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LABORATORY DATA VALIDATION FUNCTIONAL GUIDELINES FOR EVALUATING ORGANICS ANALYSES

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LABORATORY DATA VALIDATION
FUNCTIONAL GUIDELINES FOR EVALUATING ORGANICS ANALYSES

Prepared for the

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LABORATORY DATA VALIDATION

FUNCTIONAL GUIDELINES FOR EVALUATING ORGANICS ANALYSES

INTRODUCTION

This document is designed to offer guidance in laboratory data evaluation and validation. In some aspects, it is equivalent to 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. These Guidelines have been updated to include all requirements in the 10/86 Statement of Work (SOW) for Organics and 10/86 SOW for Volatiles.

Those areas where specific SOPs are possible are primarily areas in which definitive performance requirements are established. These areas also correspond to specific requirements in Agency contracts. These requirements are concerned with specifications that are not sample dependent; they specify performance requirements on matters that should be fully under a laboratory's control. These specific areas include blanks, calibration standards, performance evaluation standard materials, and tuning. In particular, mistakes such as calculation and transcription errors must be rectified by resubmission of corrected data sheets.

This document is intended for technical review. Some areas of overlap between technical review and Contract Compliance Screening (CCS) exist; however, contract compliance is not intended to be a goal of these guidelines. It is assumed that the CCS is available and can be utilized to assist in the data review procedure.

Some requirements are not identical for every Case or batch of samples. Requirements for frequency of Quality Control (QC) actions are dependent on the number of samples, sample preparation technique, time of analysis, etc. Specific Case requirements and the impact of nonconformance must be addressed on a case by case basis; no specific guidance is provided. For example, there is a contract requirement that a blank analysis be performed a minimum of once every twelve hours of analysis time. This requirement must be translated into the number of blanks required for a specific set of samples; the data reviewer may have to consider the impact on data quality for a sample analyzed thirteen hours after a blank, in terms of the acceptability of that particular sample.

At times, there may be an urgent need to use data which do not meet all contract requirements and technical criteria. Use of these data does <u>not</u> 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 or resubmit data even if the previously submitted data have been utilized due to urgent program needs; data which do not meet specified requirements are never fully acceptable. The only exception to this requirement is in the area of requirements for individual sample analysis; if the nature of the sample itself limits the attainment of specifications, appropriate allowances must be made. The overriding concern of the Agency is to obtain data which are technically valid and legally defensible.

All data reviews must have, as a cover sheet, the Organic Regional Data Assessment (ORDA) form. If mandatory actions are required, they should be specifically noted on this form. In addition, this form is to be used to summarize overall deficiencies requiring attention, as well as general laboratory performance and any discernible trends in

the quality of the data. (This form is not a replacement for the data review.) Sufficient supplementary documentation must accompany the form to clearly identify the problems associated with a Case. The form and any attachments must be submitted to the Contract Laboratory Program Quality Assurance Officer (CLP QAO), the Regional Deputy Project Officer (DPO), and the Environmental Monitoring Systems Laboratory in Las Vegas (EMSL/LV).

It is the responsibility of the data reviewer to notify the Regional DPO concerning problems and shortcomings with regard to laboratory data. If there is an urgent requirement, the DPO may be contacted by telephone to expedite corrective action. It is recommended that all items for DPO action be presented at one time. In any case, the Organic Regional Data Assessment form must be completed and submitted.

PRELIMINARY REVIEW

In order to use this document effectively, the reviewer should have a general overview of the 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 is very difficult to locate. The site project officer is the best source for answers or further direction.

CCS is a source of a large quantity of summarized information. It can be used to alert the reviewer of problems in the Case or what may be sample-specific problems. This information may be utilized in data validation. If CCS is unavailable, those criteria affecting data validity must be addressed by the data reviewer.

Cases routinely have unique samples which require special attention by the reviewer. Field blanks, field duplicates, and performance audit samples need to be identified. The sampling records should provide:

1. Project Officer for site
2. Complete list of samples with notations on
   a) sample matrix
   b) blanks*
   c) field duplicates*
   d) field spikes*
   e) QC audit sample*
   f) shipping dates
   g) labs involved

   * If applicable

The chain-of-custody record includes sample descriptions and date of sampling. Although sampling date is not addressed by contract requirements, the reviewer must take into account lag times between sampling and shipping while assessing sample holding times.

The Case Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, and unusual events should be found in the Narrative.

VOLATILES AND SEMIVOLATILES PROCEDURE

The requirements to be checked in validation are listed below: ("CCS" indicates that the contractual requirements for these items will also be checked by CCS; CCS requirements are not always the same as the data review criteria.)

I. Holding Times (CCS - Lab holding times only)

II. GC/MS Tuning

III. Calibration

- o Initial (CCS)
- o Continuing (CCS)

IV. Blanks (CCS)

V. Surrogate Recovery (CCS)

VI. Matrix Spike/Matrix Spike Duplicate (CCS)

VII. Field Duplicates

VIII. Internal Standards Performance (CCS)

IX. TCL Compound Identification

X. Compound Quantitation and Reported Detection Limits

XI. Tentatively Identified Compounds

XII. System Performance (CCS)

XIII. Overall Assessment of Data for a Case

I. HOLDING TIMES

A. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of analysis or sample preparation, as appropriate.

B. Criteria

Technical requirements for sample holding times have only been established for water matrices. The holding times for soils are currently under investigation. When the results are available they will be incorporated into the data evaluation process. On October 26, 1984 in Volume 49, Number 209 of the Federal Register, page 43260, the following holding time requirements were established under 40 CFR 136 (Clean Water Act):

Purgeables: If unpreserved, aromatic volatiles must be analyzed within 7 days and non-aromatic volatiles must be analyzed within 14 days. If preserved with hydrochloric acid and stored at 4°C, then both aromatic and non-aromatic volatiles must be analyzed within 14 days.

