STANDARD OPERATING PROCEDURES

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

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DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

1.0 OBJECTIVE

The objective of this Standard Operating Procedure (SOP) is to establish a protocol for evaluation and validation of the data generated in the REAC laboratory as well as data submitted to REAC by subcontract laboratories in preparation for inclusion into an analytical report.

2.0 APPLICABILITY

This SOP is applicable to all samples submitted to REAC for analysis, whether samples are to be subcontracted or analysis is to be done in-house.

3.0 DESCRIPTION

3.1 Sample Holding Times

3.1.1 Objective

The objective is to ascertain the quality of results based on the holding time of the sample from the time of collection to the time of analysis including sample preparation, if appropriate.

3.1.2 Requirements

Volatiles Analysis

The analysis for volatile organics (VOA) must be performed within seven days of collection for all samples (aqueous and nonaqueous).

Semivolatiles Analysis

For semivolatile analysis, all samples (aqueous and nonaqueous) must be extracted within seven days of collection. Both aqueous and nonaqueous extracts must be analyzed within 40 days of extraction.

Pesticide/PCB Analysis

For pesticide/PCB analysis, all samples (aqueous and nonaqueous) must be extracted within seven days of collection. Both aqueous and nonaqueous extracts must be analyzed within 40 days of extraction.

3.1.3 Evaluation Procedure

Volatile Analysis

For VOA analysis, holding times are determined by comparing the date of collection on the chain of custody record with the date of analysis as noted on the laboratory instrument log and sample chromatogram.

Semivolatile Analysis

For semivolatile analysis, the holding time for extraction is established by comparing the date of sample collection on the chain of custody record with the extraction date on the laboratory extraction log. The holding time for analysis is established by comparing the date of collection on the chain of custody record with the analysis date on the instrument injection log to ensure that the time from extraction to analysis is less than 40 days.

Pesticide/PCB Analysis

For pesticide/PCB analysis, the holding time for extraction is established by comparing the date of sample collection on the chain of custody record with the extraction date on the laboratory extraction log. The holding time for analysis is established by comparing the date of sample collection on the chain of custody record with the analysis date on the instrument injection log to ensure that the time from extraction to analysis is the 40 days.

3.1.4 Action

Volatile Analysis

For VOA analysis of potable water samples, the results of any samples analyzed after the holding times are rejected. For VOA analysis of all other samples, if the holding time prior to analysis is greater than seven days and less than or equal to 20 days, all results are quantitatively qualified and flagged with a "J" and all non-detects are flagged (UJ). If the holding time prior to analysis was exceeded by more than 20 days, qualify all positive results (J) and consider all nondetects unusable (R).

Semivolatile Analysis

For semivolatile analysis of potable water samples, the results of any sample extracted or analyzed after the appropriate holding time are rejected. For semivolatile analysis of all other samples (aqueous and nonaqueous), if the holding time before extraction is greater than seven days and less than or equal to 15 days, all results are quantitatively qualified (J). If the holding time before analysis and after extraction of semivolatile samples other than potable

water exceeds 40 days but is less than or equal to 50 days, all results are quantitatively qualified and flagged with a "J". If the holding time exceeds 50 days, all samples results are considered unusable (R).

Pesticide/PCB Analysis

The actions for semivolatiles as listed in the above apply to the pesticide/PCB analysis.

3.2 GC/MS Tuning and Performance (VOA and Semivolatile Analyses)

3.2.1 Objective

Tuning and performance criteria are established to ensure that the data produced by the instruments may be correctly interpreted according to the requirements of the method being used. These criteria are not sample specific; conformance is determined using standard materials. Therefore, these criteria should be met in all circumstances.

3.2.2 Requirements

Volatiles

The VOA GC/MS system must be tuned using bromofluorobenzene (BFB). The following ion abundance criteria must be met prior to any standard, blank, and samples analysis:

m/z	Ion Abundance Criteria
50	8.0 - 40.0 % of mass 95
75	30.0 - 66.0 % of mass 95
95	base peak, 100% relative abundance
96	5.0 - 9.0 % of mass 95 (see note)
173	less than 2.0 % of mass 174
174	50.0 - 120.0 % of mass 95
175	4.0 - 9.0 % of mass 95
176	93.0 - 101.0 % of mass 174
177	5.0 - 9.0 % of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

