mixtures A and B were analyzed at the proper frequency on each GC column and instrument used for analysis. Check the raw data (chromatograms and data system print outs) for each standard to verify that each of the standards was analyzed at the required concentration levels.

b. Check the raw data and determine that the midpoint standard's concentration is 4 times the concentration of the low point standard's concentration and verify that resolution is greater than 90%.

c. Check the Individual Standard Mixtures A and B data and Form VI PEST-1 and review the calculated retention time windows for calculation and transcription errors.

d. Check the Individual Standard Mixtures A and B data and Form VI PEST-2 to verify that the %RSD for the calibration factors in each of the single component pesticides and surrogates in the initial calibration analyses on both columns are in compliance with the criteria in Section III.C. Check and recalculate the calibration factors and %RSD for one or more pesticides; verify that the recalculated values agree with the reported values. If errors are detected, more comprehensive recalculation should be performed.

2. Multi-component Target Compounds

   a. Verify from the Form VIII PEST that each of the multi-component target compounds were analyzed at the required frequency. Check the raw data for the standards to verify that the multi-component analytes were analyzed at the required concentration.

   b. Check the data for the multi-component target compounds and Form PEST VI-3 to verify that at least three peaks were used for calibration and that retention time and calibration factor data are available for each peak.

E. Action

1. If the initial calibration sequence was not followed as required, then professional judgement must be used to evaluate the effect of the non-compliance on the sample data. If the requirements for the initial calibration sequence were not met, then this should be noted for TPO action on the ORDAS. If the non-compliance has a potential effect on the data, then the data should be qualified according to the professional judgement of the reviewer and this should be noted in the data review narrative.

2. If resolution criteria are not met, then the quantitative results may not be accurate due to peak overlap and lack of adequate resolution. Positive sample results for compounds that were not adequately resolved should be qualified with "J". Qualitative identifications may be questionable if coelution exists. Non-detected target compounds that elute in the region of coelution may not be valid depending on the extent of the coelution problem. Professional judgement should be used to qualify data as unusable (R).

3. If the %RSD linearity criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J". When the %RSD is grossly exceeded (i.e., >50%), use professional judgement for qualifying non-detects as "UJ".

4. Potential effects on the sample data due to problems with calibration should be noted in the data review narrative. If the data reviewer has knowledge that the laboratory has repeatedly failed to comply with the requirements for frequency, linearity, retention time, or resolution, this information should be documented in the report narrative.

IV. Continuing Calibration

A. Review Items: Form VII PEST-1 and 2, Form VIII PEST, chromatograms, and data system printouts.

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 checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To verify the calibration and evaluate instrument performance, continuing calibration is performed, consisting of the analyses of instrument blanks, the PEM, and the midpoint concentration of Individual Standard Mixtures A and B.

C. Criteria

1. An instrument blank and the PEM must bracket one end of a 12-hour period during which samples are analyzed, and a second instrument blank and the midpoint concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.

2. The resolution between any two adjacent peaks in the midpoint concentration of Individual Standard Mixtures A and B must be greater than or equal to 90.0 percent.

3. The absolute retention time for each single component pesticide and surrogate in the midpoint concentration of Individual Standard Mixtures A and B must be within the retention time windows determined from the initial calibration.

4. The RPD between the calculated amount and the true amount for each of the pesticides and surrogates in the midpoint concentration of the Individual Standard Mixtures A and B must not exceed 25.0 percent.

D. Evaluation

1. Check the Form VIII PEST to verify that the instrument blanks, PEMs, and Individual Standard Mixtures were analyzed at the proper frequency and that no more than 12 hours elapsed between continuing calibration brackets in an ongoing analytical sequence.

2. Check the data for the midpoint concentration of Individual Standard Mixtures A and B to verify that the resolution between any two adjacent peaks is greater than or equal to 90.0 percent.

3. Check the data for each of the single component pesticides and surrogates in the midpoint concentration of Individual Standard Mixtures A and B and Form VII PEST-2 to verify that the absolute retention times are within the appropriate retention time windows.

4. Check that the data from the midpoint concentration of Individual Standard Mixtures A and B and Form VII PEST-2 between the calculated amount and the true amount for each of the pesticides and surrogates is less than or equal to 25.0%.

E. Action

1. If the continuing calibration sequence was not followed as required, then professional judgement must be used to evaluate the effect of the non-compliance on the sample data. If the requirements for the continuing calibration sequence were not met, then this should be noted in the report narrative. If the non-compliance has a potential effect on the data, then the data should be qualified according to the professional judgement of the reviewer and this should be noted in the data review narrative.

2. If resolution criteria are not met then the quantitative results may not be accurate due to inadequate resolution. Positive sample results for compounds that were not adequately resolved should be qualified with "J". Qualitative identifications may be questionable if coelution exists. Non-detected target compounds that elute in the region of coelution may not be valid depending on the extent of the coelution problem. Professional judgement should be used to qualify data as unusable (R).

3. Retention time windows are used in qualitative identification. If the standards do not fall within the retention time windows, the associated sample results should be carefully evaluated. All samples injected after the last in-control standard are potentially affected.

   a. For the affected samples, check to see if the sample chromatograms contain any peaks that are close to the expected retention time window of the pesticide of interest. If no peaks are present either within or close to the retention time window of the deviant target pesticide compound, then non-detected values can be considered valid. Sample data that is potentially affected by the standards not meeting the retention time windows should be noted in the data review narrative.
   b. If the affected sample chromatograms contain peaks which may be of concern (i.e., above the CRQL and either close to or within the expected retention time window of the pesticide of interest), then the reviewer should follow the guidelines provided in Section II.E.2 to determine the extent of the effect on the data.

4. If the RPD is greater than 25% for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detects with "UJ" when the RPD is grossly exceeded (i.e., >50%).

5. Potential effects on the sample data due to problems with calibration should be noted in the data review narrative. If the data reviewer has knowledge that the laboratory has repeatedly failed to comply with the requirements for frequency, linearity, retention time, resolution, or DDT/Endrin breakdown, the data reviewer should note this in the report narrative.

V. Blanks

A. Review Items: Form I PEST, Form IV PEST, chromatograms, and data system printouts.

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 laboratory blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, field generated blanks, and sulfur cleanup 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 present in the blanks.

2. Frequency:

   a. Method Blanks - A method blank analysis must be performed for each 20 samples of similar matrix in each sample delivery group (SDG) or whenever a sample extraction procedure is performed.

   b. Instrument Blanks - An acceptable instrument blank must be run at least once every 12 hours and immediately prior to the analysis of either the performance evaluation mixture or Individual Standard Mixtures, A and B, depending on the place in the analysis sequence.

   c. Sulfur Cleanup Blanks - A sulfur cleanup blank must be analyzed whenever part of a set of samples extracted together requires sulfur cleanup. If the entire set of samples associated with a method blank requires sulfur cleanup, then the method blank also serves the purpose of a sulfur blank and no separate sulfur blank is required.

   d. Field Generated Blanks - Equipment rinsate blanks and/or field blanks may be collected and analyzed with each set of samples collected. The QAPjP will specify the type and frequency for the collection of these blanks.

D. Evaluation

1. Review the results of all associated blanks.. Form I PEST and Form IV PEST, and raw data (chromatograms and data system printouts) to evaluate the presence of target pesticides/PCBs.

2. Verify that method blank analysis has been reported per SDG, per matrix, per concentration level, for each GC system used to analyze samples, and for each extraction batch.

3. Verify that the method blank analyses do not contain any target pesticide or Aroclor/Toxaphene at greater than its Contract Required Quantitation Limits (CRQL).

4. For the surrogates in each method blank, verify that the observed retention times are within the appropriate retention time windows calculated from the initial calibration.

5. Verify that the instrument blank analysis has been performed every 12 hours as part of the continuing calibration and following a sample analysis which contains an analyte(s) at high concentration(s), and that the instrument blanks do not contain any target analytes above one-half the CRQL, assuming that the material in the instrument resulted from the extraction of a 1-L water sample.

6. Verify that the sulfur cleanup blanks were analyzed at the required frequency and that they do not contain any target compound above the CRQL, assuming that the material in the instrument resulted from the extraction of a 1-L water sample. If a separate sulfur cleanup blank was prepared, one version of Form IV PEST should be completed associating all the samples with the method blank, and a second version of Form IV PEST should be completed listing only those samples associated with the separate sulfur cleanup blank.

E. Action

If the appropriate blanks were not analyzed with the frequency described in Section V.C.2, 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.

Action in the case of unsuitable blank results depends on the circumstances and the origin of the blank. Detected compound results should be reported and qualified "B" if the concentration of the compound in the sample is less than or equal to 5 times (5x) the amount in the blank. 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. For qualification purposes, to determine the highest concentration of a contaminant, consider all blanks in a case associated with all samples, except for instrument blanks, which only affect the samples bracketed by the contaminated instrument blank. The results must not be corrected by subtracting the blank value.

Specific actions are as follows:

1. If a target pesticide or Aroclor/Toxaphene is found in the blank but not found in the sample(s), no qualification is required. If the contaminant(s) is found at level(s) significantly greater than the CRQL, then this should be noted in the report narrative.