Extractables (Includes Base/Neutrals and Acids): Both samples and extracts must be preserved at 4°C. Samples must be extracted within 7 days and the extract must be analyzed within 40 days.

C. Evaluation Procedure

Actual holding times are established by comparing sampling date on the EPA Sample Traffic Report with dates of analysis and/or extraction on Form I. Examine the sample records to determine if samples were properly preserved. (If there is no indication of preservation, it must be assumed that the samples are unpreserved.)

D. Action

If 40 CFR 136 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.

The following table illustrates when the qualifiers are to be used for volatiles:

Matrix	Preserved	> 7 Days	> 14 Days
Water	No	All aromatics	All compounds
	Yes	None	All compounds

1. If holding times are grossly exceeded, either on the first analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data and the effects of additional storage on the sample results. The reviewer may determine that non-detect data are unusable (R).

2. 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.

II. GC/MS TUNING

A. Objective

Tuning and performance criteria are established 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.

B. Criteria

1. Decafluorotriphenylphosphine (DFTPP)

m/z	ION ABUNDANCE CRITERIA
51	30.0 - 60.0 % of m/z 198
68	less than 2.0% of m/z 69
70	less than 2.0 % of m/z 69
127	40.0 - 60.0% 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 1.00% of m/z 198
441	present, but less than m/z 443
442	greater than 40.0% of m/z 198
443	17.0 - 23.0% of m/z 442

2. Bromofluorobenzene (BFB)

m/z	ION ABUNDANCE CRITERIA
50	15.0 - 40.0% of the base peak
75	30.0 - 60.0% of the base peak
95	base peak, 100% relative abundance
96	5.0 - 9.0% of the base peak
173	less than 2.0% of m/z 174
174	greater than 50.0% of the base peak
175	5.0 - 9.0% of m/z 174
176	greater than 95.0%, but less than 101.0% of m/z 174
177	5.0 - 9.0% of m/z 176

Note: As contracts are modified, new criteria would then apply.

C. Evaluation Procedure

1. Verify from the raw data that the mass calibration is correct.

2. Compare the data presented on each GC/MS Tuning and Mass Calibration (Form V) with each mass listing submitted.

3. Ensure the following:

   a. Verify that Form V is present for each 12-hour period samples are analyzed.

   b. The laboratory has not made any transcription errors.

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

   d. The laboratory has not made any calculation errors. For example, the % mass of m/z 443 relative to the mass of m/z 442 is calculated using the following equation:

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

4. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the DFTPP and BFB spectra are obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the quality assurance objectives and are therefore unacceptable.

D. Action

1. If mass calibration is in error, classify all associated data as unusable (R).

2. If ion abundance criteria are not met and the data in question are needed on a priority basis, professional judgment may be applied to determine to what extent the data may be utilized. Guidelines to aid in the application of professional judgment to this topic are discussed as follows:

   a. DFTPP — 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 198/199 and 442/443 ratios are critical. These ratios are based on the natural abundances of Carbon 12 and Carbon 13 and should always be met. Similarly, the m/z 68, 70, 197, and 441 relative abundances 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. 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- 10-30%) and other criteria are met, the deficiency is minor. The relative abundance of

m/z 365 is an indicator of suitable instrument zero adjustment. If m/z 365 relative abundance is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 1% minimum abundance criteria, the deficiency is not as serious.

b. BFB — As with DFTPP, 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 ratio, the 174/175 ratio, the 176/177 ratio, and the 174/176 ratio. The relative abundances of m/z 50 and 75 are of lower importance.

3. In line with the above discussion, an expansion of minus 25% of the low limit and plus 25% of the high limit for selected ions may be appropriate. For example, in DFTPP the m/z 51 ion abundance criteria might be expanded from 30-60% of m/z 198 to 22-75% of m/z 198.

a. The complete expanded criteria for DFTPP and BFB are as follows:

1) Decafluorotriphenylphosphine (DFTPP) (Expanded Criteria)*

m/z	ION ABUNDANCE CRITERIA
51	22.0 - 75.0% of m/z 198
68	less than 2.0% of m/z 69
70	less than 2.0% of m/z 69
127	30.0 - 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	7.0 - 37.0% of m/z 198
365	greater than 0.75% of m/z 198
441	present, but less than m/z 443
442	greater than 30.0% of m/z 198
443	17.0 - 23.0% of m/z 442

2) Bromofluorobenzene (BFB) (Expanded Criteria)*

m/z	ION ABUNDANCE CRITERIA
50	11.0 - 50.0% of the base peak
75	22.0 - 75.0% of the base peak
95	base peak, 100% relative abundance
96	5.0 - 9.0% of the base peak
173	less than 2% of the base peak
174	greater than 50% of the base peak
175	5.0 - 9.0% of m/z 174
176	greater than 95%, but less than 101% of m/z 174
177	5.0 - 9.0% of m/z 176

*Note: Does NOT change contract requirements.

b. If results fall within these expanded criteria, data may be acceptable.

c. If results fall outside these expanded criteria, all data are unusable (R).

d. These criteria do NOT establish new contract requirements. Contract laboratories meeting expanded criteria but not meeting contract requirements are NOT in compliance.

e. Decisions to use analytical data associated with DFTPP and BFB tunes not meeting contract requirements should be clearly noted on the Organic Regional Data Assessment Form.

f. If the reviewer has reason to believe that tuning criteria were achieved using techniques that distorted or skewed the spectra, full documentation on the tuning quality control should be obtained. If the techniques employed are found to be at variance with accepted practices, the quality assurance program of the laboratory may merit evaluation.

g. It is up to the reviewer's discretion, based on professional judgment, to flag data associated with tunes meeting expanded criteria, but not basic criteria. If only one element falls within the expanded criteria, no qualification may be needed. On the other hand, if several data elements are in the expanded windows, all associated data may merit an estimated flag (J). Please note that the data reviewer is not required to use expanded criteria. The reviewer may still choose to flag all data associated with a tune not meeting contract criteria as unusable (R) if it is deemed appropriate.