Semivolatiles

The semivolatile GC/MS system must be tuned using decafluorotriphenylphosphine (DFTPP). The following ion abundance criteria must be met prior to any standard, blank and sample analysis:

m/z	Ion Abundance Criteria
51	30 - 80% of mass 198 (See Note)
68	less than 2.0% of mass 69
69	mass 69 relative abundance
70	less than 2.0% of mass 69
127	25.0 - 75.0% of mass 198
197	less than 1.0% of mass 198
198	base peak, 100% relative abundance
199	5.0 to 9.0% of mass 198
275	10.0 - 30.0% of mass 198
365	greater than 0.75% of mass 198
441	present, but less than mass 443
442	40.0 - 110.0% of mass 198
443	15.0 - 24.0% of mass 442

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

In addition, the criteria must be achieved during every 12-hour period during which standards, blanks and samples are analyzed. The 12-hour time period for GC/MS system tuning begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant tune. The time period ends after 12 hours have elapsed according to the system clock.

3.2.3 Evaluation Procedure

Compare the data presented on each GC/MS Tuning and Mass Calibration Form (Environmental Protection Agency (EPA) Contract Lab Program (CLP) Statement of Work (SOW), 3/90 Edition, Form V or equivalent) with each mass listing submitted to ensure achievement of ion abundance criteria.

Ensure the following:

- The laboratory has not made any transcription errors.

- The appropriate number of significant figures has been reported (3 sig. figures).
- The laboratory has not made any calculation errors.

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

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

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 of co-elution problems, background subtraction should be straight-forward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the objectives of Quality Assurance and are therefore unacceptable.

3.2.4 Action

If the ion abundance criteria are not met, the tune is not acceptable and all associated data are considered unusable (R).

If there are calculation or transcription errors, recalculate or make the necessary corrections. If all the criteria are now met, the tune and all associated data are acceptable. If after recalculation or corrections, ion abundance criteria are still not met, the tune is not acceptable and all associated data are considered unusable (R).

If any of the information required on the GC/MS Tuning and Mass Calibration Form (EPA CLP SOW, 3/90 Edition, Form V or equivalent) is missing, this information must be obtained from the laboratory.

If any standards, blanks or samples were analyzed more than 12 hours after the instrument tune, the data for the affected samples, blanks or standards are rejected. The only exception to this action would occur if any standard, blanks or samples were analyzed between 12 and 13 hours after the associated instrument tune. Under these circumstances, the data for all samples, blanks and standards analyzed between 12 and 13 hours after the associated tune would be qualified (J).

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 affected runs are considered unacceptable and all associated data are considered unusable. In

addition, the Quality Assurance Program of the laboratory may merit evaluation.

3.3 Pesticides Instrument Performance

3.3.1 Objective

To ensure that the data obtained from the instrument are interpreted correctly and the requirements of the specific method being followed correctly.

3.3.2 Requirements

Retention Time Windows

Retention time windows must be established before any samples are analyzed. Five injections of all single component pesticide mixtures, multiresponse pesticides and PCBs are made at approximately equal intervals over a 24-hour period. From the absolute retention times for each analyte, the standard deviation is calculated. Three times the standard deviation of the mean retention time for each pesticide/PCB will be used to establish the retention time window. For multiresponse pesticides or PCBs, pattern recognition together with surrogate retention times are used to determine the existence of the compounds.

The standard deviations determined above shall be used to determine the retention time windows for a particular 24-hour sequence.

Apply plus or minus three times the standard deviations determined to the retention time of each pesticide/PCB determined for the first analysis of the pesticide/PCB standard in a given 24-hour analytical sequence. This range of retention times defines the retention time window for the compound of interest for that 24-hour sequence. Note that, by definition, the retention time of a pesticide/PCB from the first analysis of that compound in the 24-hour sequence is the center of the retention time window. Do not use the absolute retention time of the other component mixtures as the center of the retention time window.

In those cases where the retention time window for a particular pesticide/PCB is less than 0.01 minutes, the laboratory may substitute following formula.

For capillary columns, the retention time window of the particular pesticide/PCB shall be calculated as ±3% of the initial retention time of the compound in the 24-hour sequence.

The retention time windows must be reported as a range of values, not as, for example, 1.51 minutes ±1%.

The laboratory must report retention time window data on the Pesticide/PCB Standards Summary (EPA CLP SOW 3/90 Edition, Form V or equivalent) for each GC column used to analyze samples.