2. Any pesticide or Aroclor/Toxaphene detected in the sample, that was also detected in any associated blank, is qualified "B"if the sample concentration is less than five times (5x) the blank concentration.

   The reviewer should note that analyte concentrations calculated for method 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" criteria, such that a comparison of the total amount of contamination is actually made.

Additionally, there may be instances when 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 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" rule does not apply, the sample value should be reported and qualified "B" and a note should be added to the narrative.

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

4. If inordinate amounts of other target pesticides or Aroclors/Toxaphene are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted in the data revie6w narrative.

5. 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), and if so, detected compound results should be qualified. If instrument cross-contamination is suggested, then this should be noted in the data review narrative 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 CRQL, but is less than the 5x multiple of the blank result.

	5x
Blank Result	1.0
CRQL	0.5
Sample Result	4.0
Qualified Sample Result	4.0B

In this case, sample results less than 5.0 (or 5 x 1.0) would be qualified as a blank contaminant, "B".

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

	5x
Blank Result	1.0
CRQL	0.5
Sample Result	0.4J
Qualified Sample Result	0.4B

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

	5x
Blank Result	1.0
CRQL	0.5
Sample Result	10.0
Final Sample Result	10.0

In this case, the sample result exceeded the adjusted blank result (5 x 11) and the sample result is not qualified.

6. In pesticide analyses by GC/EC, contractually compliant laboratory blanks can sometimes contain interferences which obscure detection of target pesticide compounds (since the interfering compound may not actually be a pesticide). If sample quantitation limits are flagged as biased low (UL) or unreliable (R) due to interferences attributable to such laboratory blank contamination, then this issue should be addressed in the narrative.

VI. Surrogate Spikes PEST

A. Review Items: Form II PEST, Form VII PEST, chromatograms, and data system printouts.

B. Objective

Laboratory performance on individual samples is established by means of spiking samples prior to extraction and analysis to determine surrogate spike recoveries. All samples are spiked with surrogate compounds prior to sample extraction to measure extraction efficiency. The evaluation of the recovery 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 target and/or non-target 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. Two surrogate spikes, tetrachloro-m-xylene and decachlorobiphenyl, are added to all samples, Individual Standard Mixtures, PEMs, blanks, and matrix spikes to measure their recovery in sample and blank matrices.

2. The advisory limits for recovery of the surrogates tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB) are 60-150 percent for both water and soil samples.

3. The retention times of both of the surrogates in the PEM, Individual Standard Mixtures, and samples must be within the calculated retention time windows. TCX must be within $\pm$ 0.05 minutes, and DCB must be within $\pm$ 0.10 minutes of the mean retention time determined from the initial calibration.

D. Evaluation

1. Check raw data (e.g., chromatograms and data system printouts) to verify that the recoveries on the Surrogate Recovery Form II PEST are accurate and within the advisory limits and that the retention times on the Pesticide Analytical Sequence Form VIII PEST are accurate and within the retention time limits.

2. Check that the surrogate spike recoveries were calculated correctly and free from transcription errors.

3. If surrogate spike recoveries are not within limits, check the raw data for possible interferences which may have affected surrogate recoveries.

4. If retention time limits were not met, check the raw data for possible misidentification of GC peaks. Non-recovery of surrogates may be due to shifts in RT.

5. If low surrogate recoveries are observed, the reviewer should investigate whether the low recoveries were a result of sample dilution.

6. 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.

E. Action

1. If surrogate spike recoveries are outside of advisory limits (60-150%), the following guidance is suggested. Professional judgement must be used in applying these criteria.

TABLE X - Guidance for qualifying data based on surrogate recoveries outside the advisory limits (60-150%) but greater than 10%. In instances where detection limits require qualification, the qualifier begins with a U and is listed in the column titled "Value reported from the column with non-conformance".

# of outliers	Recovery	Value reported from the column with non-conformance	Value reported from the column without non-conformance
1 out	High Low	No action No action	No action No action
2 out	2 high same column 2 low same column Mixed same column 2 high different column 2 low different column Mixed different column	K L, UL J, UJ J J, UJ Prof. judgement	No action No action No action Not applicable Not applicable Not applicable
3 out	All high All low 2 high 1 low 2 low 1 high Other mix of high and low	K L, UL K (2 high) L, UJ (2 low) J, UJ	Not applicable Not applicable J (1 low 2nd column) J (1 high 2nd column) Not applicable
4 out	All high All low Mixed	K L, UL J, UJ	Not applicable Not applicable Not applicable

a. If either pesticide surrogate recovery is reported >0% but <10%, the reviewer should examine the sample chromatogram to assess the qualitative validity of the analysis. If low surrogate recoveries are found to be due to sample dilution, then professional judgement should be used to determine if the resulting data should be qualified. If sample dilution is not a factor, then detected target compounds may be qualified "L", and non-detected target compound results should be qualified unusable (R).

b. If zero pesticide surrogate recovery is reported, the reviewer should examine the sample chromatogram to determine if the surrogate may be present, but slightly outside its retention time window. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the overriding consideration is to investigate the qualitative validity of the analysis. If the surrogate is not present, qualify all non detected target compounds as unusable (R).

2. If surrogate retention times in PEMs, individual standards, and samples are outside of the retention time limits, qualification of the data is left up to the professional judgement of the reviewer. Refer to section II E.2 for more guidance.

3. Potential effects of the data resulting from surrogate recoveries not meeting the advisory limits should be noted in the data review narrative.

VII. Matrix Spikes/Matrix Spike Duplicates

A. Review Items: Form III PEST-1 and PEST-2, chromatograms, and data system printouts.

B. Objective

Data for Matrix spikes (MS) and Matrix spike duplicates (MSD) are generated to determine long-term precision and accuracy of the analytical method on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgement, MS/MSD 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 a frequency of at least one MS and MSD per 20 samples of each matrix.

2. Matrix spike recoveries should be within the advisory limits provided on Form III PEST-1 and PEST-2 and in Appendix A.

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

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 PEST-1 and PEST-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 judgement 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 sample data. The 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 some 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. For example, if the recoveries for MS and MSD are consistently low for both water and soil samples, this could be indicative of a systematic problem in the laboratory and recoveries should be examined in all associated samples.

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

5. When extremely low % recoveries are noted, qualify data for all affected compounds using professional judgement.

6. When non-spiked compounds are present in either the MS or MSD results, a table in the data review narrative is constructed showing original (unspiked) sample results for non-spiked compounds, non-spiked compounds present in the MS and MSD and the calculated % RSD.

VIII. Regional Quality Assurance and Quality Control PEST

A. Review Items: Form I PEST, chromatograms, Data system printouts, traffic reports and raw data for Regional QC samples.

B. Objective

Regional Quality Assurance and Quality Control (QA/QC) refers 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 dependent on the type of QC sample. Frequency may vary.

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

D. Evaluation

1. Evaluation of Performance Evaluation (PE) Samples are not to be presented as part of the data review. All forms associated with the Performance Evaluation Samples are to be sent (with a cover memo stating the case number and laboratory information) directly to the Quality Assurance Branch in Region III:

   U.S. Environmental Protection Agency
   Region III, Central Regional Laboratory
   Quality Assurance Branch
   201 Defense Highway, Suite 200
   Annapolis, MD 21401

   Attn: Program Support Section

E. Action

1. Field duplicate results are to be presented in a table form in the data review narrative. If target compounds were not present in either of the field duplicate samples, then a table is not required. The percent difference is to be calculated and presented in the table. (If one of the field duplicates was also used as a matrix spike/matrix spike duplicate sample, then the table should include any non-spiked compounds detected, along with the % relative standard deviation.)

2. No action is taken based on percent difference of field duplicate sample data alone. However, using informed professional judgement, the data reviewer may use the field duplicate results in conjunction with other QC criteria and determine the need for some qualification of the data.

3. Other types of Regional QC Samples

   Professional judgement is needed for evaluating other types of QC samples that may be associated with a particular case of samples. This information may be used in conjunction with other QC criteria to determine the need for qualification of data.

IX. Pesticide Cleanup Checks

A. Review Items: Form IX PEST-1 and 2, chromatograms, and data system printouts.

B. Objective

Pesticide cleanup procedures are utilized to remove matrix interferences from sample extracts prior to analysis. The use of the Florisil cartridge cleanup procedure significantly reduces matrix interferences caused by polar compounds. Gel permeation chromatography (GPC) is used to remove high molecular weight contaminants that can interfere with the analysis of target analytes. Pesticide cleanup procedures are checked by spiking the cleanup columns and cartridges and verifying the recovery of pesticides through the cleanup procedure.

C. Criteria

1. Florisil Cartridge Cleanup

   a. Florisil cartridges must be used for the cleanup of all sample extracts.

   b. Every lot number of Florisil cartridges used for sample cleanup must be checked by spiking with 2,4,5-trichlorophenol and the midpoint concentration of Individual Standard Mixture A. These compounds are listed in Appendix A.

   c. The lot of Florisil cartridges is acceptable if the recoveries for all of the pesticides and surrogates in Individual Standard Mixture A are within 80 and 120 percent, if the recovery of 2,4,5-trichlorophenol is less than 5 percent, and if no peaks interfering with the target analytes are detected.