III. CALIBRATION

A. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning, and continuing calibration checks document satisfactory maintenance and adjustment of the instrument on a day-to-day basis.

B. Criteria

1. Initial Calibration

a. Volatile and Semivolatile Fractions

1) All average Relative Response Factors ($\overline{RRF}$) for TCL compounds must be ≥ 0.05.

2) All Percent Relative Standard Deviations (%RSD) must be $\leq 30\%$.

2. Continuing Calibration

a. Volatile and Semivolatile Fractions

1) All Relative Response Factors (RRF) for TCL compounds must be ≥ 0.05.

2) All Percent Difference (%D) must be $\leq 25\%$.

C. **Evaluation Procedure**

1. Initial Calibration

a. Evaluate the $\overline{RRF}$ for all TCL compounds and verify the following:

1) Check and recalculate the RRF and $\overline{RRF}$ for one or more volatile and semivolatile TCL compounds; verify that the recalculated value(s) agrees with the laboratory reported value(s).

2) Verify that all volatile and semivolatile TCL compounds have average Relative Response Factors of at least 0.05.

b. Evaluate the Percent Relative Standard Deviation (%RSD) for all TCL compounds and verify the following:

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

$$\% \text{ RSD} = \frac{\sigma}{\bar{x}} \times 100$$

σ = Standard deviation of 5 response factors

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

1) Check and recalculate the %RSD for one or more TCL compounds; verify that the recalculated value agrees with the laboratory reported value.

2) Verify that all TCL compounds (volatile and semivolatile) have a %RSD of $\leq 30\%$.

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

2. Continuing Calibration

a. Evaluate the RRF for all TCL compounds:

1) Verify that all volatile and semivolatile TCL compounds have Relative Response Factors of at least 0.05.

b. Evaluate the Percent Difference and verify the following:

1) Check calculation of % Difference (%D) between initial calibration average Relative Response Factors and continuing calibration Relative Response Factors for one or more compounds, using the following equation:

$$\%D = \frac{\overline{RRF_I} - RRF_C}{\overline{RRF_I}} \times 100$$

where,

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

RRF_C = relative response factor from continuing calibration standard.

2) Verify that the %D is $\leq$ 25% for all volatile and semivolatile TCL compounds.

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

D. Action

1. Initial Calibration

a. If any volatile or semivolatile TCL compound result has an average Relative Response Factor of less than 0.05:

1) Flag positive results for that compound as estimated (J).

2) Flag non-detects for that compound as unusable (R).

b. If any volatile or semivolatile TCL compound has a % RSD of greater than 30%:

1) Flag positive results for that compound as estimated (J).

2) Non-detects may be qualified using professional judgment.

2. Continuing Calibration

a. If any volatile or semivolatile TCL compound has a Relative Response Factor of less than 0.05:

1) Flag positive results for that compound as estimated (J).

2) Flag non-detects for that compound as unusable (R).

b. If any volatile or semivolatile TCL compound has a % Difference between Initial and Continuing Calibration of greater than 25%:

1) Flag all positive results for that compound as estimated (J).

2) Non-detects may be qualified using professional judgment.

IV. BLANKS

A. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all data associated with the Case must be carefully evaluated to determine whether or not there is an inherent variability in the data for the Case, or if the problem is an isolated occurrence not affecting other data.

B. Criteria

No contaminants should be present in the blank(s).

C. Evaluation Procedure

1. Review the results of all associated blank(s), Form I(s) and raw data (chromatograms, reconstructed ion chromatograms, quantitation reports or data system printouts).

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

D. Action

Action in the case of unsuitable blank results depends on the circumstances and origin of the blank. No positive sample results should be reported unless the concentration of the compound in the sample exceeds 10 times the amount in any blank for the common contaminants listed below, 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 compound is found in a blank but not found in the sample, no action is taken.

2. Any compound (other than the five listed below) detected in the sample, which was also detected in any associated blank, must be qualified when the sample concentration is less than five times the blank concentration. For the following five compounds, the results are qualified by elevating the limit of detection when the sample concentration is less than 10 times the blank concentration.

   Common lab contaminants:

   a. Methylene chloride
   b. Acetone
   c. Toluene
   d. 2-butanone
   e. Common phthalate esters

   The reviewer should note that the blank analyses 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 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. 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 rule does not apply; the sample value should be reported as a non-detect.

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

   Case 1: Sample result is greater than the Contract Required Quantitation Limit (CRQL), but is less than the required amount (5x or 10x) from the blank result.

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

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

Case 2: Sample result is less than CRQL, and is also less than the required amount (5x or 10x) from the blank result.

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

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

Case 3: Sample result is greater than the required amount (5x or 10x) from the blank result.

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

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

4. If gross contamination exists (i.e., saturated peaks by GC/MS), all compounds affected should be flagged as unusable (R), due to interference, in all samples affected.

5. If inordinate amounts of other TCL compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted in the data review comments which are forwarded to the DPO.

6. Similar consideration should be given to TIC compounds which are found in both the sample and associated blank(s). (See Section XI for TIC guidance.)

V. SURROGATE RECOVERY

A. 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 review and validation 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.

B. Criteria

Sample and blank surrogate recoveries for volatiles and semivolatiles must be within limits as per applicable SOW (Form II).

