United States
Environmental Protection
Agency

Office of
Solid Waste and
Emergency Response

Publication 9240.1-05
EPA-540/R-94/012
PB94-963501

Superfund

February 1994

Karen

EPA

USEPA CONTRACT LABORATORY PROGRAM NATIONAL FUNCTIONAL GUIDELINES FOR ORGANIC DATA REVIEW

ER ID# 58690

AUG 0 4 1998
SM

14024

Publication 9240.1-05
PB94-963501
EPA540/R-94/012
February 1994

USEPA CONTRACT LABORATORY PROGRAM NATIONAL FUNCTIONAL GUIDELINES FOR ORGANIC DATA REVIEW

Office of Emergency and Remedial Response
U.S. Environmental Protection Agency
Washington, DC 20460

NOTICE

The policies and procedures set forth here are intended as guidance to the Agency and other governmental employees. They do not constitute rulemaking by the agency, and may not be relied on to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

Additional copies of this document can be obtained from:

National Technical Information Service (NTIS)
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650
Document Number: PB94-963501

TABLE OF CONTENTS

		Page
INTRODUCTION		1
PRELIMINARY REVIEW		2
DATA QUALIFIER DEFINITIONS		4
VOLATILE DATA REVIEW		5
I.	Holding Times	6
II.	GC/MS Instrument Performance Check	9
III.	Initial Calibration	12
IV.	Continuing Calibration	17
V.	Blanks	20
VI.	System Monitoring Compounds	26
VII.	Matrix Spikes/Matrix Spike Duplicates	30
VIII.	Laboratory Control Samples	32
IX.	Region Quality Assurance and Control	34
X.	Internal Standards	35
XI.	Target Compound Identification	37
XII.	Compound Quantitation and Reported Contract Required Quantitation Limits	39
XIII.	Tentatively Identified Compounds	41
XIV.	System Performance	45
XV.	Overall Assessment	47
SEMIVOLATILE DATA REVIEW		48
I.	Holding Times	49
II.	GC/MS Instrument Performance Check	51
III.	Initial Calibration	55

IV. Continuing Calibration 59
V. Blanks 62
VI. Surrogate Spikes 66
VII. Matrix Spikes/Matrix Spike Duplicates 69
VIII. Laboratory Control Samples 71
IX. Region Quality Assurance and Control 73
X. Internal Standards 74
XI. Target Compound Identification 76
XII. Compound Quantitation and Reported Contract Required Quantitation Limits 78
XIII. Tentatively Identified Compounds 80
XIV. System Performance 84
XV. Overall Assessment 86

PESTICIDE/AROCLOR DATA REVIEW 87

I. Holding Times 88
II. GC/ECD Instrument Performance Check 90
III. Initial Calibration 96
IV. Calibration Verification 100
V. Blanks 103
VI. Surrogate Spikes 108
VII. Matrix Spikes/Matrix Spike Duplicates 111
VIII. Laboratory Control Samples 113
IX. Region Quality Assurance and Control 115
X. Pesticide Cleanup Checks 116
XI. Target Compound Identification 119
XII. Compound Quantitation and Reported Contract Required Quantitation Limits 122
XIII. Overall Assessment 124

INTRODUCTION

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

These guidelines include the requirements for the Organic Analysis Multi-Media Multi-Concentration method, and for the Low Concentration Water Organic Analysis method. *To ensure that the data review guidelines that are unique to the Low Concentration Water Samples are easily identified, these requirements and procedures are presented in italics and contained within brackets ([ ]) throughout the 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. 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 of the reviewer.

At times, there may be a need to use data which does 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 program needs. Data which do not meet specified requirements are never fully acceptable. The only exception to this condition is in the area of the requirements for individual sample analysis; if the nature of the sample itself inhibits the attainment of specifications, appropriate allowances must be made.

PRELIMINARY REVIEW

In order to use this document effectively, the reviewer should have a general overview of the sample delivery group (SDG) or sample 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.

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 identify:

1. The Project Officer for site.

2. The 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,
   g. preservatives, and
   h. 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 start of 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, preservation, 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 written in the method), signed by the laboratory manager or his designee. This statement authorizes the validation and release of the sample data results. In addition, the laboratory must also provide comments in the SDG narrative describing in detail any problems encountered in processing the samples in the data package.

For every data package, the reviewer must verify that the laboratory certification statement is present, exactly stated as in the method (i.e., verbatim to the statement in the method), 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 any associated problem(s).

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

A data review narrative generally accompanies the laboratory data forwarded to the intended data recipient (client) or user to promote communications. A copy of the data review narrative should be submitted to the Regional CLP Technical Project Officer (TPO) assigned oversight responsibility for the laboratory producing the data.

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

DATA QUALIFIER DEFINITIONS

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

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

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

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

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

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

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

VOLATILE DATA REVIEW

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

The volatile data requirements to be checked are listed below:

I. Holding Times (Method Holding Times)

II. GC/MS Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration

V. Blanks

VI. System Monitoring Compounds

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Laboratory Control Samples

IX. Regional Quality Assurance and Quality Control

X. Internal Standards

XI. Target Compound Identification

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

XIII. Tentatively Identified Compounds

XIV. System Performance

XV. Overall Assessment of Data

I. Holding Times

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

B. **Objective:**

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

C. **Criteria:**

Technical requirements for sample holding times have only been established for water matrices.