2. Gel Permeation Chromatography (GPC)

   a. GPC is used for the cleanup of all soil sample extracts and for water sample extracts that contain high molecular weight components that interfere with the analysis of the target analytes.

   b. At least once every 7 days, the calibration of the GPC unit must be checked by spiking with two check mixtures: the matrix spiking solution and a mixture of 0.2 ug/mL Aroclors 1016 and 1260. The matrix spiking solution compounds for the GPC Check are:

Pesticide	Ug/mL
gamma-BHC(Lindane)	0.5
4,4'-DDT	1.0
Endrin	1.0
Heptachlor	0.5
Aldrin	0.5
Dieldrin	1.0

c. The GPC calibration is acceptable if the recovery of the pesticides in the matrix spiking solution are within 80 to 110 percent, and the Aroclor patterns should match those generated for previously run standards.

d. A GPC blank must be analyzed after each GPC calibration and is acceptable if the blank does not exceed one-half the CRQL for any target analytes.

D. Evaluation

1. Florisil Cartridge Check

Check the data from the Florisil cartridge solution analyses and the Form IX-PEST-1 and recalculate some of the percent recoveries to verify that the percent recoveries of the pesticides and surrogates in Individual Standard Mixture A are within 80-120%, the recovery of 2,4,5-trichlorophenol is less than 5%, and no interfering peaks are present. Compare the raw data to the reported results and verify that no calculation or transcription errors have occurred.

2. **Gel Permeation Chromatography (GPC)**

Check the data from the GPC calibration check analyses and the Form IX PEST-2 and recalculate some of the percent recoveries to verify that the percent recoveries of the pesticides in the matrix spike solution are within 80-110% and that the Aroclor patterns are similar to those of previous standards. Check to make sure that no transcription errors have occurred.

E. Action

1. If Florisil Cartridge Check criteria are not met, the raw data should be examined for the presence of polar interferences and professional judgement should be used in qualifying the data. If a laboratory chooses to analyze samples under an unacceptable Florisil Cartridge Check, then this should be noted in the data review narrative.

2. If Gel Permeation Criteria are not met, the raw data should be examined for the presence of high molecular weight contaminants and professional judgement should be used in qualifying the data. If a laboratory chooses to analyze samples under an unacceptable Gel Permeation Criteria, then 8this should be noted in the data review narrative.

3. If zero recovery was obtained for the pesticide compounds and surrogates during either check, then the non-detected target compounds may be suspect and the data may be qualified unusable (R).

4. If high recoveries (i.e., greater than 120%) were obtained for the pesticides and surrogates during either check, use professional judgement to qualify detected target compounds as biased high (K). Non-detected target compounds do not require qualification.

5. Potential effects on the sample data resulting from the pesticide cleanup analyses not yielding acceptable results should be noted in the data review narrative.

X. Target Compound Identification

A. Review Items: Form I PEST, Form X PEST-1 and PEST-2, chromatograms, and data system printouts.

B. Objective

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present).

C. Criteria

1. The retention times of both of the surrogates, matrix spikes, and reported compounds in each sample must be within the calculated retention time windows on both columns. TCX must be within ± 0.05 minutes of the mean retention time determined from the initial calibration and DCB must be within ± 0.10 minutes of the mean retention time determined from the initial calibration.

2. GC/MS confirmation is required if the concentration of a compound exceeds 10 ng/uL in the final sample extract. Pesticides that are confirmed by GC/MS should be identified with a "C" in the Q column on Form I PEST.

3. When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.

4. Chromatograms must display single component pesticides detected in the sample and the largest peak of any multicomponent analyte detected in the sample at less than full scale.

5. If an extract must be diluted, chromatograms must display single component pesticides between 10 and 100 percent of full scale, and multicomponent analytes between 25 and 100 percent of full scale.

6. For any sample, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and also return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

7. If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram, and both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

D. Evaluation

1. Review Form I PEST, the associated raw data (chromatograms and data system printouts) and Form X PEST-1 and PEST-2. Confirm reported detected analytes by comparing the sample

chromatograms to the tabulated results and verifying peak measurements and retention times. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate retention time windows (to evaluate sample data for false positives and false negatives).

2. For multi-component target compounds (Toxaphene and Aroclors), the retention times and relative peak heights ratios of major component peaks should be compared against the appropriate standard chromatograms.

3. Verify that GC/MS confirmation was performed for pesticide concentrations in the final sample extract which exceeded 10 ng/uL.

E. Action

1. If the qualitative criteria for both columns were not met, all target compounds that are reported detected should be considered non-detected. The reviewer may use professional judgement to qualify reported compounds "N", tentatively identified, or "R", rejected. In the case of multi-component compounds, the reviewer can accept the reported compound based on pattern recognition and relative peak height ratios. The reviewer should use professional judgement to assign an appropriate quantitation limit using the following guidance:

   a. If the misidentified peak was sufficiently outside the target pesticide retention time window, then the reported values may be a false positive and should be replaced with the sample CRQL value.

   b. If the misidentified peak poses an interference with potential detection of a target peak, then the reported value should be considered and qualified as unusable (R).

2. If the data reviewer identifies a peak in both GC column analyses that falls within the appropriate retention time windows, but was reported as a non-detect, then the compound may be a false negative. Professional judgement should be used to decide if the compound should be included. All conclusions made regarding target compound identification should be included in the data review narrative.

3. If multi-component target compounds exhibit marginal pattern-matching quality, professional judgement should be used to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of a multi-component pesticide is strongly suggested, results should be reported as presumptively present (N). If an observed pattern closely matches more than one Aroclor, professional judgement should be used to decide whether the neighboring Aroclor is a better match, or if multiple Aroclors are present.

4. If it is determined that qualitative criteria for two-column confirmation were not met, all such data should be reported as not detected and it should be clearly noted in the narrative.

5. When all qualitative criteria for identification have been met, single-peak pesticides which are not confirmed by GC/MS should be noted in the narrative, indicating that supporting data may be necessary to rely upon these results. If supporting data exist (site-related records, GC/MS confirmations of other samples, etc.), the reviewer should discuss the type of supporting data in the narrative. Whenever single-peak pesticides are confirmed by an acceptable GC/MS spectrum and retention time match against standards, confirmation should be noted in the narrative.

XI. Compound Quantitation and Reported CROLS

A. Review Items: Form I PEST, Form X PEST-1 and PEST-2, sample preparation log sheets, chromatograms, case narrative, and data system printouts.

B. Objective

The objective is to ensure that the reported quantitative results and contract required quantitation limits (CRQLs) are accurate.

C. Criteria

Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the equations provided in Appendix A (also found in Section D/Pest of the Statement of Work).

D. Evaluation

1. Raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Data system printouts, chromatograms, and sample preparation log sheets should be compared to the reported positive sample results and quantitation limits. Verify that the sample values are reported correctly. Calculation errors can sometimes be revealed by abnormally high surrogate recoveries, matrix spike recoveries, or inappropriately high results for certain compounds.

2. 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. Quantitation limits affected by large, off-scale peaks should be qualified as unusable (R). If the interference is on-scale, the reviewer can provide an approximated quantitation limit (UJ) for each affected compound.

Note: Single-peak pesticide results are checked for rough agreement between quantitative results obtained by the two GC columns. The potential for co-elution should be considered and the reviewer should use professional judgement to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interfering compound is indicated, professional judgement must be used to determine how best to report, and if necessary, qualify the data. Contractually the lower of the two values is reported.

2. 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 decide which value is the best value. Under these

circumstances, the reviewer may determine if qualification of the 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.

3. If the calculated concentrations of detected compounds do not agree ±25% on both columns, qualify the reported value "J", estimated.

XII. Overall Assessment

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. 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. Reference the Region III Data Validation Reports Requirements, found in Appendix B.

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 in the calculation of the percent relative abundance.

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

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

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

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 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 Compounds

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 Compounds (continued)

Volatile Compound	Minimum RRF
Trichloroethene	0.300
Dibromochloromethane	0.100
1,1,2-Trichloroethane	0.100
Benzene	0.500
trans-1,2-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

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

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

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

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

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

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

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% criterion.

Contractual 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 specified 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 RRF and continuing calibration RRF is calculated using equation IV.1.

$$\%\ D = \frac{\overline{RRF_i} - RRF_c}{\overline{RRF}} \times 100\% \qquad (IV.1)$$

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 X1.3. 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:

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

Concentration for low level soils:
(Dry weight basis)

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

Concentration for medium level soils:
(Dry weight basis)

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

where:

A_x = 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%
V_t = volume of methanol (ml)*
V_i = volume of extract added (ul) for purging
D_f = 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_o) 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:

$$AdjustedCRQL = Non\text{-}adjustedCRQL \times Sample\ Dilution\ Factor \qquad (X1.4)$$

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:

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

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
Bromodichloroemethane	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	91	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

APPENDIX A

MULTI-MEDIA, MULTI-CONCENTRATION 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:

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

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-n-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
Acenaphthylene	0.800
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
4-Chorophenyl-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 (pg.A-2, Appendix A) and III.4 (pg.A-3, Appendix A).