Primary Column Analysis

At the beginning of the first 24-hour period all standards must be analyzed. The evaluation mixes include Endrin and 4,4'-DDT. The 24-hour sequence is as follows:

1. Standard Mix (20 ppb)
2. Standard Mix (50 ppb)
3. Standard Mix (100 ppb)
4. Standard Mix (200 ppb)
5. Standard Mix (500 ppb)
6. Evaluation Standard
7. Toxaphene
8. Aroclor 1016/1260
9. Aroclor 1221
10. Aroclor 1232
11. Aroclor 1242
12. Aroclor 1248
13. Aroclor 1254
14. 5 Samples
15. Standard Mix (100 ppb)
16. 5 Samples
17. Standard Mix (100 ppb)
18. 5 Samples
19. Standard Mix (100 ppb)
20. 5 Samples
21. Standard Mix (100 ppb)
22. 5 Samples

23. Repeat sequence from Step 15 above
24. Pesticide/PCB analysis must end with Standard Mix (100 ppb) regardless of number of samples analyzed.

At the second 24-hour period, a continuing 100 ppb Standard Mix is used to replace the initial five levels. A breakdown Standard Mix is followed if all criteria meet, continue sample analysis from Sequence #14.

Confirmation Column Analysis

The confirmation column analytical sequence is the same as for the primary analysis.

DDT/Endrin Degradation Check

The breakdown for either DDT or Endrin must be less than 20%. Percent breakdown is the amount of decomposition Endrin and DDT undergo when subjected to chromatographic conditions as specified by the method.

3.3.3 Evaluation Procedure

Retention Time Window

Verify that Retention Time Windows are reported on EPA CLP SOW, 3/90 Edition, Form IX (or equivalent). Compare the retention times from Form IX to the retention times on the standard chromatograms and verify that they are within the appropriate retention time windows.

DDT/Endrin Degradation Check

Verify that the breakdown for Endrin and DDT does not exceed 20% in all Evaluation Mix B standards. Use the following formula for calculating DDT/Endrin breakdown on all columns used for sample analysis.

$$\%\ Breakdown\ of\ DDT = \frac{DDE\ Peak\ Area + DDD\ Peak\ Area}{DDT\ Peak\ Area} \times 100$$

$$\%Breakdown\ of\ Endrin = \frac{Endrin\ Aldehyde\ Peak\ Area + Endrin\ Ketone\ Peak\ Area}{Endrin\ Peak\ Area} \times 100$$

3.3.4 Action

Retention Time Windows

Retention Time Windows are used in qualitative identification. When retention time windows have not been established by the laboratory, positive results reported by the laboratory, are, at best, tentative. The data reviewer must use professional judgement in determining the effect of no retention time windows on sample data quality. Sample chromatograms with no peaks or sample chromatograms with multipeak pesticide/PCB patterns would not be affected as greatly as sample chromatograms containing single peak

pesticide patterns. When retention times have not be established, positive results reported by the laboratory must be flagged as tentative (N). Resampling and reanalysis are required to confirm/negate this tentative call.

Analytical Sequence

If the proper analytical sequence is not followed, the reviewer must use professional judgement to determine the extent of effect and qualification of data.

DDT/Endrin Degradation Check

a. If DDT breakdown is greater than 20% on quantitation column beginning with the samples following the last in control standard:

   1. Flag all positive DDT results "J".

   2. If DDT was not detected but DDD and/or DDE are positive, flag the DDT non-detect "R".

   3. Flag positive DDD and DDE results "JN".

   4. If DDT breakdown is greater than 20% on the confirmation column and DDT is identified on quantitation column but not on the confirmation column, use professional judgement to determine whether DDT should be reported (if reported, flag result "N").

b. If Endrin breakdown is greater than 20% on the quantitation column, beginning with the samples following the last in control standard:

   1. Flag all positive Endrin results "J".

   2. If Endrin was not detected, but Endrin Aldehyde and/or Endrin Ketone are positive, flag the Endrin non-detect "R".

   3. Flag Endrin Ketone positive results "JN".

   4. If Endrin breakdown is greater than 20% on confirmation column and Endrin is identified on quantitation column but not on confirmation column, use professional judgement to determine whether Endrin should be reported (if reported, flag result "N").

c. If the combined breakdown is used when Endrin Aldehyde and 4,4-DDD co-elute or

their RT windows overlap, and there is a peak at their retention time, and is greater than 20% on quantitation column beginning with the last in control standard, take the actions specified in a and b above. If the combined breakdown is greater than 20% on confirmation column and Endrin or DDT is identified on quantitation column but not on confirmation column, use professional judgement to determine whether Endrin or DDT should be reported (if reported, flag result "N").