C. **Evaluation Procedure**

1. Check raw data (i.e., chromatograms, quant list, etc.) to verify the recoveries on the Surrogate Recovery (Form II).

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

   a. If any two surrogates within a base/neutral or acid fraction (or one surrogate for the VOA fraction) are out of specification, or if any one base/neutral, acid or VOA surrogate has a recovery of less than 10%, then there should be a reanalysis with surrogate results still outside the criteria. (Note: When there are unacceptable surrogate recoveries followed by successful re-analyses, the labs are required to report only the successful run.)

   b. The lab has failed to perform satisfactorily if surrogate recoveries are out of specification with no evidence of repurging, reinjection, or re-extraction.

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

3. 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:

   a. Surrogate recovery (marginal vs. gross deviation).

   b. Holding times.

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

D. **Action**

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 at least two surrogates in a base/neutral or acid fraction or one surrogate in the volatile fraction are out of specification, but have recoveries greater than 10%:

   a. Positive results for that fraction are flagged as estimated (J).

b. Negative results for that fraction are flagged with the sample quantitation limit as estimated (UJ).

2. If any surrogate in a fraction shows less than 10% recovery:

a. Positive results for that fraction are flagged as estimated (J).

b. Negative results for that fraction are flagged as unusable (R).

3. No qualification with respect to surrogate recovery is placed on data unless at least two surrogates are out of specification in the base/neutral or acid fraction, or one in the volatile fraction, or unless any surrogate has a less than 10% recovery.

4. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems remain that must be corrected by the laboratory.

VI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A. Objective

These data 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.

B. Criteria

1. Spike recoveries must be within the advisory limits established in the appropriate IFB and on Form III.

2. Relative Percent Differences (RPD) between matrix spike and matrix spike duplicate recoveries must be within the advisory limits established in the appropriate IFB and on Form III.

C. Evaluation Procedure

1. Inspect results for the Matrix Spike/Matrix Spike Duplicate Recovery (Form III).

2. Verify transcriptions from raw data and verify calculations.

D. **Action**

No action is taken on Matrix Spike/Matrix Spike Duplicate (MS/MSD) data alone to qualify an entire Case. 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.

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.

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 lab is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

Note: If a field blank was used for the MS/MSD, the information must be included on the ORDA form.

VII. FIELD DUPLICATES

A. **Objective**

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and lab precision; therefore, the results may have more variability than lab duplicates which measure only lab performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

B. **Criteria**

There are no specific review criteria for field duplicate analyses comparability.

C. **Evaluation Procedures**

Samples which are field duplicates should be identified using EPA Sample Traffic Reports or sample field sheets. The reviewer should compare the results reported for each sample and calculate the Relative Percent Difference (RPD).

D. **Action**

Any evaluation of the field duplicates should be provided with the reviewer's comments.

VIII. INTERNAL STANDARDS PERFORMANCE

A. Objective

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

B. Criteria

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

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

C. **Evaluation Procedure**

1. Check raw data (i.e., chromatograms, quantitation lists, etc.) to verify the recoveries reported on the Internal Standard Area Summary (Form VIIIA, VIIIB).

2. Verify that all retention times and IS areas are acceptable.

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

   a. Magnitude of the shift.

   b. Holding times.

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

D. **Action**

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

   a. Positive results for compounds quantitated using that IS are flagged as estimated (J) for that sample fraction.

   b. Non-detects for compounds quantitated using that IS are flagged with the sample quantitation limit classified as estimated (UJ) for that sample fraction.

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

2. If an IS retention time varies by more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction.

IX. TCL COMPOUND IDENTIFICATION

A. 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 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.

B. 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

   b. The relative intensities of ions specified above 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 greater than 10% in the <u>sample</u> spectrum but not present in the <u>standard</u> spectrum must be considered and accounted for.

C. Evaluation Procedure

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

2. Check the laboratory standard spectra vs. the sample compound spectra.

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

D. **Action**

1. The application of qualitative criteria for GC/MS analysis of TCL compounds requires professional judgment. If it is determined that incorrect identifications were made, all such data should be flagged as not detected (U) or unusable (R).

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

X. COMPOUND QUANTITATION AND REPORTED DETECTION LIMITS

A. **Objective**

The objective is to ensure that the reported quantitation results and CRQLs are accurate.

B. **Criteria**

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

2. Compound RRF must be calculated based on the IS specified in the SOW for that compound. Quantitation must be based on the quantitation ion (m/z) specified in the SOW. The compound quantitation must be based on the RRF from the appropriate daily standard.

C. **Evaluation Procedure**

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.

2. Verify that the correct internal standard, quantitation ion, and RRF were used to quantitate the compound.

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.

D. **Action**

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 qualification of data is warranted.

XI. TENTATIVELY IDENTIFIED COMPOUNDS

A. Objective

Chromatographic peaks in volatile and semivolatile fraction analyses that are not target compound list (TCL) analytes, surrogates, or internal standards are potential tentatively identified compounds (TIC). TICs must be qualitatively identified by (GC/MS) library search and the identifications assessed by the data reviewer.

B. Criteria

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

   Note: SOW revision October 1986 does not allow the laboratory to report as tentatively identified compounds (TICs) any TCL compound which is properly reported in another fraction. (For example, late eluting volatile TCL compounds must not be reported as BNA TICs.)

2. Guidelines for tentative identification are as follows:

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

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

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

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

C. Evaluation Procedure

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

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

3. All mass spectra in every sample and blank must be examined.

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

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

   Examples:

   a. Common lab contaminants: CO_2 (m/e 44), siloxanes (m/e 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), phthalates at levels less than 100 ug/l or 4000 ug/kg.