The technical holding time criteria for water samples are 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 (with HCl to pH 2 or below) water samples is 14 days from sample collection.

Water samples that have not been maintained at 4°C (± 2°C) and preserved to a pH of 2 or below should be analyzed within 7 days from sample collection. If insufficient ice is used to ship samples, the laboratory may receive samples with no ice left in the cooler. Under these circumstances, the temperature of the samples may exceed 4°C.

NOTE: It is further recommended that volatile compounds in properly preserved (4°C ± 2°C) non-aqueous samples be analyzed within 14 days of sample collection.

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

D. **Evaluation:**

Technical holding times are established by comparing the sampling dates on the EPA Sample Traffic Report with dates of analysis on Form I VOA *[Form I LCV]* and the raw data. Information contained in the complete SDG file 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. Review the SDG narrative to determine if samples were preserved. If there is no indication in the SDG narrative or the sample records that there was a problem with the samples (e.g., samples not maintained @ 4°C or containing headspace in the samples), then the integrity of samples can be assumed to be good. If it is indicated that there were problems with the samples, then the integrity of the sample may have been compromised and professional judgement should be used to evaluate the effect of the problem on the sample results.

E. **Action:**

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

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

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

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

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

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

VOA

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

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

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

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

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

II. GC/MS Instrument Performance Check

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

B. Objective:

Gas chromatograph/mass spectrometer (GC/MS) instrument performance checks 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.

VOA

D. **Evaluation:**

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

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

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

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

   d. The laboratory has not made calculation errors.

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

3. Verify that the ion abundance criteria was met. The criteria for m/z 173, 175, 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. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not subtract as part of the background the BFB peak.

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

E. Action:

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

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

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

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

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

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

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

III. Initial Calibration

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

B. **Objective:**

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

C. **Criteria:**

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

   [For data generated through the Low Concentration Water Method: Initial calibration standards containing both volatile target compounds and system monitoring compounds are analyzed at concentrations of 1, 2, 5, 10, and 25 ug/L for non-ketones and 5, 10, 25, 50, and 125 ug/L for ketones at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met.

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

3. Initial calibration standard Relative Response Factors (RRFs) for all volatile target compounds and system monitoring compounds must be greater than or equal to 0.05. (Contractual initial calibration RRF criteria are listed in the appropriate Method.)

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

D. **Evaluation:**

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

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

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

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

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

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

   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.

<u>NOTE</u>: The criteria employed for technical data review purposes are different from those used in the method. The laboratory 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-Dichloroethane (total)†	1,2-Dichloroethane-d4†
trans-1,2-Dichloroethene ‡	*1,2-Dibromo-3-chloropropane* ‡
cis-1,2-Dichloroethene ‡	

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

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

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

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

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

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

E. Action:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

VOA

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

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

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

IV. Continuing Calibration

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

B. Objective:

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

C. Criteria:

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

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

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

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

D. Evaluation:

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

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

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

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

NOTE: The criteria employed for data review purposes are different from those defined in the method. The compounds listed in Table 2 (VOA Section III.D.4) have no method maximum %D criteria. The laboratory 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 ± 25.0% for all volatile target compounds and system monitoring compounds. Note those compounds which have a %D outside the ± 25.0% criterion. The method 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 ± 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 ± 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 ± 25.0% criterion and the continuing calibration RRF is greater than or equal to 0.05, qualify non-detected volatile target compounds with "UJ".

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

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

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

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

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

V. Blanks

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

B. **Objective:**

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

C. **Criteria:**

1. No contaminants should be found in the blanks.

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

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

4. A storage blank must be prepared upon receipt of the first samples from an SDG, and stored with samples until analysis. The storage blank must be analyzed once per SDG.

5. An instrument blank must 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 *[Form IV LCV]*) to identify the samples associated with each method blank.

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

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

E. **Action:**

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

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

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. If the contaminants found are volatile target compounds (or interfering non-target compounds) at significant concentrations above the CRQL, then this should be noted for TPO action.

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

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

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

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

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

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

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

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

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

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

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.

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

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

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

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

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

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

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

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

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

For both the "10x" and "5x" rules, sample results exceeded the adjusted blank results of 100 (or 10x10) and 50 (or 5x10), respectively, and therefore are not qualified.

VI. System Monitoring Compounds

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

B. Objective:

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

C. Criteria:

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

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

2. Recoveries for system monitoring compounds in volatile samples and blanks must be within the limits specified in the Method.

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 *[Form II LCV]*. Check for any calculation or transcription errors.

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

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 acceptable re-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.

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

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

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

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

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

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

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

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

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

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

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

4. In the special case of a blank analysis with system monitoring compounds 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. However, even if this judgment allows some use of the affected data, analytical problems should be noted for TPO action. Also note if there are potential contractual problems associated with the lack of reanalysis of samples that were out of specification.

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

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

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

B. **Objective:**

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

C. **Criteria:**

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

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

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

D. **Evaluation:**

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

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

3. Verify transcriptions from raw data and verify calculations.

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

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

E. Action:

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

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

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

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

NOTE: If a field blank was used for the MS/MSD, the TPO must be notified.