3.4 Initial Calibration

3.4.1 Objective

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

3.4.2 Requirements

Volatile Analysis

Initial calibration of volatile compounds and surrogates are required at 20, 50, 100, 150 and 200 µg/L. Surrogate and internal standards shall be used with each of the calibration standards. If an analyte saturates at the 200-µg/L concentration level and the GC/MS system is calibrated to achieve a detection sensitivity of no less than the routine method detection limit (see Appendix A), the laboratory must document it on EPA CLP SOW, 3/90 Edition, Form VI (or equivalent) and in the Case Narrative, and attach a quantitation report and Reconstructed Ion Chromatogram (RIC). In this instance, the laboratory should calculate the results based on a four-point initial calibration for the specific analyte that saturates. The use of a secondary ion for quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, the laboratory must document the reasons in the Case Narrative. All method blanks and standards must be analyzed under the same conditions as the samples.

All volatile compounds must have an average response factor greater than 0.050 in the initial calibration for VOA analysis.
All compounds must have less than 30% relative standard deviation (RSD) in response factors in the initial calibration for VOA analysis.

All samples or blanks must be analyzed within 12 hours of the initial calibration unless a subsequent continuing calibration is performed. The 12-hour time period for GC/MS standards calibration begins at the moment of injection of the last injection of the initial calibration standards. The time period ends after 12 hours have elapsed according to the system clock.

Semivolatile Analysis

Initial calibration of the semivolatile compounds is required at 20, 50, 80, 120 and 160 total nanograms (ng). Surrogate and internal standards shall be used with each of the calibration standards. If an analyte saturates at the 160 total nanogram concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity of no less than the routine method detection limit (see Appendix B), the laboratory must document it on EPA CLP SOW, 3/90 Edition, Form VI (or equivalent) and in the Case Narrative, and attach a quantitation report and Reconstructed Ion Chromatogram (RIC). In this instance, the laboratory should calculate the results based on a four-point initial calibration for the specific analyte. The use of a secondary ion for quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, the laboratory must document the reasons in the Case Narrative. Nine compounds: Benzoic Acid, 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-Methylphenol, and Pentachlorophenol will only require a four-point initial calibration at 50, 80, 120, and 160 total nanograms since detection at less than 50 nanograms is difficult. All method blanks and standards must be analyzed under the same conditions as the samples.

All compounds must have an average response factor greater than 0.050.

All compounds must not exceed 30% relative standard deviation (RSD) in response factors for the initial calibrations.

All samples or blanks must be analyzed within 12 hours of the calibration unless a subsequent continuing calibration is performed. The 12-hour time period for GC/MS system standards calibration begins at the moment of injection of the last standard in the initial calibration.

Pesticide/PCB

Five levels of initial calibration standards are evaluated at the beginning of each 24-hour period. Calibration factors for each compound are calculated. The %RSD must be no greater than 25%.

3.4.3 Evaluation Procedure

Volatile Analysis

Review the results contained on EPA CLP SOW, 3/90 Edition, Form VI (or equivalent), the standard chromatograms and the associated quantitation reports to verify the following:

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

Verify that the correct internal standards (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5) were used.

Check and recalculate the mean relative response factor for one or more analyte quantitated from each internal standard, verify that the recalculated values agree with the laboratory reported value. The relative response factor (RRF) for a compound can be calculated as follows:

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

where,

A_X = Area of characteristic ion for the compound to be measured
C_{IS} = Concentration of the internal standard (µg/µL)
A_{IS} = Area of characteristic ion for the specific internal standards
C_X = Concentration of the compound to be measured (µg/µL)

Verify that all volatile compounds in the initial calibration data have average RRF values greater than 0.050.

Check and recalculate the %RSD for one or more analytes quantitated from each internal standard; verify that the recalculated value agrees with the laboratory reported value. The percent relative standard deviation for a compound can be calculated as follows:

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

where,

RSD = Relative standard deviation
SD = Standard deviation of initial relative response factors (per compound)

where SD = $\sum_{i=1}^{N} \frac{(X_i - X)^2}{N - 1}$

X = mean of initial relative response factors (per compound)

Verify that all volatile compounds in the initial calibration have a %RSD less than 30%.

Verify that all samples and blanks were analyzed within 12 hours of the last injected standard of the initial calibration or within 12 hours of the continuing calibration standard.