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 (reference p.A-2), and evaluate the %D between initial calibration RRF and continuing calibration RRF using equation IV.1 (reference p.A-3).

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 - 144	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-Fluoprophenol	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. (Reference p.A-4)

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-proplyamine	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-Nitrolaniline
1,2-Dichlorobenzene	2,4-Dichlorophenol	Dimethyl phthalate
2-Methylphenol	1,2,4-Trichlorobenzene	Acenaphthylene
2,2'-oxybis-(1-Chloropropane)	Napththalene	3-Nitroaniline
4-Methylphenol	4-Chloroaniline	Acenaphthene
N-Nitroso-Di-n-propylamine	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
2-Flurorophenol (surr)	2-Methylnaphthalene	Dibenzofuran
Phenol-d_5 (surr)	2-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 below. Equation XI.4 (reference p.A-6) 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 Arolclors are contained in Table A.13.

Concentration for waters:

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

Concentration for soils/sediments:
(Dry weight basis)

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

where:

A_x = 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%
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.

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

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-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	128, 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 A.11 Characteristic Ions for Semivolatile Target Compounds (Continued)

Parameter	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
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
Benz(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279

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

Analyte	Primary Ion	Secondary Ion(s)
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 expoxide	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
1,4'-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
Aroclor-1016	222	260, 292
Aroclor-1221	190	222, 260
Aroclor-1232	190	222, 260
Aroclor-1242	222	256, 292
Aroclor-1248	292	362, 326
Aroclor-1254	292	362, 326
Aroclor-1260	360	362, 394

Calibration standards are prepared at a minimum of five concentration levels (20, 50, 80, 120, and 160 total ng). Eight compounds listed below require only a four-point initial calibration at 50, 80, 120 and 160 total ng.

2,4 - Dinitro phenol
2,3,4 - Trichlorophenol
2 - Nitroaniline
3 - Nitroaniline
4 - Nitroaniline
4 - Nitrophenol
4,6 - Dinitro-2-methylphenol
Pentachlorophenol

APPENDIX A

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

II. GC/ECD Instrument Performance Check

Check the Performance Evaluation Mixture calculations to ensure correct calculation of DDT and Endrin breakdown. When using equations II.2 and II.3, values for the amount found and the amount injected should be reported in nanograms (ng). The breakdown of DDT and Endrin in both of the PEM injections must be less than 20.0 percent, and the combined breakdown of DDT and Endrin must be less than 30.0 percent.

$$\%\ Breakdown\ DDT = \frac{Amount\ found\ (DDD+DDE)\ x\ 100}{Amount\ of\ DDT\ injected} \qquad (II.2)$$

$$\%\ Breakdown\ Endrin = \frac{Amount\ found\ (Endrin\ aldehyde\ +\ Endrin\ ketone)\ x\ 100}{Amount\ of\ Endrin\ injected} \qquad (II.3)$$

$$Combined\ \%\ Breakdown = \%\ Breakdown\ DDT + \%\ Breakdown\ Endrin \qquad (II.4)$$

All peaks in both injections of the Performance Evaluation Mixture must be 100 percent resolved on both columns. The relative percent difference of the calculated amount and the true amount for each of the single component pesticides and surrogates in the PEMs must be less than or equal to 25.0 percent using equation II.5.

$$RPD = \frac{|C_{nom} - C_{cal}|}{(½)(C_{nom} + C_{cal})}\ x\ 100 \qquad (II.5)$$

Where:

C_{nom} = True concentration of each analyte
C_{cal} = Calculated concentration of each analyte from the analysis of the standard

III. Initial Calibration

Retention time windows for each analyte and surrogate are calculated using Table A.14. Windows are centered around the mean absolute retention time for the analyte established during the initial calibration. For example, for a given pesticide the mean retention time is first determined from the initial calibration is found to be 12.69 minutes. The retention time window for this pesticide is ± 0.05 minutes. Therefore, the calculated retention time window would range from 12.64 to 12.74 minutes.

Table A.14 Retention Time Windows for Pesticide Target Compounds

Pesticide Compounds	Retention Time Windows in Minutes
alpha-BHC	±0.05
beta-BHC	±0.05
gamma-BHC	±0.05
delta-BHC	±0.05
Hepatachlor	±0.05
Aldrin	±0.05
alpha-Chlordane	±0.07
gamma-Chlordane	±0.07
Heptachlor epoxide	±0.07
Dieldrin	±0.07
Endrin	±0.07
Endrin aidehyde	±0.07
Endrin ketone	±0.07
DDD	±0.07
DDE	±0.07
DDT	±0.07
Endosulfan I	±0.07
Endosulfan II	±0.07
Endosulfan sulfate	±0.07
Methoxychlor	±0.07
Aroclors	±0.07
Toxaphene	±0.07
Tetrachloro-m-xylene	±0.05
Decachlorobiphenyl	±0.10

The % RSD of the calibration factors for each single component target must be less than or equal to 20.0 percent. The % RSD for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds per column may exceed the 20.0 percent limit for % RSD, but those compounds must have a % RSD of less than or equal to 30.0 percent. Calibration factors are calculated using equations III.5 and III.6 and the % RSD is calculated using equations III.3 and III.4.

$$\%RSD = \frac{Standard Deviation}{Mean} \times 100 \qquad (III.3)$$

where,

$$Standard\ Deviation = \left|\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}\right|^{1/2} \qquad (III.4)$$

Where:

x_i = each individual value used to calculate the mean
x = the mean of n values
n = the total number of values

$$CF = \frac{Peak\ Area\ of\ the\ Standard}{mass\ injected} \qquad (III.5)$$

$$\overline{CF} = \sum_{i=1}^{n} \frac{CF_i}{n} \qquad (III.6)$$

Where:

$\overline{CF}$ = Mean calibration factor of a n values
CF_i = i^{th} calibration factor
n = Total number of values

IV. Continuing Calibration

The retention time (RT) for each target compound and surrogate must be within RT window as calculated above using the mean absolute RT established during the three-point initial calibration. The relative percent difference of the calculated amount and the true amount for each of the compounds in the mid point concentration of the individual Standard mixtures must be less than or equal to 25.0 percent, using equation II.5.

VI. Surrogate Spikes

The advisory limits for recovery of tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB) are 60-150 percent for both water and soil samples. The surrogate percent recovery is calculated using equation VI.1. The retention time of both surrogates must be within the calculated retention time windows, i.e., TCX must be within ±0.05 minutes of the mean retention time determined from the initial calibration and DCB must be within ±0.10 minutes of the mean retention time determined from the initial calibration.

$$\textit{Surrogate Percent Recovery} = \frac{Q_d}{Q_a} \times 100 \qquad (VI.1)$$

Where:

Q_d = Quantity determined by analysis
Q_a = Quantity added to sample/blank

VII. Matrix Spikes/Matrix Spike Duplicate

The matrix spike/matrix spike duplicate recovery and RPD requirements are listed in Table A.15. The matrix spike recoveries and RPD are calculated using equations VII.1 and VII.2.

Table A.15 MS/MSD Contractual Requirements

Compound	% Recovery Water	RPD Water	% Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56-123	15	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	18	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50

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

Where:

SSR = Spike 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

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

IX. Pesticide Cleanup Check

Every lot number of Florisil cartridges used for sample cleanup must be checked by spiking with 2,4,5-trichlorophenol and midpoint concentration of Individual Standard Mixture A. The recoveries for all of the pesticides and surrogates in Individual Standard Mixture A must be within 80 to 120 percent, the recovery of 2,4,5-trichlorophenol must be less than 5 percent, and no peaks must interfere with the target analytes. Percent recovery is determined using equation IX.1.

$$Percent\ Recovery = \frac{Q_d}{Q_a} \times 100 \qquad (IX.1)$$

Where:

Q_d = Quantity determined by analysis
Q_a = Quantity added to sample/blank

The gel permeation chromatography (GPC) apparatus must be calibrated every 7 days. The calibration is acceptable if the recovery of each single component analyte is within 80-110 percent and the Aroclor patterns match patterns previously generated by standards.

X. Target Compound Identification

Retention times of surrogates, matrix spikes, and reported compounds must fall within the retention time windows established using the initial three-point calibration.

XI. Compound Quantitation and Reported CRQLs

The concentration of the single component pesticides are calculated using equations XI.1 and XI.2, as appropriate. The dilution factor for both soil and water samples is calculated using equation XI.3 and the adjusted CRQL is calculated using equation XI.4. Equation XI.5 is used to adjust the CRQL for the samples's dry weight. The percent difference (%d) is calculated comparing calculated concentrations for both columns using equation XI.6.

Concentration for water samples:

$$Concentration \quad ug/L = \frac{(A_x)(V_t)(D_f)}{(CF)(V_o)(V_i)} \qquad (XI.1)$$

Where:

A_x = Area of the peak for the compound to be measured.