VIII. Laboratory Control Samples
(Low Concentration Water)

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

B. Objective:

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

C. Criteria:

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

2. *The LCS contains the following volatile compounds, in addition to the required SMC (Bromofluorobenzene):*

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

3. *The percent recoveries for the LCS compounds must be within the QC limits. The LCS must meet this recovery criteria for the sample data to be accepted.*

4. *The criteria for system monitoring compound recovery and internal standard performance also apply.*

D. Evaluation:

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

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

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

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

E. Action:

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

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

2. *If the LCS recovery criteria are not met, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution. Professional judgement should be used to qualify data for compounds other than those compounds that are included in the LCS. Professional judgement to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in performance of the LCS compound to the non-LCS compound.*

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

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

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

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

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

IX. Regional Quality Assurance and Quality Control

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

B. **Objective:**

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

C. **Criteria:**

Criteria are determined by each Region.

1. Performance evaluation sample frequency may vary.

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

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

D. **Evaluation:**

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

E. **Action:**

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

X. Internal Standards

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

B. Objective:

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

C. Criteria:

1. Internal standard area counts must not vary by more than a factor of two (-50% to +100%) from the associated 12hr calibration standard.

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

2. The retention time of the internal standard must not vary more than ±30 seconds from the retention time of the associated 12hr calibration standard.

   [For data generated through the Low Concentration Water Method: The retention time of the internal standard must not vary more than ± 20.0 seconds from the retention time of the associated 12hr calibration standard.]

D. Evaluation:

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

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

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

   a. Magnitude and direction of the IS area shift.

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

   c. Technical holding times.

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

   e. Other QC.

E. **Action:**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

XI. Target Compound Identification

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

B. Objective:

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

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

C. Criteria:

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

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

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

      [For data generated through the Low Concentration Water Method: All ions present in the standard mass spectrum at a relative intensity greater than 25% <u>must</u> 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 <u>sample</u> mass spectrum but not present in the <u>standard</u> spectrum must be considered and accounted for.

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

D. Evaluation:

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

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

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

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

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

E. Action:

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

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

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

XII. Compound Quantitation and Reported CRQLs

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

B. **Objective:**

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

C. **Criteria:**

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

2. Compound RRFs must be calculated based on the internal standard (IS) associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the Method for both the IS and target analytes. The compound quantitation must be based on the RRF from the appropriate daily standard.

D. **Evaluation:**

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

2. Verify that the correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout, in both the calibration as well as the quantitation process.

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

E. Action:

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

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

XIII. Tentatively Identified Compounds

A. Review Items: Form I VOA-TIC *[Form I LCV-TIC]*, chromatograms, and library search printouts and spectra for the 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 via a forward search of the NIST/EPA/NIH and/or Wiley Mass Spectral Library, 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 appropriate number of the largest volatile fraction peaks which are not system monitoring compound, internal standard, or target compounds, but which have area or height greater than 10 percent of the area or height of the nearest internal standard. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I VOA-TIC).

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

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

D. Evaluation:

1. Guidelines for tentative identification are as follows:

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

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

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

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

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

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

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

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

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

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

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

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

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

Examples:

a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or 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.

E. Action:

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

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

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

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

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

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

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

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

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

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

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

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

XIV. System Performance

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

B. **Objective:**

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

C. **Criteria:**

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

D. **Evaluation:**

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

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

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

   b. Excessive baseline rise at elevated temperature.

   c. Extraneous peaks.

   d. Loss of resolution.

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

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

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

E. Action:

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

XV. Overall Assessment of Data

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

B. **Objective:**

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

C. **Criteria:**

Assess the overall quality of the data.

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

D. **Evaluation:**

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

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

E. **Action:**

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

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

SEMIVOLATILE DATA REVIEW

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

The semivolatile data requirements to be checked are listed below:

I. Holding Times (Method Holding Times)

II. GC/MS Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration

V. Blanks

VI. Surrogate Spikes

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Laboratory Control Samples

IX. Regional Quality Assurance and Quality Control

X. Internal Standards

XI. Target Compound Identification

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

XIII. Tentatively Identified Compounds

XIV. System Performance

XV. Overall Assessment of Data

I. Holding Times

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

B. Objective:

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

C. Criteria:

Technical requirements for sample holding times have only been established for water matrices.

The technical holding time criteria for water samples, are as follows:

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

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

The method 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.

[For data generated through the Low Concentration Method: The method holding times requirements are that the extraction of all samples must be started within 5 days of the VTSR, and the extracts must be analyzed within 40 days of VTSR.

D. **Evaluation:**

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

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

E. **Action:**

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

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

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

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

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

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

II. GC/MS Instrument Performance Check

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

B. Objective:

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

C. Criteria:

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

Decafluorotriphenylphosphine (DFTPP)

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

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

D. **Evaluation:**

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

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

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

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

   d. The laboratory has not made any calculation errors.

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

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

4. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the DFTPP spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not subtract as part of the background the DFTPP peak.