Semivolatile Analyses

Review the results contained on EPA CLP SOW, 3/90 Edition, Form VI (or equivalent) the standards chromatograms and the associated quantitation reports to verify the following:

- Time(s), date(s) and instrument ID of calibration standard analyses are consistent on all forms and raw data sheets.
- Calibration standard analyses are associated with an acceptable instrument tune.
- A five-point calibration (four-point where applicable) was conducted using the proper standards concentrations.

Verify that the correct internal standards (1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were used.

Check and recalculate the average relative response factor (RRF) for one or more analyte quantitated from each internal standard; verify that the recalculated value agrees with the laboratory reported value. The relative response factor for a compound can be calculated as described in the volatiles portion of this section.

Verify that all other semivolatile compounds have an average relative response factor greater than 0.050.

Check and recalculate the %RSD for one or more compounds; verify that all recalculated values agree with the laboratory reported value. The percent relative standard deviation for a compound can be calculated as described as above.

Verify that all semivolatile compounds have a %RSD of less than 30.0%.

Verify that all samples and blanks were analyzed within 12 hours of the instrument tune associated with the initial calibration unless a subsequent instrument tune was performed or within 12 hours of an instrument tune associated with the continuing calibration.

Pesticide/PCB Analysis

Check and recalculate the calibration factor for one or more compounds in the calibration standard mix. The calibration factor can be determined as follows:

$$Calibration\ Factor = \frac{Total\ Area\ of\ Peak}{Mass\ Injected\ (in\ nanograms)} *$$

* peak height may be substituted for peak area

Check and recalculate the %RSD for one or more compounds in the calibration standard Mix. The %RSD for a given compound is determined as follows:

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

where:

RSD	=	relative standard deviation
X	=	mean calibration factor for a given compound
SD	=	standard deviation of calibration factors for a given compound

Verify that all compounds in the initial calibration standard have a %RSD less than 25% for a

three-point curve or a five-point curve.

3.4.4 Action

Volatile and Semivolatile Analyses

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

If the calibration standard analyses are not associated with an acceptable instrument tune, all calibration data are considered unusable (R).

If the initial calibration did not consist of five points, determine if a four-point calibration is applicable (see Section 3.4.2). If a three or four-point (other than those described in Section 3.4.2) initial calibration was performed, determine the range of concentrations used in the calibration. All analytical results reported outside the calibration concentration range for sample or blanks associated with such calibrations must be quantitatively qualified (J). Two and one-point initial calibrations are unacceptable; all such calibrations must be considered unusable (R).

If incorrect internal standards are used, all calibration data for the compounds associated with an incorrect internal standard are rejected.

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

If any compound has a average relative response factor of less than 0.050, all positive results for that compound in samples and blanks associated with the initial calibration are quantitatively qualified (J). In addition, all non-detected results for that compound in samples and blanks associated with the initial calibration are considered unusable (R).

If any compound has a %RSD for response factor greater than 30% RSD, all positive results for the given compounds in samples and blanks associated with the initial calibration are quantitatively qualified (J); all non-detects should be flagged as unusable (R) only when %RSD is greater than 90%.

If any samples or blanks are analyzed more than 12 hours after the moment of injection of the last standard in the initial calibration without a subsequent calibration performed, the data for the affected samples or blanks are considered unusable (R). The only exception to this action

would occur if any samples or blanks were analyzed between 12 and 13 hours after the associated tune. Under those circumstances, the data for all samples and blanks analyzed between 12 and 13 hours after the associated tune are quantitatively qualified (J).

Pesticide/PCB Analysis

If any %RSD is greater than 25%, qualify all associated positive results generated during the entire analytical sequence (J), and all non-detects (UJ). When % RSD is greater than 90%, flag all non-detects for the analyte unusable (R).

3.5 Continuing Calibration

3.5.1 Objective

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

3.5.2 Requirements

Volatile Analysis

Continuing calibration of volatile compounds is required at 50 µg/L. Surrogate and internal standards shall be used with the continuing calibration standard. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, the laboratory must document the reasons in the case narrative. All method blanks and standards must be analyzed under the same conditions as the samples.

Minimum response factor is 0.050 for all compounds.

Maximum percent difference (%D) between continuing calibration response factor and average response factor from initial calibration is 25% for all compounds.

All blanks and samples must be analyzed within 12 hours of the continuing calibration unless a subsequent calibration is performed. The 12-hour time period for GC/MS standards continuing calibration begins at the moment of injection of the continuing calibration. The time period ends after 12 hours have elapsed according to the system clock.