CF = Calibration factor for the mid point concentration external standard (area per ng).

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

V_i = Volume of extract injected in microliters (uL). (If a single injection is made on to two columns, use one half the volume in the syringe as the volume injected on to each column.)

V_t = Volume of the concentrated extract in microliters (uL) (this volume must be 10000 uL, see Section II, 7.2.3).

Df = Dilution Factor. The dilution factor for analysis of water samples by this method is defined as follows:

$$\frac{uL \text{ most conc. extract used for dilution} + uL \text{ clean solvent}}{uL \text{ most conc. extract used for dilution}} \qquad (XI.3)$$

If no dilution is performed, Df = 1.0

If GPC is performed on a water sample extract, V_t becomes 5000 uL, and a factor of 2 must be added to the numerator, as described below for soil/sediment samples.

Concentration for soil samples (Dry weight basis)

$$Concentration\ \ ug/Kg = \frac{(A_x)(V_t)(Df)(2.0)}{(CF)(V_i)(W_s)(D)} \qquad (X1.2)$$

Where:

A_x and CF are as given for water, above.

V_t = Volume of the concentrated extract in microliters (uL) (this volume must be 5000 uL, see Section II, 7.2.3)

V_i = Volume of extract injected in microliters (uL) (If a single injection is made on to two columns, use one half the volume in the syringe as the volume injected on to each column.)

$D = \frac{100 - \%\ moisture}{100}$

W_s = Weight of sample extracted in grams (g).

D_f = Dilution Factor. The dilution factor for analysis of soil samples by this method is defined as follows:

Dilution factor (D_f):

$$D_f = \frac{uL\ most\ conc.\ extract\ used\ for\ dilution + uL\ clean\ sovent}{uL\ most\ conc.\ extract\ used\ for\ dilution} \qquad (X1.3)$$

If no dilution is performed, $D_f = 1.0$.

The factor of 2.0 in the numerator is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 5.0 mL rather than 10.0 mL for water samples not subjected to GPC (see Section II. 7.2.3 in the CLP SOW OLM01.0 or subsequent revision), maintains the sensitivity of the soil method comparable to that of the water method, but correction of the numerical result is still required.

Dilution factor (D_f):

$$D_f = \frac{uL\ most\ conc.\ extract\ used\ for\ dilution + uL\ clean\ solvent}{uL\ most\ conc.\ extract\ used\ for\ dilution} \qquad (X1.3)$$

CRQL (Adjusted for dilution)

$$(CRQL)\ (D_f) = Adjusted\ CRQL \qquad (X1.4)$$

Where:

CRQL = contract required quantitation limit

D_f = Dilution factor

CRQL (Adjusted for samples dry weight)

$$\frac{(CRQL)(D_f)}{D} \qquad (X1.5)$$

Where:

D = $\frac{100 - \%\ moisture}{100}$

CRQL = contract required quantitation limit

D_f = dilution factor

If no dilution is performed, $D_f = 1.0$

If a sample extract cannot be concentrated to the protocol-specified volume, this fact must be accounted for in reporting the sample quantitation limit. (SOW: Exhibit C)

Percent difference:

$$\%\ D = \frac{Conc_H - Conc_L}{Conc_L} \times 100 \qquad (X1.6)$$

Where:

$Conc_H$ = The higher of the two concentrations for the target compound in question

$Conc_L$ = The lower of the two concentrations for the target compound in question

APPENDIX B

REGION III STANDARD OPERATING PROCEDURE

FOR DATA VALIDATION REPORTS

ORGANIC DATA VALIDATION REPORT PREPARATION

1.0 Purpose

The purpose of this procedure is to establish a report format for organic data review report writing according to EPA Region III protocol and is based on and applies to organic data review level M3 only.

2.0 Discussion

After completion of data review, the data reviewer will be responsible for compiling review notes and writing a report. The outline below describes the steps to follow in preparing the organic data review report.

3.0 Procedure

3.1 Organic Data Validation Narrative

The validation narrative is for the data user. Because the data user may not be familiar with EPA abbreviations, it is necessary to write out commonly used acronyms such as RAS, DAS, etc..

3.1.1 The first page of the report should be printed on letterhead. The address of the report should include the following information and be in the established format for Region III, as:

Date: Month DD, YEAR (Date report is sent to EPA)

Subject: Organic Data Validation for Case (case #)
Site (write site name)

From: Reviewer Name — Oversight Reviewer Name
Reviewer Title — Reviewer Title

To: Remedial Project Manager
EPA Region III

3.1.2 Overview

The first section of the report is the overview, and is presented in paragraph form after the title "**OVERVIEW**". Information in this paragraph should include:

- Case or DAS (Delivered Analytical Services) Number
- Analytes
- Number of samples
- Matrix (or matrices and number of samples of each matrix)
- Number of QC samples (field and/or equipment blanks, trip blanks, field duplicates, etc.)
- The SOW under which the laboratory performed the analyses
- Laboratory name and its CLP Code

A statement should also be made that the samples were analyzed through the Contract Laboratory Program (CLP),

and whether they were performed as a Routine Analytical Services (RAS) or Delivered Analytical Services (DAS). If results exceeded the levels identified in the EPA 10-day Chemical Health Advisory Levels (Attachment A), such exceedances are mentioned in the overview paragraph(s).

3.1.3 **Summary**

The summary section, written below the title "**SUMMARY**", is a general statement noting whether the samples were successfully analyzed or if there were any analyses determined unsuccessful (e.g., data were qualified unusable).

3.1.4 **Major Problems**

After the section title, "**MAJOR PROBLEMS**", any problems identified during the validation that seriously affect data usability and any data that are qualified unusable, "R", is noted in this portion of the narrative. Identification of the support documentation included in the appendices of the report (see Section 3.1.8) which identifies each problem is referenced. Each identified problem is reported in a separate paragraph.

NOTE: Paragraphs in the major and minor problems sections and the "Notes" section are presented in "bulleted" format.

3.1.5 **Minor Problems**

The section title, "**MINOR PROBLEMS**" is followed by a series of bulleted paragraphs describing biases identified during the data review which may qualify data as "J", "UJ", "K", "L", or "UL". Examples of these problems are discussed thoroughly in the Functional Guidelines for Organic Data Validation as Modified by Region III. As in the reporting of major problems, support documentation is referenced for each problem described.

Problems listed in this section of the narrative are listed according to the hierarchy of qualifiers, beginning with the most serious ("J", "UJ") first. If problems are identified in more than one organic fraction, each fraction is identified.

3.1.6 **Notes**

This section follows the minor problems section and is used to identify issues and information which may be beneficial to the data user, and includes a paragraph describing any blank contamination found and its possible effects on sample results. Maximum levels of the blank contaminants are listed in tabular form. Common lab contaminants are identified with an asterisk (*). Other information which shall be included in the "Notes" section includes, but is not limited to: variances in methodology which did not affect samples, dilutions used, non-spiked MS/MSD comparisons, a field duplicate

comparison summary (in tabular form with relative percent differences [RPDs]), and a general statement regarding actions taken during the review of tentatively identified compounds (TICs). As in the problems descriptions, reference is made to support documentation included in the appendices of the report.

3.1.7 **Report Content Statement**

A short paragraph, not bulleted, follows the notes section stating that the data were reviewed in accordance with the Functional Guidelines for Evaluating Organic Analyses, as modified for use in Region III, and that the text of the report only addresses those problems which affect data usability.

3.1.8 **Attachments**

Under the section title "**ATTACHMENTS**", a list of appendices and their contents is included. The appendices normally listed and their order are:

Appendix A - Glossary of Data Qualifiers
Appendix B - Data Summary Forms
Appendix C - Laboratory Reported Results
Appendix D - Laboratory Reported TICs
Appendix E - Support Documentation

3.2 **Appendices**

Appendices are separated from the main body of the report by title pages containing, centered on the page, the appendix name and title.

3.2.1 **Appendix A - Glossary of Data Qualifier Codes**

A listing of all organic data qualifiers used in Region III and their definitions is included in Attachment D.

3.2.2 **Appendix B - Data Summary Forms**

3.2.2.1 The full title of this appendix is "Data Summary. These include:
(a) All positive results for target compounds with qualifier codes where applicable.
(b) All unusable detection limits (qualified "R")."

3.2.2.2 Included are Data Summary Forms for all fractions analyzed, sequentially numbered beginning with the volatile organic fraction, for all samples analyzed. Information on the Data Summary Forms includes: organic fraction identified, sample matrix, concentration units, site, case number, SDG number if multiple SDGs are reported, sampling date(s), sample numbers, dilution factors used (if none, identified as 1.0), sample locations, sample identifications (e.g., trip blank, field duplicate), contract required quantitation limit for each analyte, all target analytes, all positive results and

quantitation limits with qualifier codes where applicable, and all unusable detection limits qualified "R".

NOTE: Standard generation of the Data Summary Forms can be done on a spreadsheet program. Blank Data Summary Forms for both aqueous and solid samples are included in Attachment E.