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

E. Action:

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

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

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

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

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

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

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

5. Decisions to use analytical data associated with DFTPP instrument performance checks not meeting method 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 method and Section 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. Concerns or questions regarding laboratory performance should be noted for TPO action. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the DFTPP peak), then this should be noted for TPO action.

III. Initial Calibration

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

B. **Objective:**

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

C. **Criteria:**

1. Initial calibration standards containing both semivolatile target compounds and surrogates are analyzed at concentrations of 20, 50, 80, 120, and 160 ng/2uL at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.

   [For data generated through the Low Concentration Method: Initial calibration standards containing both semivolatile TCL compounds and surrogates are analyzed at concentrations of 5, 10, 20, 50, and 80 ng/2uL 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. The following nine compounds require initial calibration at 20, 50, 80, 100, and 120 ng/2uL: 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3, nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, pentachlorophenol, and 2,4,6-tribromophenol (surrogate).]

2. Minimum Relative Response Factor (RRF) criteria must be greater than or equal to 0.05. (Initial RRF criteria are listed in the appropriate method.)

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 ng/2uL). For the eight compounds with higher CRQLs, only a four-point initial calibration is required (i.e., 50, 80, 120, and 160 ng/2uL).

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

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

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

NOTE: The criteria used for data review purposes are different from those used for contractual purposes. The laboratory must meet a minimum RRF criteria of 0.01, however, for data review purposes, the "greater than or equal to 0.05" criterion is applied to all semivolatile compounds.

Table 4. Semivolatile Target Compounds Exhibiting Poor Response

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

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

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

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

   b. Verify that all semivolatile target compounds have a %RSD of less than 30%. The method 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 $\leq$30.0% criterion.

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

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

E. **Action:**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

IV. Continuing Calibration

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

B. **Objective:**

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

C. **Criteria:**

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

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

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

D. **Evaluation:**

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

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

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

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

NOTE: The criteria employed for the data review purposes are different from those used for contractual purposes. The laboratory 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 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 ± 25.0% criterion, for all semivolatile target compounds and surrogates. Note those compounds which have a %D outside the ± 25.0% criterion. The method 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 ± 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 ± 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 ± 25.0% criterion and the continuing calibration RRF is greater than or equal to 0.05, qualify non-detected semivolatile target compounds "UJ".

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

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

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

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

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

V. Blanks

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

B. **Objective:**

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

C. **Criteria:**

1. No contaminants should be found in the blanks.

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

D. **Evaluation:**

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

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

E. **Action:**

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

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

Specific actions are as follows:

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

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

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

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

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

4. If inordinate amounts of other target compounds are found at low levelt 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 XIII for TIC guidance.)

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

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

	Rule	
	10x	5x
Blank Result	12	12
CRQL	10	10
Sample Result	50	40
Qualified Sample Result	50U	40U

In the example for the "10x" rule, sample results less than 120 (or 10 x 12) would be qualified as non-detects. In the case of the "5x" rule, sample results less than 60 (or 5 x 12) would be qualified as non-detects.

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

	Rule	
	10x	5x
Blank Result	12	12
CRQL	10	10
Sample Result	8J	8J
Qualified Sample Result	10U	10U

Note that data are not reported as 8U, as this would be reported as a detection limit below the CRQL.

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

	Rule	
	10x	5x
Blank Result	15	15
CRQL	10	10
Sample Result	160	80
Qualified Sample Result	160	80

For both the "10x" and "5x" rules, sample results exceeded the adjusted blank results of 150 (or 10x15) and 75 (or 5x15), respectively, and therefore are not qualified.

VI. Surrogate Spikes

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

B. **Objective:**

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

C. **Criteria:**

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

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

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

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

D. **Evaluation:**

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

2. Check that the surrogate spike recoveries were calculated correctly. The equation can be found in the method

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

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

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

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

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

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

   a. Surrogate recovery (marginal versus gross deviation).

   b. Technical holding times.

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

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

E. Action:

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

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

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

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

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

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

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

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

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

3. In the case where two or more surrogates are out in either semi-volatile fraction; one with a recovery greater than the upper acceptance-limit and one with a recovery greater than or equal to 10% but less than the lower acceptance limit, qualify as described in SV Section VI.E.2 a., b., & c. above.

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

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

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

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

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.

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. Additionally, the lack of reanalysis of samples that were out of specification should be noted for TPO action.

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

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

B. **Objective:**

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

C. **Criteria:**

1. A matrix spike and matrix spike duplicate are extracted and analyzed for every 20 field samples of similar matrix in an SDG, whenever samples are extracted by the same procedure.

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

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

D. **Evaluation:**

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

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

3. Verify transcriptions from raw data and verify calculations.

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

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

E. **Action:**

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

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

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

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

NOTE: If a field blank was used for the MS/MSD, the TPO must be notified.

VIII. Laboratory Control Samples
(Low Concentration Water)

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

B. Objective:

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

C. Criteria:

1. *Laboratory control samples are prepared, extracted, analyzed, and reported once per SDG. The LCS must be extracted and analyzed concurrently with the samples in the SDG, using the same instrumentation as the samples in the SDG.*

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

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

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

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

D. Evaluation:

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

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

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

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

E. *Action:*

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

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

2. *If the LCS recovery criteria are not met, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution. Professional judgement should be used to qualify data for compounds other than those compounds that are included in the LCS. Professional judgement to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in performance of the LCS compound to the non-LCS compound.*

3. *If the LCS recovery is greater than the upper acceptance limit, then positive sample results for the effected compound(s) should be qualified with a "J".*

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

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

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

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

IX. Regional Quality Assurance and Quality Control

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

B. Objective:

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

C. Criteria:

Criteria are determined by each Region.