Semivolatile Analysis

Continuing calibration of semivolatile compounds is required at 50 total nanograms. Surrogate and internal standards shall be used with the continuing calibration standard. Secondary ion quantification is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, the laboratory must document the reasons in the case narrative. All method blanks and standards must be analyzed under the same conditions as the samples.

All compounds must have a response factor greater than 0.050 and must have a %D no greater than 25%.

All blanks and samples must be analyzed within 12 hours of the continuing calibration. The 12-hour time period for GC/MS standards continuing calibration begins at the moment of injection of the continuing calibration standard. The time period ends after 12 hours have elapsed according to the system clock.

Pesticide/PCB Analysis

Individual Standard Mixtures are analyzed at the beginning of each 24-hour period and analyzed at the intervals specified in the analytical sequence (see Section 3.3.2), and whenever sample analysis is completed. The Calibration Factor for each standard quantitated must not exceed a 20.0%D for a quantitation run.

3.5.3 Evaluation Procedures

Volatile Analysis

Review the results contained on EPA CLP SOW, 3/90 Edition, Form VII (or equivalent), the standard chromatograms and the associated quantitation reports to verify the following:

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

Verify that the correct internal standards (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5) were used.

Check and recalculate the RRF for one or more analyte quantitated under each internal standard; verify that the recalculated value agrees with the laboratory reported value. The RRF for a compound can be calculated as follows:

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

where:

A_X = area of characteristic ion for the compound to be measured
C_{IS} = concentration of the internal standard
A_{IS} = area of the characteristic ion for the specific internal standard
C_X = concentration of the compound to be measured

Verify that all volatile compounds in the continuing calibration data have RRF values greater than 0.050.

Check and recalculate the %D for one or more analytes quantitated from each internal standard; verify that the recalculated value agrees with the laboratory reported value. The %D for a compound can be calculated as follows:

$$\%\ Difference = \left| \frac{RRF_I - RRF_C}{RRF_I} \right| \times 100$$

where:

RRF_I = average relative response factor from initial calibration
RRF_C = relative response factor from current calibration check standard

Verify that all volatile compounds in the continuing calibration have a %D no greater than 25%.

Verify that all samples and blanks were analyzed within 12 hours of continuing calibration.

Semivolatile Analysis

Review the results contained on EPA CLP SOW, 3/90 Edition, Form VII (or equivalent), the standards chromatographs and the associated quantitation reports to verify the following:

- Time(s), date(s) and instrument ID of calibration standard analyses are consistent on all forms and raw data sheets.

- Calibration standard analyses are associated with an acceptable instrument tune.

Verify that the correct internal standards (1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) were used.

Check and recalculate the RRF for one or more analyte quantitated from each internal standard; verify that the recalculated value agrees with the laboratory reported value. The relative response factor for a compound can be calculated as described in the volatile part of this section.

Verify that all semivolatile compounds have a relative response factor of greater than 0.050.

Check and recalculate the %D for one or more analytes quantitated from each internal standard; verify that the recalculated value agrees with the laboratory reported value. The percent difference of relative response factors for a compound can be calculated as described in the above.

Verify that all semivolatile compounds have a %D no greater than 25%.

Verify that all samples and blanks were analyzed within 12 hours of the continuing calibration.

Pesticide/PCB Analysis

Review the calibration standard chromatograms, and associated quantitative reports to verify that time(s), date(s), chromatograph column and instrument ID of standard analyses are consistent on all forms and raw data sheets.

Check and recalculate the calibration factor for one or more compounds in the calibration standard mixes. The Calibration Factor (ratio of the total area to the mass injected) for a compound can be determined as follows:

$$Calibration\ Factor = \frac{Total\ Area\ of\ Peak}{Mass\ Injected\ (in\ nanograms)} *$$

*peak height may be substituted for peak area

Check and recalculate the %D for approximately 10% of the reported values. The %D for a given compound is determined as follows:

$$Percent\ Difference = \left| \frac{R_1 - R_2}{R_1} \right| \times 100$$

where:

R_1 = average calibration factor from the initial calibration
R_2 = calibration factor from the continuing calibration

Verify that all compounds in the continuing calibration check standard have a %D no greater than 25%.

3.5.4 Action

Volatile and Semivolatile Analyses

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

If the calibration standard analyses are not associated with an acceptable instrument tune, all calibration data are considered unusable (R).

If incorrect internal standards are used, all calibration data for the compounds associated with the incorrect internal standards are considered unusable (R).