3.2.3 **Appendix C - Results as Reported by the Laboratory for all Target Compounds**

After the title page, Appendix C contains photocopies of all of the Form Is. The Form Is for all samples for the volatile organics fraction are included first, followed by Form Is for all samples for semivolatile organic compounds and pesticides/PCBs. The sample order of the Form Is should match the sample order as listed on the Data Summary Forms.

3.2.4 **Appendix D - Reviewed and Accepted (Corrected) Tentatively Identified Compounds**

Appendix D contains photocopies of the Tentatively Identified Compounds forms (Form I VOA - TIC and Form I SV - TIC) for each sample, with all volatile organics forms preceding all semivolatile organics forms. If corrections to the TIC forms are made during validation, use the word "corrected" in the appendix title. All TIC forms are included even if no TICs were identified by the laboratory.

3.2.5 **Appendix F - Support Documentation**

Appendix F for the organic data review report includes all support documentation needed to substantiate the findings described in the narrative. In addition to copies of specific supporting forms from the data package, the appendix will include:

3.2.5.1 Table I, "Calibration Outliers", is a compilation of all Response Factors (RFs), percent Relative Standard Deviations (%RSDs), and percent Differences (%Ds) which were outside of the control limits for both volatile and semivolatile organic compounds. Examples of Table I are included in Attachment F. Table I also includes the qualifiers applied during validation to compound results because of these outliers, and the definitions of the qualifier codes used.

3.2.5.2 Initial and continuing calibration data are included for all volatile and semivolatile compounds (Forms VI VOA, VII VOA, VI SV-1 and -2, and VII SV-1 and -2), with a reviewer-written list of samples affected by each calibration.

3.2.5.3 Copies of the laboratory case narrative, sample traffic report/chain of custody (TR/COC), and EPA Shipping Log.

4.0 Assembling the Report

The organic report shall be assembled in the order presented in Sections 3.1 and 3.2 of this document. The narrative is followed by the Appendices as described.

5.0 Review and Distribution

After the report is completed and assembled, it should be reviewed internally by optional peer review(s), oversight chemist review(s), and team manager review.

5.1 The report should be submitted to a senior oversight chemist for its first internal review. The internal review may be assigned to another validator or be performed by the oversight chemist.

5.1.1 The reviewer will review the document. Any deficiencies, inconsistencies, or other comments should be returned to the validator.

5.1.2 The reviewer will return the review to the validator, who will make the required corrections.

5.1.3 The process will continue (Steps 5.1 - 5.1.2) until the document requires no further revision.

5.1.4 The validator will initial the first page of the narrative next to his/her name.

5.1.5 The final review is performed by the team manager, who will read and review the document. If the report is acceptable to the team manager, he will initial the narrative next to his name.

5.2 The completed report is submitted to the EPA oversight chemist for review.

5.2.1 All internal review checklists are removed, and the rest of the document is copied for the validator files. The internal review checklists and document copy are then placed in a filing area.

5.2.2 The original document is placed in an inter-office envelope addressed to the EPA RPM.

5.3 Upon completion of review by the EPA oversight chemist, the document will either be approved as submitted or revisions will be required.

5.3.1 If revisions are required by the EPA oversight chemist, the validator must complete those revisions and submit the document for internal review as outlined above beginning in section 5.1.

5.3.1.1 All resubmissions are labelled as revision 1 (or subsequent).

ATTACHMENT A

Chemical Ten Day Health Advisory List

Organics
Water (µg/L)

Acrylamide	300
Alachlor	15000
Aldicarb	12
Benzene	233
Carbofuran	50
Carbon Tetrachloride	160
Chlordane	63
Chlorobenzene	1800
2,4-D	300
DBCP	50
1,3-dichlorobenzene	8930
1,4-dichlorobenzene	10700
1,2-dichloroethane	740
1,1-dichloroethylene	1000
cis-1,2-dichloroethylene	1000
trans-1,2-dichloroethylene	2720
Dichloromethane	1500
1,2-dichloropropane	90
p-Dioxane	568
Dioxin	1×10^{-4}
EDB	8
Endrin	5
Epichlorohydrin	140
Ethylbenzene	2100
Ethylene glycol	5500
Heptachlor	10
Hexachlorobenzene	50
n-Hexane	4000
Lindane	1200
Methoxychlor	2000
Methyl ethyl ketone (2-butanone)	7500
Oxamyl	350
Pentachlorophenol	300
Styrene	20000
Tetrachloroethylene	34000
Toluene	6000
Toxaphene	80
2,4,5-TP (Silvex)	200
1,1,1-trichloroethane	35000
Vinyl chloride	2600
Xylenes	7800
PCB	hundreds

Metals
Water (µg/L)

Arsenic	50
Cadmium	8
Chromium	1400
Lead	20
Nickel	1000

Soil (ppm)

Lead	500

Inorganics

Nitrate	
	10 mg/L - 4 kg
	111 mg/L - other
Nitrite	
	1 mg/L - 1 kg
	11 mg/L - other
Cyanide	220 µg/L

RD0073A23.LIS

ATTACHMENT B

GLOSSARY OF DATA QUALIFIER CODES (ORGANIC)

CODES RELATED TO IDENTIFICATION

(confidence concerning presence or absence of compounds)

U = Not detected. The associated number indicates approximate sample concentration necessary to be detected.

NO CODE = Confirmed identification.

B = Not detected substantially above the level reported in laboratory or field blanks.

R = Unusable result. Analyte may or may not be present in the sample.

N = Tentative identification. Consider present. Special methods may be needed to conform its presence or absence in future sampling efforts.

CODES RELATED TO QUANTITATION

(can be used for both positive results and sample quantitation limits):

J = Analyte present. Reported value may not be accurate or precise.

K = Analyte present. Reported value may be biased high. Actual value is expected to be lower.

L = Analyte present. Reported value may be biased low. Actual value is expected to be higher.

UJ = Not detected. Quantitation limit may be inaccurate or imprecise.

UL = Not detected. Quantitation limit is probably higher.

OTHER CODES

NJ = Qualitative identification questionable due to poor resolution. Presumptively present at approximate quantity.

Q = No analytical result.

Attachment C

Data Summary Forms

DATA SUMMARY FORM: V O L A T I L E S 1 Page _____ of _____

Site Name:

WATER SAMPLES
(ug/L)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRDL * Dilution Factor)

	Sample No.								
	Dilution Factor								
	Location								
CRQL	COMPOUND								
10	Chloromethane								
10	Bromomethane								
10	*Vinyl Chloride								
10	Chloroethane								
10	*Methylene Chloride								
10	Acetone								
10	Carbon Disulfide								
10	*1,1-Dichloroethene								
10	1,1-Dichloroethane								
10	*Total 1,2-Dichloroethene								
10	Chloroform								
10	*1,2-Dichloroethane								
10	*2-Butanone								
10	*1,1,1-Trichloroethane								
10	*Carbon Tetrachloride								
10	Bromodichloromethane								

CRQL = Contract Required Quantitation Limit

*Action Level Exists

SEE NARRATIVE FOR CODE DEFINITIONS

revised 07/90

DATA SUMMARY FORM: V O L A T I L E S 2 Page _____ of _____

Site Name:

WATER SAMPLES
(ug/L)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRDL * Dilution Factor)

	Sample No.								
	Dilution Factor								
	Location								
CRQL	COMPOUND								
10	*1,2-Dichloropropane								
10	Cis-1,3-Dichloropropene								
10	Trichloroethene								
10	Dibromochloromethane								
10	1,1,2-Trichloroethane								
10	*Benzene								
10	Trans-1,3-Dichloropropene								
10	Bromoform								
10	4-Methyl-2-pentanone								
10	2-Hexanone								
10	*Tetrachloroethene								
10	1,1,2,2-Tetrachloroethane								
10	*Toluene								
10	*Chlorobenzene								
10	*Ethylbenzene								
10	*Styrene								
10	*Total Xylenes								

CRQL = Contract Required Quantitation Limit

*Action Level Exists

SEE NARRATIVE FOR CODE DEFINITIONS

revised 07/90

DATA SUMMARY FORM: V O L A T I L E S 1 Page _____ of _____

Site Name:

SOIL SAMPLES
(ug/Kg)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRQL * Dilution factor / ((100 - %moisture)/100)

	Sample No.								
	Dilution Factor								
	% Moisture								
	Location								
CRQL	COMPOUND								
10	Chloromethane								
10	Bromomethane								
10	Vinyl Chloride								
10	Chloroethane								
10	Methylene Chloride								
10	Acetone								
10	Carbon Disulfide								
10	1,1-Dichloroethene								
10	1,1-Dichloroethane								
10	Total 1,2-Dichloroethene								
10	Chloroform								
10	1,2-Dichloroethane								
10	2-Butanone								
10	1,1,1-Trichloroethane								
10	Carbon Tetrachloride								
10	Bromodichloromethane								

CRQL = Contract Required Quantitation Limit

SEE NARRATIVE FOR CODE DEFINITIONS

revised 07/90

DATA SUMMARY FORM: V O L A T I L E S 2 Page _____ of _____

Site Name:

SOIL SAMPLES
(ug/Kg)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRQL * Dilution factor / ((100 - %moisture)/100)

	Sample No.								
	Dilution Factor								
	% Moisture								
	Location								
CRQL	COMPOUND								
10	1,2-Dichloropropane								
10	Cis-1,3-Dichloropropene								
10	Trichloroethene								
10	Dibromochloromethane								
10	1,1,2-Trichloroethane								
10	Benzene								
10	Trans-1,3-Dichloropropene								
10	Bromoform								
10	4-Methyl-2-pentanone								
10	2-Hexanone								
10	Tetrachloroethene								
10	1,1,2,2-Tetrachloroethane								
10	Toluene								
10	Chlorobenzene								
10	Ethylbenzene								
10	Styrene								
10	Total Xylenes								

CRQL = Contract Required Quantitation Limit

SEE NARRATIVE FOR CODE DEFINITIONS

revised 07/90

DATA SUMMARY FORM: B N A 1 Page _____ of _____

Site Name:

WATER SAMPLES
(ug/L)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRDL * Dilution Factor)

	Sample No.								
	Dilution Factor								
	Location								
CRQL	COMPOUND								
10	Phenol								
10	bis(2-Chloroethyl)ether								
10	2-Chlorophenol								
10	*1,3-Dichlorobenzene								
10	*1,4-Dichlorobenzene								
10	1,2-Dichlorobenzene								
10	2-Methylphenol								
10	2,2'-oxybis(1-chloropropane)								
10	4-Methylphenol								
10	N-Nitroso-di-n-propylamine								
10	Hexachloroethane								
10	Nitrobenzene								
10	Isophorone								
10	2-Nitrophenol								
10	2,4-Dimethylphenol								
10	bis(2-Chloroethoxy)methane								
10	2,4-Dichlorophenol								
10	1,2,4-Trichlorobenzene								
10	Naphthalene								
10	4-Chloroaniline								

CRQL = Contract Required Quantitation Limit

*Action Level Exists

SEE NARRATIVE FOR CODE DEFINITIONS

revised 07/90

DATA SUMMARY FORM: B N A 2

Page _____ of _____

Site Name:

WATER SAMPLES
(ug/L)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRDL * Dilution Factor)

	Sample No.									
	Dilution Factor									
	Location									
CRQL	COMPOUND									
10	Hexachlorobutadiene									
10	4-Chloro-3-methylphenol									
10	2-Methylnaphthalene									
10	Hexachlorocyclopentadiene									
10	2,4,6-Trichlorophenol									
25	2,4,5-Trichlorophenol									
10	2-Chloronapthalene									
25	2-Nitroaniline									
10	Dimethylphthalate									
10	Acenaphthylene									
10	2,6-Dinitrotoluene									
25	3-Nitroaniline									
10	Acenaphthene									
25	2,4-Dinitrophenol									
25	4-Nitrophenol									
10	Dibenzofuran									
10	2,4-Dinitrotoluene									
10	Diethylphthalate									
10	4-Chlorophenyl-phenylether									
10	Fluorene									
25	4-Nitroaniline									
25	4,6-Dinitro-2-methylphenol									

CRQL = Contract Required Quantitation Limit

*Action Level Exists

SEE NARRATIVE FOR CODE DEFINITIONS

revised 07/90

DATA SUMMARY FORM: B N A 3

Page _____ of _____

Site Name:

WATER SAMPLES
(ug/L)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRDL * Dilution Factor)

CRQL	COMPOUND	Sample No.								
		Dilution Factor								
		Location								
10	N-Nitrosodiphenylamine									
10	4-Bromophenyl-phenylether									
10	*Hexachlorobenzene									
25	*Pentachlorophenol									
10	Phenanthrene									
10	Anthracene									
10	Carbazole									
10	Di-n-butylphthalate									
10	Fluoranthene									
10	Pyrene									
10	Butylbenzylphthalate									
10	3,3'-Dichlorobenzidine									
10	Benzo(a)anthracene									
10	Chrysene									
10	bis(2-Ethylhexyl)phthalate									
10	Di-n-octylphthalate									
10	Benzo(b)fluoranthene									
10	Benzo(k)fluoranthene									
10	Benzo(a)pyrene									
10	Indeno(1,2,3-cd)pyrene									
10	Dibenz(a,h)anthracene									
10	Benzo(g,h,i)perylene									

CRQL = Contract Required Quantitation Limit

*Action Level Exists

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DATA SUMMARY FORM: B N A 1 Page _____ of _____

Site Name:

SOIL SAMPLES
(ug/Kg)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRQL * Dilution factor / ((100 - %moisture)/100)

	Sample No.								
	Dilution Factor								
	% Moisture								
	Location								
CRQL	COMPOUND								
330	Phenol								
330	bis(2-Chloroethyl)ether								
330	2-Chlorophenol								
330	1,3-Dichlorobenzene								
330	1,4-Dichlorobenzene								
330	1,2-Dichlorobenzene								
330	2-Methylphenol								
330	2,2'-oxybis(1-chloropropane)								
330	4-Methylphenol								
330	N-Nitroso-di-n-propylamine								
330	Hexachloroethane								
330	Nitrobenzene								
330	Isophorone								
330	2-Nitrophenol								
330	2,4-Dimethylphenol								
330	bis(2-Chloroethoxy)methane								
330	2,4-Dichlorophenol								
330	1,2,4-Trichlorobenzene								
330	Naphthalene								
330	4-Chloroaniline								

CRQL = Contract Required Quantitation Limit

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DATA SUMMARY FORM: B N A 2 Page _____ of _____

Site Name:

SOIL SAMPLES
(ug/Kg)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRQL * Dilution factor / ((100 - %moisture)/100)

CRQL	COMPOUND									
	Sample No.									
	Dilution Factor									
	% Moisture									
	Location									
330	Hexachlorobutadiene									
330	4-Chloro-3-methylphenol									
330	2-Methylnaphthalene									
330	Hexachlorocyclopentadiene									
330	2,4,6-Trichlorophenol									
800	2,4,5-Trichlorophenol									
330	2-Chloronapthalene									
800	2-Nitroaniline									
330	Dimethylphthalate									
330	Acenaphthylene									
330	2,6-Dinitrotoluene									
800	3-Nitroaniline									
330	Acenaphthene									
800	2,4-Dinitrophenol									
800	4-Nitrophenol									
330	Dibenzofuran									
330	2,4-Dinitrotoluene									
330	Diethylphthalate									
330	4-Chlorophenyl-phenylether									
330	Fluorene									
800	4-Nitroaniline									
800	4,6-Dinitro-2-methylphenol									

CRQL = Contract Required Quantitation Limit

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DATA SUMMARY FORM: B N A 3 Page _____ of _____

Site Name:

SOIL SAMPLES
(ug/Kg)

Case #: Sampling Date(s):

To calculate sample quantitation limits:
(CRQL * Dilution factor / ((100 - %moisture)/100)

	Sample No.									
	Dilution Factor									
	% Moisture									
	Location									
CRQL	COMPOUND									
330	N-Nitrosodiphenylamine									
330	4-Bromophenyl-phenylether									
330	Hexachlorobenzene									
800	Pentachlorophenol									
330	Phenanthrene									
330	Anthracene									
330	Carbazole									
330	Di-n-butylphthalate									
330	Fluoranthene									
330	Pyrene									
330	Butylbenzylphthalate									
330	3,3'-Dichlorobenzidine									
330	Benzo(a)anthracene									
330	Chrysene									
330	bis(2-Ethylhexyl)phthalate									
330	Di-n-octylphthalate									
330	Benzo(b)fluoranthene									
330	Benzo(k)fluoranthene									
330	Benzo(a)pyrene									
330	Indeno(1,2,3-cd)pyrene									
330	Dibenz(a,h)anthracene									
330	Benzo(g,h,i)perylene									

CRQL = Contract Required Quantitation Limit

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DATA SUMMARY FORM: P E S T I C I D E S A N D P C B S Page _____ of _____

Site Name:

WATER SAMPLES
(ug/L)

To calculate sample quantitation limits:
(CRDL * Dilution Factor)

Case #: Sampling Date(s):

CRQL	COMPOUND	Sample No.									
		Dilution Factor									
		Location									
0.05	alpha-BHC										
0.05	beta-BHC										
0.05	delta-BHC										
0.05	*gamma-BHC (Lindane)										
0.05	*Heptachlor										
0.05	Aldrin										
0.05	Heptachlor Epoxide										
0.05	Endosulfan I										
0.10	Dieldrin										
0.10	4,4'-DDE										
0.10	*Endrin										
0.10	Endosulfan II										
0.10	4,4'-DDD										
0.10	Endosulfan Sulfate										
0.10	4,4'-DDT										
0.50	*Methoxychlor										
0.10	Endrin Ketone										
0.10	Endrin Aldehyde										
0.05	*alpha-Chlordane										
0.05	*gamma-Chlordane										
5.0	*Toxaphene										
1.0	*Aroclor-1016										
2.0	*Aroclor-1221										
1.0	*Aroclor-1232										
1.0	*Aroclor-1242										
1.0	*Aroclor-1248										
1.0	*Aroclor-1254										
1.0	*Aroclor-1260										