1. Performance evaluation sample frequency may vary.

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

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

D. Evaluation:

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

E. Action:

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

X. Internal Standards

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

B. **Objective:**

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

C. **Criteria:**

1. Internal standard area counts for samples and blanks must not vary by more than a factor of two (- 50% to + 100%) from the associated 12hr 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 12hr calibration standard.

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

D. **Evaluation:**

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

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

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

   a. Magnitude and direction of the IS area shift.

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

   c. Technical holding times.

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

E. **Action:**

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

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

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

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

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

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

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

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

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

XI. Target Compound Identification

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

B. **Objective:**

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

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

C. **Criteria:**

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

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

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

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

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

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

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

D. Evaluation:

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

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

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

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

E. Action:

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

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

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

XII. Compound Quantitation and Reported CRQLS

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

B. **Objective:**

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

C. **Criteria:**

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

2. Compound area responses must be calculated based on the internal standard (IS) associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the method for both the IS and target analytes. The compound quantitation must be based on the RRF from the appropriate daily calibration standard.

D. **Evaluation:**

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

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

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

E. Action:

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

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

XIII. Tentatively Identified Compounds

A. **Review Items:** Form I SV-TIC *[Form I LCSV-TIC]*, chromatograms, and library search printouts with spectra for the 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 appropriate number of the 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. Peaks that are suspected to be part of an alkane series shall be library searched and reported, as the alkane series (e.g., C_5-C_9), as a single entry along with the estimate for the total concentration of the series. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I SV-TIC).

[For data generated through the Low Concentration Method: For each sample, the laboratory must conduct a mass spectral search of the NIST library and report the possible identity for the appropriate number of the largest semivolatile fraction peaks which are not surrogates, internal standards, or TCL compounds, but which have an area greater than 50 percent of the area of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the TCL compounds, using total ion areas for the TIC and the internal standard, and assuming a relative response factor of 1.0. Peaks that are suspected to be part of an alkane series shall be library searched and reported, as the alkane series (e.g., C_5-C_9), as a single entry along with the estimate for the total concentration of the series. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I LCSV-TIC).]

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

D. **Evaluation:**

1. Guidelines for tentative identification are as follows:

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

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

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

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

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

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

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

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

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

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

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

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

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

6. Check the raw data to verify that the laboratory has properly identified and assigned peaks to the alkane series.

7. 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, cyclohexanone, 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.

8. 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.

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

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

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

E. Action:

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

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

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

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

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

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

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

6. The reviewer may elect to report all similar isomers as a total. All alkanes may be summarized and reported as total hydrocarbons (e.g., alkane series C_5-C_9). Reporting an alkane series counts only as one of the 30 most intense non-target semi-volatile compounds.

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

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

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

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

XIV. System Performance

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

B. **Objective:**

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

C. **Criteria:**

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

D. **Evaluation:**

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

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

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

   b. Excessive baseline rise at elevated temperature.

   c. Extraneous peaks.

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

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

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

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

E. Action:

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

XV. Overall Assessment of Data

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

B. **Objective:**

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

C. **Criteria:**

Assess the overall quality of the data.

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 usability 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 usability of the data within the given context.

PESTICIDE/AROCLOR DATA REVIEW

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

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

I. Holding Times (Method Holding Times)

II. GC/ECD Instrument Performance Check

III. Initial Calibration

IV. Calibration Verification

V. Blanks

VI. Surrogate Spikes

VII. Matrix Spikes/Matrix Spike Duplicates

VIII. Laboratory Control Samples

IX. Regional Quality Assurance and Quality Control

X. Pesticide Cleanup Checks

XI. Target Compound Identification

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

XIII. Overall Assessment of Data

I. Holding Times

A. **Review Items:** Form I PEST *[Form I LCP]*, EPA Sample Traffic Report, and/or chain-of-custody, raw data, sample extraction sheets, 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 sample extraction and analysis.

C. **Criteria:**

Technical requirements for sample holding times have only been established for water matrices.

The technical holding time criteria for water samples, are as follows:

For pesticides and Aroclors in cooled (@ 4°C) water samples, 7 days from sample collection to time of extraction and then 40 days from sample extraction to analysis.

It is recommended that pesticides and Aroclors in soil samples be extracted within 14 days of sample collection.

The method 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.

[For data generated through the Low Concentration Method: The holding times requirements are that the extraction of all samples must be started within 5 days of the VTSR, and the extracts must be analyzed within 40 days of VTSR.]

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 *[Form I LCP]* 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 *[Form I LCP]*.

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

E. **Action:**

1. If technical holding times are exceeded, 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.

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

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

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

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

II. GC/ECD Instrument Performance Check

A. **Review Items:** Form VI PEST-4,-5 *[Form VI LCP-4,-5]*, Form VII PEST-1 *[Form VII LCP-1]*, Form VIII PEST *[Form VIII LCP]*, 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 Mixtures

   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. All peaks in the Performance Evaluation Mixture injections must be greater than or equal to 90 percent resolved on each GC column. This applies to both initial and continuing calibrations.