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

If any compound has a relative response factor of less than 0.050, all positive results for that compound in samples and blanks associated with the continuing calibration are quantitatively qualified (J). In addition, all nondetected results for that compound in samples and blanks associated with the continuing calibration are considered unusable (R).

If any compound has a %D for response factor greater than the 25%, all positive results for

the given compounds in samples and blanks associated with the initial calibration are quantitatively qualified (J), any non-detects between 50 - 90% will be qualified (UJ), any non-detects greater than 90%, will be considered unusable (R). If any compound has a %D for response factor less than 50%, no qualifiers will be used for non-detects.

If any samples or blanks are analyzed more than 12 hours after the continuing calibration, the data for the affected samples or blanks are considered unusable (R). The only exception to this action would occur if any samples or blanks were analyzed between 12 and 13 hours after the associated instrument tune. Under these circumstances, the data for all samples and blanks analyzed between 12 and 13 hours after the associated tune are quantitatively qualified (J).

Pesticide/PCB Analysis

If the %D for any compound is greater than 25% (primary column), all positive results for that compound are qualified (J), non-detects are qualified (UJ). If the %D is greater than 90%, all non-detects considered unusable (R).

3.6 Blanks

3.6.1 Objective

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

3.6.2 Requirements

Volatile Analysis

The only in-house blank the laboratory is responsible for reporting is the method blank. The method blank for aqueous samples is a volume of deionized, distilled, and boiled water allowed to cool to room temperature, carried through the entire analytical scheme. The aqueous method blank volume must be approximately equal to the sample volumes being analyzed. For soil/sediment samples the method blank consists of purified solid matrix at the same approximate weight as the highest weight sample associated with the method blank and five mL of deionized, distilled, and boiled water, allowed to cool to room temperature,

carried through the entire analytical scheme. For medium level samples (which are methanol dilutions), the method blank consists of the largest volume of the methanol being aliquoted for dilutions made up to five mL in deionized, distilled, boiled water allowed to cool to room temperature and carried through the entire analytical scheme.

All samples and MS/MSD must be analyzed within 12 hours of an acceptable method blank. In the event a sample has very high concentrations of compounds present, good laboratory practice may suggest additional blank analyses to check for carryover of contamination from one sample to another.

The method blank must contain less than or equal to five times the method detection limit for methylene chloride, acetone, toluene, and 2-butanone, and less than or equal to the method detection limit of any other volatile target compound.

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

Semivolatile Analysis

The only in-house blank the laboratory is responsible for reporting is the method blank. A method blank is a volume of deionized, distilled laboratory water for associated aqueous samples, and purified solid matrix for nonaqueous samples carried through the entire analytical scheme. The method blank volume must be approximately equal to the sample volumes or sample weights being processed.

For the analysis of semivolatile compounds, a method blank analysis must be performed once each sample batch; with every 10 sample of similar concentration (i.e., low or medium soil analysis) and/or sample matrix; for each extraction technique used (e.g., separatory funnel, continuous extractor or soxhlet extractor); or whenever samples are extracted, whichever is more frequent.

The method blank must contain less than or equal to five times the method detection limit of phthalate esters listed in the target compound list (see Appendix B) and less than or equal to the method detection limit of all other semivolatile compounds.

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

Pesticide/PCB Analysis

The only in-house blank the laboratory is responsible for reporting is the method blank. A

method blank is a volume of deionized, distilled laboratory water for aqueous samples, and a purified solid matrix for nonaqueous samples, carried through the entire analytical scheme. The method blank volume must be approximately equal to the sample volumes or sample weights being processed.

For the analysis of pesticides/PCBs, a method blank analysis must be performed once each sample batch; with every 10 samples of similar concentration (i.e., low or medium soil analysis) and/or sample matrix; for each extraction technique used (e.g., separatory funnel or continuous extractor); or whenever samples are extracted, which ever is more frequent.

The method blank must contain less than the method detection limit (MDL) for all pesticide/PCB compounds.

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

3.6.3 Evaluation Procedure

Volatile Analysis

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

- Time(s), date(s) and instrument ID of method blank analyses are consistent on all forms and raw data sheets.
- Method blank analyses are associated with an acceptable instrument tune and within 12 hours of the tune.
- Method blank analyses are associated with an initial and, if applicable, continuing calibration.
- A given method blank analysis can be associated with a given group of samples.
- The proper number of method blanks were analyzed.

Verify that each volatile method blank contains less than five times the method detection limit of methylene chloride, acetone, toluene, and 2-butanone, and less than or equal to the method detection limit (MDL) for all other volatile compounds.