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

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

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

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

D. Action

1. All TIC results should be flagged as tentatively identified with estimated concentrations (JN).

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-TCL 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, 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 contaminant, the result may be flagged as unusable (R).

5. In deciding whether a library search result for a TIC represents a realistic identification, professional judgment must be exercised. If there is more than one reasonable 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 (1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (2-methyl, 3-ethyl benzene to substituted aromatic compound).

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

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

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

XII. SYSTEM PERFORMANCE

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.

Some examples of instrument performance indicators for various factors are as follows:

1. Abrupt, discrete shifts in reconstructed ion chromatogram (RIC) baseline may indicate gain or threshold changes.

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

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

   b. Excessive baseline rise at elevated temperature.

c. Extraneous peaks.

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

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

Continued analytical activity with degraded performance suggests lack of attention or professional experience. Based on the instrument performance indicators, the data reviewer must decide if the system has degraded to the point of affecting data quality or validity. If data quality may have been affected, data should be qualified using the reviewer's best professional judgment.

XIII. OVERALL ASSESSMENT OF DATA FOR A CASE

It is appropriate for the data reviewer to make professional judgments and express concerns and comments on the validity of the overall data package for a Case. This is particularly appropriate for Cases in which there are several QC criteria out of specification. The additive nature of QC factors out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform users concerning data quality and data limitations in order to assist that user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

PESTICIDES PROCEDURE

The requirements to be checked in validation are listed below. ("CCS" indicates that the contract requirements for these items will also be checked by CCS; CCS requirements are not always the same as the data review criteria.)

I. Holding Times (CCS - Lab holding times only)

II. Pesticides Instrument Performance (CCS)

III. Calibration

- o Initial (CCS)
- o Analytical Sequence (CCS)
- o Continuing (CCS)

IV. Blanks (CCS)

V. Surrogate Recovery

VI. Matrix Spike/Matrix Spike Duplicate (CCS)

VII. Field Duplicates

VIII. Compound Identification

IX. Compound Quantitation and Reported Detection Limits

X. Overall Assessment of Data for a Case

I. HOLDING TIMES

A. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of analysis or sample preparation, as appropriate.

B. Criteria

Technical requirements for sample holding times have only been established for water matrices. The holding times for soils are currently under investigation. When the results are available they will be incorporated into the data evaluation process. On October 26, 1984 in Volume 49, Number 209 of the Federal Register, page 43260, the holding time requirements for pesticides were established under 40 CFR 136 (Clean Water Act). Samples must be extracted within 7 days and the extract must be analyzed within 40 days. Both samples and extracts must be stored at 4° C.

C. Evaluation Procedure

Actual holding times are established by comparing sampling date on the EPA Sample Traffic Report with dates of analysis and extraction on Form I. Examine the sample records to determine if samples were properly preserved. (If there is no indication of preservation, it must be assumed that the samples are unpreserved.)

D. Action

If 40 CFR 136 holding times are exceeded, flag all positive results as estimated (J) and sample quantitation limits as estimated (UJ) and document to the effect that holding times were exceeded.

1. If holding times are grossly exceeded, either on the first analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data and the effect of additional storage on the sample results. The reviewer may determine non-detect data are unusable (R).

2. 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.

II. PESTICIDES INSTRUMENT PERFORMANCE

A. Objective

These criteria are established to ensure that adequate chromatographic resolution and instrument sensitivity are achieved by the chromatographic system. These criteria are not sample specific; conformance is determined using standard materials. Therefore, these criteria should be met in all circumstances.

B. Criteria

1. DDT Retention Time

DDT must have retention time on packed columns (except OV-1 and OV-101) greater than or equal to 12 minutes.

2. Retention Time Windows

The laboratory must report retention time window data on the Pesticide/PCB Standards Summary (Form IX) for each GC column used to analyze samples.

3. DDT/Endrin Degradation Check

The total percent breakdown for neither DDT nor endrin may exceed 20%. The percent breakdown is the amount of decomposition that endrin and 4,4'-DDT undergo when analyzed by the chromatographic system.

a. For endrin, the percent breakdown is determined by the presence of endrin aldehyde and/or endrin ketone in the GC chromatogram.

b. 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.

c. A combined percent breakdown must be calculated if there is evidence of a peak at the retention time of endrin aldehyde/4,4'-DDD, which co-elute on the OV-1 packed column (or an equivalent column).

d. Percent breakdown is calculated using the following equations:

$$\text{\% Breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\text{\% Breakdown for endrin} = \frac{\text{Degradation Peak Areas (endrin aldehyde + endrin ketone)}}{\text{Peak Area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

<u>Note 1</u>: Peak area of endrin aldehyde must be measured during the degradation check to verify system performance. Endrin aldehyde is not reported on Form I because it is removed by alumina cleanup.

<u>Note 2</u>: The term "peak height" may be substituted for the term "peak area".

$$\text{Combined \% Breakdown} = \frac{\text{Total degradation peak areas (DDE + DDD + endrin aldehyde + endrin ketone)}}{\text{Total DDT and endrin peak areas (DDT + DDE + DDD + endrin + endrin aldehyde + endrin ketone)}}$$

4. DBC Retention Time Check

The retention time of DBC in each analysis must be compared to the retention time of DBC in Evaluation Standard Mix A. The Percent Difference (%D) must not exceed 2.0% for packed columns, 0.3% for narrow-bore capillary columns, and 1.5% if wide-bore capillary columns are used.

$$\%D = \frac{RT_I - RT_S}{RT_I} \times 100$$

where,

RT_I = Absolute retention time of dibutylchlorendate in the initial standard (Evaluation Standard Mix A).

RT_S = Absolute retention time of dibutylchlorendate in the subsequent analyses.