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 calibration using the Individual Standard Mixtures.

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 minutes.

d. The percent difference between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM analyses on each GC column must be greater than or equal to -25.0 percent, AND less than or equal to 25.0 percent using the equation as specified in the method.

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.

i. The 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 *[Form VIII LCP]* 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 *[Form VI LCP-4]* to verify that the resolution criterion between two adjacent peaks for the required compounds is greater than or equal to 60%.

2. Performance Evaluation Mixture

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

b. Check the PEM data from Form VI PEST-5, and the initial and continuing calibrations to verify that the resolution between adjacent peaks is greater than or equal to 90 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 retention time from the three-point initial calibration.

d. Verify that the percent difference between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM analyses on each GC column must be greater than or equal to -25.0 percent, AND less than or equal to 25.0 percent.

e. Verify that the individual breakdowns for 4,4'-DDT and Endrin are 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

a. If the Resolution Check Mixture was not analyzed with the frequency described in PEST Section II. C. 1, 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. This situation should be brought to the attention of the TPO.

b. 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 co-elution 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 Frequency:

If the Performance Evaluation Mixture was not analyzed with the frequency described in PEST Section II. 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. This situation should be brought to the attention of the TPO.

3. Performance Evaluation Mixture Resolution:

If PEM 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 co-elution 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).

4. 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. It should be noted for TPO action if the PEM retention time criteria are grossly exceeded.

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 effect 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 compounds "NJ" and non-detected target compounds "UJ". 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 by using the mean retention times of the standards.

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 cannot do anything with the data to resolve the problem of concern, all positive results and quantitation limits should be qualified "R."

5. If percent difference 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."

6. 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 "J". 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 "J". 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 Aldehyde and Endrin ketone 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. The reviewer should consider the degree of individual breakdown of DDT and Endrin and apply qualifiers as described above.

7. Potential effects on the sample data resulting from the instrument performance check criteria 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 notify the TPO.

III. Initial Calibration

A. **Review Items:** Form VI PEST-1, 2, 3, and 4 *[Form VI LCP-1, 2, 3, and 4]*, Form VII PEST-1 *[Form VII LCP-1]*, Form VIII PEST *[Form VIII LCP]*, 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 compounds on the Target Compound List (TCL). 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 each column.

   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. The retention time window for each single component compound can be found in the appropriate method. An example for determining retention time windows is given in PEST Section II. C. 2. c above.

   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) are as follows:

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 stated 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, as stated in the appropriate method.

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 *[Form VIII LCP]* 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 Forms VII PEST-6,-7 with the raw data, and determine that the midpoint standard concentration is 4 times the concentration of the low point standard concentration and verify that resolution is greater than 90%.

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

d. Check the chromatograms and verify that at least one chromatogram from each of the Individual Standard mixtures A and B yields peaks registering recorder/printer deflections between 50 and 100 percent of full scale.

e. Verify that the concentrations of the low, medium and high level standards of Individual Mixtures A and B meet the criteria in PEST Section III. C. 1. above.

f. Check the Individual Standard Mixtures A and B data and Form VI PEST-2 *[Form VI LCP-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 PEST Section III. C above. 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 and review should be performed.

2. Multi-component Target Compounds

a. Verify from the Form VIII PEST *[Form VIII LCP]* 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 *[Form VI LCP-3]* to verify that at least three peaks were used for calibration and that retention time windows were calculated as required.

c. Check the data to verify that calibration factors have been determined for each selected 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. 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 retention time windows, are not calculated correctly, recalculate the windows and use the corrected values for all evaluations.

4. If the chromatogram display (recorder deflection) criteria are not met, use professional judgement to evaluate the effect on the data. If the data reviewer has knowledge that the laboratory has repeatedly failed to comply with this requirement, the data reviewer should notify the TPO.

5. If the sample concentration exceeds the linearity of the calibration curve, and the sample is not properly diluted and re-analyzed, flag the positive results "J".

6. If the standard concentration criteria are not met, use professional judgement to evaluate the affect on the data and notify the TPO. This is especially critical for the low level standards and non-detects.

7. If the %RSD linearity criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

8. 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, the data reviewer should notify the TPO.

IV. Calibration Verification

A. **Review Items:** Form VI PEST-6 and 7, Form VII PEST-1 and 2 *[Form VII LCP-1 and 2]*, Form VIII PEST *[Form VIII LCP]*, 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. Calibration verification checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, calibration verification 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 percent difference 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 $\pm$ 25.0 percent.

D. **Evaluation:**

1. Check the Form VIII PEST *[Form VIII LCP]* to verify that the instrument blanks, PEMs, and Individual Standard Mixtures were analyzed at the proper frequency and that no more than 12:00 hours was elapsed between continuing calibration brackets in an ongoing analytical sequence.

2. Check Forms VI-6 and 7, and 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 *[Form VII LCP-2]* to verify that the absolute retention times are within the appropriate retention time windows.