CRQL = Contract Required Quantitation Limit *Action Level Exists SEE NARRATIVE FOR CODE DEFINITIONS

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DATA SUMMARY FORM: P E S T I C I D E S A N D P C B S

Page _____ of _____

Site Name:

SOIL SAMPLES
(ug/Kg)

To calculate sample quantitation limits:
(CRQL * Dilution factor / ((100 - %moisture)/100)

Case #: Sampling Date(s):

CRQL	COMPOUND									
	Sample No.									
	Dilution Factor									
	% Moisture									
	Location									
1.7	alpha-BHC									
1.7	beta-BHC									
1.7	delta-BHC									
1.7	gamma-BHC (Lindane)									
1.7	Heptachlor									
1.7	Aldrin									
1.7	Heptachlor Epoxide									
1.7	Endosulfan I									
3.3	Dieldrin									
3.3	4,4'-DDE									
3.3	Endrin									
3.3	Endosulfan II									
3.3	4,4'-DDD									
3.3	Endosulfan Sulfate									
3.3	4,4'-DDT									
17	Methoxychlor									
3.3	Endrin Ketone									
3.3	Endrin Aldehyde									
1.7	alpha-Chlordane									
1.7	gamma-Chlordane									
170	Toxaphene									
33	Aroclor-1016									
67	Aroclor-1221									
33	Aroclor-1232									
33	Aroclor-1242									
33	Aroclor-1248									
33	Aroclor-1254									
33	Aroclor-1260									

CRQL = Contract Required Quantitation Limit

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Attachment D

Table I

TABLE I Page___of___

ENVIRONMENTAL PROTECTION AGENCY REGION III
CALIBRATION OUTLIERS
VOLATILE HSL COMPOUNDS

CASE/SAS No._____ CONTRACTOR _____

Instrument#	Init. Cal.			Cont. Cal.			Cont. Cal.		
DATE/TIME:									
	RF	%RSD	*	RF	%D	*	RF	%D	*
Chloromethane									
Bromomethane									
Vinyl Chloride									
Chloroethane									
Methylene Chloride									
Acetone									
Carbon Disulfide									
1,1-Dichloroethene									
1,1-Dichloroethane									
Total-1,2-Dichloroethene									
Chloroform									
1,2-Dichloroethane									
2-Butanone									
1,1,1-Trichloroethane									
Carbon Tetrachloride									
Bromodichloromethane									
1,2-Dichloropropane									
cis-1,3-Dichloropropene									
Trichloroethene									
Dibromochloromethane									
1,1,2-Trichloroethane									
Benzene									
trans-1,3-Dichloropropene									
Bromoform									
4-Methyl-2-Pentanone									
2-Hexanone									
Tetrachloroethene									
1,1,2,2-Tetrachloroethane									
Toluene									
Chlorobenzene									
Ethylbenzene									
Styrene									
Total Xylenes									

AFFECTED SAMPLES:

Reviewer Initials/Date:_____

* See last page of this table for DEFINITION OF CODES.

TABLE I Page___of___

ENVIRONMENTAL PROTECTION AGENCY REGION III
CALIBRATION OUTLIERS
SEMIVOLATILE HSL COMPOUNDS (Part 1 of 2)

CASE/SAS No._____ CONTRACTOR _____

Instrument#	Init. Cal.			Cont. Cal.			Cont. Cal.			Cont.Cal.		
DATE/TIME:												
	RF	%RSD	*	RF	%D	*	RF	%D	*	RF	%D	*
Phenol												
bis(2-Chloroethyl)ether												
2-Chlorophenol												
1,3-Dichlorobenzene												
1,4-Dichlorobenzene												
1,2-Dichlorobenzene												
2-Methylphenol												
bis(2-Chloroisopropyl)ether												
4-Methylphenol												
N-Nitroso-di-n-propylamine												
Hexachloroethane												
Nitrobenzene												
Isophorone												
2-Nitrophenol												
2,4-Dimethylphenol												
bis(2-Chloroethoxy)methane												
2,4-Dichlorophenol												
1,2,4-Trichlorobenzene												
Naphthalene												
4-Chloroaniline												
Hexachlorobutadiene												
4-Chloro-3-Methylphenol												
2-Methylnaphthalene												
Hexachlorocyclopentadiene												
2,4,6-Trichlorophenol												
2,4,5-Trichlorophenol												
2-Chloronaphthalene												
2-Nitroaniline												
Dimethylphthalate												
Acenaphthylene												
2,6-Dinitrotoluene												
3-Nitroaniline												
Acenaphthene												
2,4-Dinitrophenol												
4-Nitrophenol												

AFFECTED SAMPLES:

Reviewer Initials/Date:_____

* See last page of this table for DEFINITION OF CODES.

TABLE I Page___of___

ENVIRONMENTAL PROTECTION AGENCY REGION III
CALIBRATION OUTLIERS
SEMIVOLATILE HSL COMPOUNDS (Part 2 of 2)

Instrument#	Init. Cal.			Cont. Cal.			Cont. Cal.			Cont.Cal.		
DATE/TIME:												
	RF	%RSD	*	RF	%D	*	RF	%D	*	RF	%D	*
Dibenzofuran												
2,4-Dinitrotoluene												
Diethylphthalate												
4-Chlorophenyl-phenylether												
Fluorene												
4-Nitroaniline												
4,6-Dinitro-2-methylphenol												
N-Nitrosodiphenylamine												
4-Bromophenyl-phenylether												
Hexachlorobenzene												
Pentachlorophenol												
Phenanthrene												
Anthracene												
Carbazole												
Di-n-butylphthalate												
Fluoranthene												
Pyrene												
Butylbenzylphthalate												
3,3'-Dichlorobenzidine												
Benzo(a)anthracene												
Chrysene												
bis(2-ethylhexyl)phthalate												
Di-n-octylphthalate												
Benzo(b)fluoranthene												
Benzo(k)fluoranthene												
Benzo(a)pyrene												
Indeno(1,2,3-cd)pyrene												
Dibenz(a,h)anthracene												
Benzo(g,h,i)perylene												

AFFECTED SAMPLES:

Reviewer Initials/Date:_____

* See last page of this table for DEFINITION OF CODES.

DEFINITION OF CODES USED IN TABLE I

I = %RSD exceeded 30% in the initial calibration, positive results are qualified "J". When the %RSD exceeded 50%, quantitation limits are qualified "UJ".

C = %D exceeded 25% in the continuing calibration, positive results are qualified "J". When the %D exceeded 50%, quantitation limits are qualified "UJ".

F = RF less than 0.05 in the calibration. All quantitation limits are qualified "R" and positive results are qualified "L".

+ = The "B" qualifier, denoting blank contamination, supersedes the qualifier issued in this table.

R = The "R" qualifier, denoting unusable results, supersedes the qualifier issued in this table.

APPENDIX C

CONTRACTUAL REQUIREMENT COMPARISON TABLES

APPENDIX C

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: ± 30 sec. 3 compounds: Chlorobenzene-d_5 1,4-Difluorobenzene Bromochloromethane	IS Area: ± 40% IS RT Shift: ± 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 ≥ 10% of nearest IS	largest 10 ≥ 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: ± 30 sec.	IS Area: - 50% to 100% IS RT Shift: ± 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 ≥ 10% of nearest IS	largest 20 ≥ 50% of nearest IS

APPENDIX D

PROPOSED GUIDANCE FOR TENTATIVELY IDENTIFIED COMPOUNDS (VOA AND SV)

APPENDIX D

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 (LCSs). 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 (MW). 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 nitrogen

  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 the 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-trichloromenthane), 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-pentatone, 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 XII.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 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

Equation 1:

$$RI = \frac{RTunk - RTz}{RTz+1 - RTz} + 100Z$$

where: RTunk is the retention time of the unknown
RTz is the retention time of the preceding retention index standards
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 found 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

1. Lee, M.L. Vassilaros, D.L., White. C.mM., and Novotny, M., "Retention Indices for Programmed-Temperature Capillary-Column Gas Chromatography of Polycyclic Aromatic Hydorcarbons", Analytical Chemistry, V.51, no. 6, 1979, pp. 768-773.

2. Rostad, C.E., and Pereira, W.E., "Kovats and Lee Retention Indices Determined by Gas Chromatography/Mass Spectrometry for Organic Compounds of Environmental Interest." J. High Resolution Chrom. and Chrom. Commun.., vol.9, 1986, pp. 328-334.

3. Silverstein, R.M., Bassier, 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 polyclyclic Aromatic Compounds. Critical Evaluation and Additional Indices". J. of Chromatography, 252 (1982) pp. 1-20.

APPENDIX D

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 1 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 (R) 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 proceeding 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:

- 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.

- 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 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=317.10). 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-pentatone, 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 E

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 Chromatograph/Electron capture
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 (Aroclor is a trademark)

PE	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
$\overline{\text{RRF}}$	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.