C. **Evaluation Procedure**

1. Check raw data to verify that DDT retention time is greater than 12 minutes on the standard chromatogram and that there is adequate resolution between peaks.

2. Check raw data to verify that retention time windows are reported on Form IX, and that all pesticide standards are within the established retention time windows.

3. Check raw data to verify that the percent breakdown for endrin and 4,4'-DDT, or the combined percent breakdown, does not exceed 20% in all Evaluation Standard Mix B analyses on Form VIII D.

4. Check raw data to verify that the percent difference in retention time for dibutylchlorendate in all standards and samples is $\leq$ 2.0% for packed column analysis, $\leq$ 0.3% for capillary column analysis, and $\leq$ 1.5% for wide-bore capillary column analysis on Form VIII E.

D. **Action**

1. DDT Retention Time

If the retention time of DDT is less than 12 minutes (except on OV-1 and OV-101), a close examination of the chromatography is necessary to ensure that adequate separation of individual components is achieved. If adequate separation is not achieved, flag all affected compound data as unusable (R).

2. Retention Time Windows

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 chromatograms contain any peaks within an expanded window surrounding 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, there is usually no effect on the data. (Non-detected values can be considered valid.)

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 two options are available to the reviewer to determine the extent of the effect on the data.

1) If no additional effort is warranted by the reviewer, flag all positive results and quantitation limits as unusable (R). The narrative should emphasize the possibility of either false negatives or false positives, as appropriate.

2) In some cases, additional effort is warranted by the reviewer (e.g., if the data are needed on a priority basis and if the peak(s) present might represent a level of concern for that particular pesticide). In these situations, the reviewer may undertake the following additional efforts to determine a usable retention time window for affected samples:

(a) The reviewer should 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.

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

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

(d) 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.

3. DDT/Endrin Degradation Check

a. If DDT breakdown is greater than 20%, beginning with the samples following the last <u>in-control</u> standard:

1) Flag all quantitative results for DDT as estimated (J). If DDT was not detected, but DDD and DDE are positive, then flag the quantitation limit for DDT as unusable (R).

2) Flag results for DDD and/or DDE as presumptively present at an estimated quantity (NJ).

b. If endrin breakdown is greater than 20%:

1) Flag all quantitative results for endrin as estimated (J). If endrin was not detected, but endrin aldehyde and endrin ketone are positive, then flag the quantitation limit for endrin as unusable (R).

2) Flag results for endrin ketone as presumptively present at an estimated quantity (NJ).

4. Retention Time Check

a. If the retention time shift for dibutylchlorendate (DBC) is greater than 2.0% for packed column, greater than 0.3% for narrow-bore capillary column, or greater than 1.5% for wide-bore capillary column, the analysis may be flagged unusable for that sample(s) (R), but qualification of the data is left up to the professional judgment of the reviewer.

b. The retention time shift cannot be evaluated in the absence of DBC.

III. CALIBRATION

A. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning, and continuing calibration checks document satisfactory maintenance and adjustment of the instrument over specific time periods.

B. Criteria

1. Initial Calibration Linearity Check

The Percent Relative Standard Deviation (%RSD) of calibration factors for aldrin, endrin, DDT, and dibutylchlorendate must not exceed 10%. If toxaphene is identified and quantified, a three-point calibration is required. If the calibration factor for DDT or toxaphene is outside the 10% RSD window, calibration curves must be used for quantitation of DDT, DDE, DDD, or toxaphene.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass Injected (ng)}}$$

$$\%RSD = \frac{\sigma}{CF} \times 100$$

where,

σ = Standard Deviation

CF = Mean Calibration Factor

Note: The 10% RSD linearity check is required only for columns which are used for quantitative determinations. Quantitation of the surrogate requires the use of a column shown to meet the 10% linearity criterion. Columns used only to provide qualitative confirmation are not required to meet this criterion.

2. Analytical Sequence

a. Primary Analysis

At the beginning of each 72-hour period all standards must be analyzed.

b. Confirmation Analysis

1) Evaluation Standard Mix A, B, and C are required for the curve.

2) Only the standards containing the compound(s) to be confirmed are required. These standards must be repeated after every five samples.

3) Evaluation Mix B is required after every ten samples.

3. Continuing Calibration

The calibration factor for each standard must be within 15% of the standard at the beginning of the analytical sequence on quantitation columns (20% on confirmation columns).

C. **Evaluation Procedure**

1. Initial Calibration

a. Inspect the Pesticide Evaluation Standards Summary (Form VIII) and verify agreement with the raw GC data (chromatograms and data system printouts).

b. Check the raw data and recalculate some of the calibration factors and the percent relative standard deviations (%RSD) for aldrin, endrin, 4,4'-DDT, and dibutylchlorendate at the three calibration concentrations.

c. Verify that the %RSD for the calibration factor of each specific pesticide is less than or equal to 10% for each 72-hour period.

d. If errors are detected, more comprehensive recalculation should be performed.

e. If toxaphene or the DDT series was identified and quantitated, verify that a three-point calibration was established.

2. Verify that all standards were analyzed in the 72-hour sequence.

3. Continuing Calibration

a. Review the pesticide sample data to verify whether the standard was used as a quantitation standard or as a confirmation standard.

b. For the quantitation standards, check the raw data to verify the percent difference (%D), using the following formula, for approximately ten percent of the reported values by recalculation.

$$\%D = \frac{R_1 - R_2}{R_1} \times 100$$

where,

R_1 = Calibration Factor from first analysis

R_2 = Calibration Factor from subsequent analysis

D. Action

1. Initial Calibration

If criteria for linearity are not met, flag all associated quantitative results as estimated (J).

2. Analytical Sequence

If the proper standards have not been analyzed, data may be affected. The data reviewer must use professional judgment to determine severity of the effect and qualify the data accordingly.