4. Check the data from the midpoint concentration of Individual Standard Mixtures A and B and Form VII PEST-2 *[Form VII LCP-2]* to verify that the percent difference between the calculated amount and the true amount for each of the pesticides and surrogates (must be within $\pm$ 25).

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 for TPO action. 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 <u>in-control</u> 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. If the retention time window criteria are grossly exceeded, then this should be noted for TPO action.

   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 Pesticide Section III. E. 3 to determine the extent of the effect on the data.

4. If the percent difference 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".

5. Potential effects on the sample data due to problems with calibration should be noted in the data review narrative.

V. Blanks

A. **Review Items:** Form I PEST *[Form I LCP]*, Form IV PEST *[Form IV LCP]*, 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, 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. Method Blanks

   a. 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. The method blank should be analyzed on each GC system used to analyze that set of associated samples.

3. Instrument Blanks

   a. 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 position in the analytical sequence.

4. Sulfur Cleanup Blanks

   a. 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. The sulfur cleanup blank should be analyzed on each GC system used to analyze the associated samples.

D. **Evaluation:**

1. Review the results of all associated blanks, Form I PEST *[Form I LCP]* and Form IV PEST *[Form IV LCP]*, and raw data (chromatograms and data system printouts) to evaluate presence of target or non-target analytes in the blanks.

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. The reviewer can use Form IV PEST *[Form IV LCP]* to assist in identifying samples associated with each blank.

3. Verify that the method blank analysis(es) contains less than the Contract Required Quantitation Limit (CRQL) of any target pesticide or Aroclor/Toxaphene or any interfering peak.

4. Verify that the instrument blank analysis has been performed every 12 hours as the first analysis of the continuing calibration sequence. All acceptable sample analysis are to be bracketed by acceptable instrument blanks. Additionally, the instrument blank must follow sample analysis which contain an analyte at high concentration. Evaluate the results from the various instrument blanks to verify that they do not contain any target analytes above one-half the CRQL values for water samples (assuming a 1-L extraction of a water sample).

5. Verify that the sulfur cleanup blanks were analyzed at the required frequency and that (assuming a 1-L extraction of a water sample) the sulfur blanks do not contain any target compound above the CRQL. If a separate sulfur cleanup blank was prepared, one version of Form IV PEST *[Form IV LCP]* should be completed associating all the samples with the method blank, and a <u>second</u> version of Form IV PEST *[Form IV LCP]* 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 the previous PEST Section V. C., then the data reviewer should use professional judgement to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should be brought to the attention of the TPO.

Action in the case of unsuitable blank results depends on the circumstances and the origin of the blank. Detected compounds should be reported unless the concentration of the compound in the sample is less than or equal to 5 times (5x) the amount in any blank. In instances where more than one blank is associated with a given sample, <u>qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant</u>. The results <u>must not</u> 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 contaminants found are at levels significantly greater than the CRQL, then this should be noted in for TPO action.

2. Any pesticide or Aroclor/Toxaphene detected in the sample, that was also detected in any associated blank, is qualified if the sample concentration is less than five times (5x) the blank concentration. The quantitation limit may also be elevated. Typically, the sample CRQL is elevated to the concentration found in the sample. The reviewer should use professional judgement to determine if further elevation of the CRQL is required.

   The reviewer should note that analyte concentrations calculated for method, sulfur, or instrument 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 as a non-detected target compound, "U". An explanation of the rationale for this determination should be provided in the narrative.

3. If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" 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, and as a TPO action item if the contamination is suspected of having an effect on the sample results.

4. If inordinate amounts of target pesticides, Aroclors/Toxaphene, or other interfering non-target compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted for TPO action.

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, and for TPO action, if the cross-contamination is suspected of having an affect on the sample results.

The following are examples of applying the blank qualification 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	4.0U

In this case, sample results less than 5.0 (or 5 x 1.0) would be qualified as non-detected target compounds.

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
Final Sample Result	0.5U

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
Qualified Sample Result	10.0

In this case, the sample result exceeded the adjusted blank result (5 x 1.0) and the sample result is not qualified.

VI. Surrogate Spikes

A. **Review Items:** Form II PEST *[Form II LCP]*, Form VIII PEST *[Form VIII LCP]*, 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. 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 limits for recovery of the surrogates tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB) are 30-150 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 the raw data (e.g., chromatograms and data system printouts) to verify that the recoveries on the Surrogate Recovery Form II PEST *[Form II LCP]* are calculated and transcribed correctly.

2. If recoveries are not within limits, check the raw data for possible interferences which may have affected surrogate recoveries. If low surrogate recoveries are observed, the reviewer should investigate whether the low recoveries were a result of sample dilution.

3. Check the raw data (e.g., chromatograms and data system printouts) to verify that the retention times on Form VIII PEST *[Form VIII LCP]* are accurate and within retention time windows.

4. If retention times were not met, check the raw data for possible mis-identification of GC peaks. Non-recovery of surrogates may also be due to shifts in retention times.

E. Action:

1. If either surrogate spike recovery is outside of advisory limits, the following guidance is suggested. Professional judgement must be used in applying these criteria, as surrogate recovery problems may not directly apply to target analytes.

   a. If low recoveries (i.e., between 10 and 30 percent) are obtained, associated detected compounds should be qualified "J" and quantitation limits "UJ".

   b. If high recoveries (i.e., greater than 150%) are obtained, this may be an indication of a high bias due to co-eluting interferences. Using professional judgement, qualify associated detected compound data with "J", non-detected analytes do not require qualification.

   c. If either pesticide surrogate recovery is reported as between 0% and 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 "J" and non-detected target compound results should be qualified unusable (R).

   d. 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 nondetected target compounds as unusable (R).

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

3. 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. Data is qualified on the professional judgement of the reviewer.

4. Extreme or repeated analytical problems with surrogate recoveries should be noted for TPO action.

5. If possible, the impact on 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
(Not Required for Low Concentration Water Data)

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 information on other deficiencies.

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.

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

D. **Evaluation:**

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

2. Check the raw data and Forms III PEST-1 and PEST-2 to verify that the results for matrix spike recoveries were calculated and transcribed correctly.

3. Check the raw data and Forms III PEST-1 and PEST-2 to verify that the matrix spike Relative Percent Difference (RPD) was calculated and transcribed correctly.

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

E. **Action:**

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

2. The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated sample 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. 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.

NOTE: If a field blank was used for the MS/MSD, unless designated as such by the Region, the TPO must be notified.

VIII. Laboratory Control Samples (Low Concentration Water)

A. Review Items: Form I LCP, Form III LCP, LCS chromatograms and data system printouts.

B. Objective:

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

C. Criteria:

1. *Laboratory control samples are analyzed at a frequency of once per SDG.*
2. *The LCS contains the following pesticides: gamma-BHC, heptachlor epoxide, dieldrin, 4,4'-DDE, endrin, endosulfan sulfate, and gamma-chlordane, in addition to the two required surrogates.*
3. *The percent recoveries for the LCS compounds must be within the QC limits provided on Form III LCP. The LCS must meet the recovery criteria for the sample data to be accepted.*
4. *The criteria for surrogate recovery and target compound identification also apply.*

D. Evaluation:

1. *Verify that LCS samples were analyzed at the required frequency.*
2. *Verify that the LCS recoveries reported on Form III LCP are within the QC limits.*
3. *Check that the LCS recoveries were calculated correctly.*
4. *Verify transcriptions from raw data to Forms I and III LCP.*

E. Action:

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

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

2. *If the LCS recovery criteria are not met, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution. If the LCS recovery exceeds the upper acceptance limit, detected target compounds may be qualified "J". If the LCS recovery exceeds the lower acceptance limit, detected target compounds may be qualified "J" and non-detects may be qualified unusable (R). Professional judgement should be used to qualify data for compounds other than those compounds that are included in the LCS. Professional judgement to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in performance of the LCS compound to the non-LCS compound.*

3. *If more than half of the compounds in the LCS are not within the recovery criteria, then all of the associated detected target compounds may be qualified "J" and all associated non-detected target compounds may be qualified unusable (R).*

4. *It should be noted for TPO action if a laboratory fails to analyze an LCS with each SDG, or if the reviewer has knowledge that a laboratory consistently fails to generate acceptable LCS recoveries.]*

IX. Regional Quality Assurance and Quality Control

A. Review Items: Form I PEST *[Form I LCP]*, 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 QA/QC samples.)

C. Criteria:

Criteria are determined by each Region.

1. Performance evaluation sample frequency may vary.

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

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

D. Evaluation:

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

E. Action:

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

X. Pesticide Cleanup Checks

A. **Review Items:** Form IX PEST-1 and 2 *[Form IX LCP]*, GPC/Florisil raw data, 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.

   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 to 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 Aroclors 1016 and 1260.

   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 *[Form IX LCP]*. 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. Aroclor pattern comparison within a laboratory can be checked if more than one GPC calibration was performed in for that SDG. The Region may devise other means to compare this information. 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 analyzes samples under an unacceptable Florisil Cartridge Check, then the TPO should be notified.

2. If Gel Permeation Criteria are not met, the raw data should be examined for the presence of high molecular weight contaminants, subsequent sample data should be examined for unusual peaks, and professional judgement should be used in qualifying the data. If a laboratory chooses to analyze samples under unacceptable Gel Permeation Criteria, then the TPO should be notified.

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. 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.

XI. Target Compound Identification

A. **Review Items:** Form I PEST *[Form I LCP]*, Form X PEST-1 and PEST-2 *[Form X LCP-1]* and LCP-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 *[Form I LCP]*.

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 *[Form I LCP]*, the associated raw data (chromatograms and data system printouts) and Form X PEST-1 and PEST-2 *[Form X LCP-1 and LCP-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 height 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 <u>not</u> met, all target compounds that are reported detected should be considered non-detected. The reviewer may need to use the qualifiers that are specific to pesticides. 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 GC/MS confirmation was required but not performed, the reviewer should report this for TPO action.

XII. Compound Quantitation and Reported CRQLS

A. **Review Items:** Form I PEST *[Form I LCP]*, Form X PEST-1 and PEST-2 *[Form X LCP-1 and LCP-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 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.

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 on the two GC columns. The potential for co-elution should be considered and the reviewer should use professional judgment 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.

XIII. 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. 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.