3. Continuing Calibration

a. If the %D between calibration factors is greater than 15% for the compound(s) being quantitated (20% for compounds being confirmed), flag all associated positive quantitative results as estimated (J).

IV. BLANKS

A. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all data associated with the Case must be carefully evaluated to determine whether or not there is an inherent variability in the data for the Case, or the problem is an isolated occurrence not affecting other data.

B. Criteria

No contaminants should be present in the blank(s).

C. Evaluation Procedure

1. Review the results of all associated blank(s), Form I(s) and raw data (chromatograms, quantitation reports or data system printouts).

2. Verify that the method blank analysis(es) contains less than the Contract Required Quantitation Limits (CRQL) of any Pesticide/PCB or interfering peak.

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

D. Action

Action in the case of unsuitable blank results depends on the circumstances and the origin of the blank. No positive sample results should be reported unless the concentration of the compound in the sample exceeds 5 times the amount in the blank. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting the blank value. Specific actions are as follows:

1. If a Pesticide/PCB is found in the blank but not found in the sample(s), no action is taken.

2. Any Pesticide/PCB detected in the sample and also detected in any associated blank, must be qualified when the sample concentration is less than 5 times the blank concentration.

   The reviewer should note that the blank analyses 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 where little or no contamination was present in the associated blanks, but qualification of the sample was deemed

necessary. 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 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-detect.

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

Case 1: Sample result is greater than the CRQL, but is less than the required amount (5x) from the blank result.

	5x
Blank Result	1.0
CRQL	.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-detects.

Case 2: Sample result is greater than the required amount (5x) from the blank result.

	5x
Blank Result	1.0
CRQL	.5
Sample Result	6.0
Qualified Sample Result	6.0

V. SURROGATE RECOVERY

A. Objective

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with a surrogate compound 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 review and validation 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.

B. **Criteria**

Sample and blank recoveries of dibutylchlorendate must be within limits as per applicable SOW (Form II).

C. **Evaluation Procedure**

1. Check raw data (i.e., chromatograms, quant list, etc.) to verify the recoveries on the Surrogate Recovery (Form II).

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

D. **Action**

If pesticide surrogate recoveries are outside of advisory windows, the following guidance is suggested:

1. If low recoveries are obtained, flag associated positive results and quantitation limits as estimated (J).

2. If high recoveries are obtained, professional judgment should be used to determine appropriate action. A high bias may be due to co-eluting interferences.

3. 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, flag all negative results as unusable (R).

VI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A. **Objective**

These data 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.

B. **Criteria**

1. Advisory limits are established for spike recovery limits in the appropriate SOW and on Form III.

2. Advisory limits are established for relative percent difference between matrix spike and matrix spike duplicate recoveries in the appropriate SOW and on Form III.

C. **Evaluation Procedure**

1. Inspect results for the Matrix Spike/Matrix Spike Duplicate Recovery (Form III).

2. Verify transcriptions from raw data and verify calculations.

D. *Action*

No action is taken on Matrix Spike/Matrix Spike Duplicate (MS/MSD) data alone to qualify an entire Case. 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.

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.

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 lab is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

VII. FIELD DUPLICATES

A. **Objective**

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and lab precision; therefore, the results may have more variability than lab duplicates which measure only lab performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

B. **Criteria**

There are no specific review criteria for field duplicate analyses comparability.

C. **Evaluation Procedures**

Samples which are field duplicates should be identified using EPA Sample Traffic Reports or sample field sheets. The reviewer should compare the results reported for each sample and calculate the Relative Percent Difference (RPD).

D. Action

Any evaluation of the field duplicates should be provided with the reviewer's comments.

VIII. COMPOUND IDENTIFICATION

A. 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).

B. Criteria

1. Retention times of reported compounds must fall within the calculated retention time windows for the two chromatographic columns.

2. GC/MS confirmation is required if the concentration of a compound exceeds 10 ng/uL in the final sample extract.

C. Evaluation Procedure

1. Review Form I, the associated raw data (chromatograms and data system printouts) and the Pesticide/PCB Identification Summary (Form X). Confirm reported positive detects, using appropriate retention times and retention time windows, and verify that the compounds listed as "not detected" are correct.

2. Verify that positive identifications have dissimilar column analysis. (The 3% OV-1 column cannot be used for confirmation if both dieldrin and DDE are identified.)

3. For multipeak pesticides (chlordane and toxaphene) and PCBs, the retention times and relative peak height ratios of major component peaks should be compared against the appropriate standard chromatograms.

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

D. Action

1. If the qualitative criteria for two-column confirmation were not met, all reported positive detects should be considered non-detects. The reviewer should use professional judgment 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 CRQL can be reported.

   b. If the misidentified peak poses an interference with potential detection of a target peak, then the reported value should be considered and flagged as the estimated quantitation limit (UJ).

2. If PCBs or multipeak pesticides exhibit marginal pattern-matching quality, professional judgment should be used to establish whether the differences are attributable to environmental "weathering". If the presence of a

PCB/multipeak pesticide is strongly suggested, results should be reported as presumptively present (N).

If an observed pattern closely matches more than one Aroclor, professional judgment should be used to decide whether the neighboring Aroclor is a better match, or if multiple Aroclors are present.

3. If GC/MS confirmation was required but not performed, the reviewer should notify the DPO.

IX. COMPOUND QUANTITATION AND REPORTED DETECTION LIMITS

A. Objective

The objective is to ensure that the reported quantitation results and CRQLs are accurate.

B. Criteria

Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the appropriate SOW.

C. Evaluation Procedure

1. Raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation reports, chromatograms, and sample preparation log sheets should be compared to the reported positive sample results and quantitation limits.

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.

D. Action

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

Note: Simple-peak pesticide results can be checked for rough agreement between quantitative results obtained on the two GC columns. 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, the lower of the two values should be reported and qualified as presumptively present at an estimated quantity (NJ). This necessitates a determination of an estimated concentration on the confirmation column. The narrative should indicate that the presence of interferences has obscured the attempt at a second column confirmation.

X. OVERALL ASSESSMENT OF DATA FOR A CASE

It is appropriate for the data reviewer to make professional judgments and express concerns and comments on the validity of the overall data package for a Case. This is particularly appropriate for Cases in which there are several QC criteria out of specification. The additive nature of QC factors out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform users concerning data quality and data limitations in order to assist that user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

GLOSSARY A

Data Qualifier Definitions

For the purposes of this document the following code letters and associated definitions are provided.

U - The material was analyzed for, but was not detected. The associated numerical value is the sample quantitation limit.

J - The associated numerical value is an estimated quantity.

R - The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification.

N - Presumptive evidence of presence of material.

NJ - Presumptive evidence of the presence of the material at an estimated quantity.

UJ - The material was analyzed for, but was not detected. The sample quantitation limit is an estimated quantity.

The reviewer may determine that qualifiers other than those used in this document are necessary to describe or qualify the data. In these instances, it is the responsibility of each Region to thoroughly document/explain the qualifiers used.

GLOSSARY B

Other Terms

BFB	Bromofluorobenzene — volatile tuning compound
BNA	Base/Neutral/Acid Compounds — compounds analyzed by semivolatile technique
Case	A finite, usually predetermined number of samples collected over a given time period for a particular site. A case consists of one or more Sample Delivery Group(s).
CCC	Calibration Check Compound
CCS	Contract Compliance Screening - process in which SMO inspects analytical data for contractual compliance and provides results to the Regions, laboratories and EMSL/LV.
CF	Calibration Factor
CRQL	Contract Required Quantitation Limit
DFTPP	Decafluorotriphenylphosphine — semivolatile tuning compound
DPO	Deputy Project Officer
EICP	Extracted Ion Current Profile
GC/EC	Gas Chromatography/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GPC	Gel Permeation Chromatography - A sample clean-up technique that separates compounds by size and molecular weight. Generally used to remove oily materials from sample extracts.
IS	Internal Standards - Compounds added to every VOA and BNA standard, blank, matrix spike duplicate, and sample extract at a known concentration, prior to instrumental analysis. Internal standards are used as the basis for quantitation of the target compounds.
MS/MSD	Matrix Spike/Matrix Spike Duplicate
m/z	The ratio of mass (m) to charge (z) of ions measured by GC/MS
OADS	Organic Analysis Data Sheet (Form I)
ORDA	Organic Regional Data Assessment
PCB	Polychlorinated biphenyl

PE Sample	Performance Evaluation Sample
Primary Analysis	One of two types of pesticide/PCB analysis by GC/EC techniques, the other being confirmation analysis. If the two analyses are run at separate times, the primary analysis is the first analysis chronologically, and is used to establish the tentative identification of any pesticides/PCBs detected. The identification is then confirmed in the confirmation analysis. If the two analyses are done simultaneously, either may be considered the primary analysis. Either may be used for quantitation if contract criteria are met.
QA	Quality Assurance - Total program for assuring the reliability of data.
QC	Quality Control - Routine application of procedures for controlling the monitoring process.
RIC	Reconstructed Ion Chromatogram
RPD	Relative Percent Difference (between matrix spike and matrix spike duplicate)
RRF	Relative Response Factor
$\overline{RRF}$	Average Relative Response Factor
RRT	Relative Retention Time (with relation to internal standard)
RSD	Relative Standard Deviation
RT	Retention Time
SDG	Sample Delivery Group - Defined by one of the following, whichever occurs first: o Case of field samples o Each 20 field samples within a Case o Each 14-day calendar period during which field samples in a Case are received, beginning with receipt of the first sample in the SDG. (For VOA contracts, the calendar period is 7-day.)
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
SPCC	System Performance Check Compound
SV	Semivolatile analysis - Method based on analysis by GC/MS for BNA organic compounds.
TCL	Target Compound List
TIC	Tentatively Identified Compound - A compound not on the TCL.

VOA	Volatile Organic Analysis - Method based on the purge and trap technique for organic compound analysis.
VTSR	Validated Time of Sample Receipt — Time of sample receipt at the laboratory as recorded on the shipper's delivery receipt and Sample Traffic Report.
σ	Standard Deviation Estimate (of a sample)

Region _____

ORGANIC REGIONAL DATA ASSESSMENT

CASE NO. _____ SITE _____

LABORATORY _____ NO. OF SAMPLES/ MATRIX _____

SDG # _____ REVIEWER (IF NOT ESD) _____

SOW# _____ REVIEWER'S NAME _____

DPO: ACTION _____ FYI _____ COMPLETION DATE _____

DATA ASSESSMENT SUMMARY

		VOA	BNA	PEST	OTHER
1.	HOLDING TIMES				
2.	GC/MS TUNE/INSTR. PERFORM.				
3.	CALIBRATIONS				
4.	BLANKS				
5.	SURROGATES				
6.	MATRIX SPIKE/DUP				
7.	OTHER QC				
8.	INTERNAL STANDARDS				
9.	COMPOUND IDENTIFICATION				
10.	SYSTEM PERFORMANCE				
11.	OVERALL ASSESSMENT				

O = Data had no problems/or qualified due to minor problems.
M = Data qualified due to major problems.
Z = Data unacceptable.
X = Problems, but do not affect data.

ACTION ITEMS: _____

AREAS OF CONCERN: _____

NOTABLE PERFORMANCE: _____