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

Trip and field blanks are evaluated as if they are "true" samples. If, however, trip and/or field blanks contain compounds that cannot be attributed to method blank contamination, the trip and/or field blank results must be evaluated against associated samples.

Semivolatile Analysis

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

- Time(s), date(s) and instrument ID of method blank analyses are consistent on all forms and raw data sheets.
- Method blank analyses are associated with an acceptable instrument tune and within 12 hours of the tune.
- Method blank analyses are associated with an initial and, if applicable, continuing calibration.
- A given method blank analysis can be associated with a given group of samples.
- The proper number of method blanks were analyzed.

Verify that each semivolatile method blank contains less than five times the method detection limit of di-n-butylphthalate, bis(2-ethylhexyl)phthalate, and di-n-octylphthalate, and less than or equal to the method detection limit (MDL) of all other semivolatile compounds.

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

Field blanks are evaluated as if they are "true" samples. If field blanks contain compounds that cannot be attributed to method blank contamination, the field blank results must be evaluated against associated samples.

Pesticide/PCB Analyses

Review the results tables, extraction log, method blank chromatogram and associated quantitation reports to verify the following:

- Time(s), date(s) and instrument ID of method blank analyses are consistent on all forms and raw data sheets.
- Method blank analyses are associated with an initial and continuing calibration.
- A given method blank analysis can be associated with a given group of samples.
- The proper number of method blanks were analyzed.

Verify that each method blank contains less than the method detection limit (MDL) for all pesticide/PCB compounds.

Verify that method blanks results were not subtracted from associated sample results.

3.6.4 Action

Volatile Analyses

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

If the method blank analyses are not associated with an acceptable instrument tune, all method blank data are considered unusable (R).

If the method blank analyses are associated with unusable (R) initial and/or continuing calibrations, all method blank data are considered unusable (R). If the method blank analyses are associated with qualified (J) initial and/or continuing calibrations, the proper qualifications must be applied to the method blank analyses.

If any samples are analyzed more than 12 hours after the last method blank analysis, all data for the affected samples are unusable (R). The only exception to this action would occur if any samples were analyzed for volatiles between 12 and 13 hours after the last method blank analysis. Under these circumstances, the volatile data for all affected samples analyzed between 12 and 13 hours after the last method blank are qualified (J).

If any samples are not associated with a volatile method blank, all associated positive volatile data from the affected samples are qualified (J).

If methylene chloride, acetone, toluene and 2-butanone are present in the method blank greater than five times the MDL, all positive data for that compound in all associated samples are considered unusable (R). If any other volatile compound is present in a method blank at greater than the MDL, all positive data in all associated samples are considered unusable (R).

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

If the concentration of a given analyte in a sample is less than five times the concentration of that analyte in the associated method blank, (10 times for common contaminants) the presence of that analyte in the sample is negated due to laboratory contamination, as indicated by the method blank. Positive hits are flagged nondetect (U).

Semivolatile Analysis

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

If the method blank analyses are not associated with an acceptable instrument tune, all method blank data are considered unusable (R).

If the method blank analyses are associated with unusable (R) initial and/or continuing calibrations, all method blank data are unusable (R). If the method blank analyses are associated with qualified (J) initial and/or continuing calibrations, the proper qualifications must be applied to the method blank analyses.

If any samples are not associated with a semivolatile method blank, all positive semivolatile data from the affected samples are qualified (J).

If di-n-butylphthalate, bis(2-ethylhexyl)phthalate and di-n-octylphthalate are present at greater than five times the method detection limit (MDL) or any other semivolatile compound is present in the method blank at greater than the method detection limit (MDL) all positive data for that compound in all associated samples are considered unusable (R).

If the method blank semivolatile results were subtracted from associated sample results, add the method blank results to the sample results. The laboratory must be notified of the data reporting error and a revised data report package must be submitted.

If the concentration of a given analyte in a sample is less than five times the concentration of that analyte in the associated method blank, (10 times for common contaminants) the

presence of that analyte in the sample is negated due to laboratory contamination, as indicated by the method blank. Associated positive hits are flagged non-detect (U).

Pesticide/PCB Analyses

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

If the method blank analyses are associated with qualified (J) initial and/or continuing calibrations, the proper qualifications must be applied to the method blank analyses.

If any samples are not associated with a pesticide/PCB method blank, all positive pesticide/PCB data from the affected samples are qualified (J).

If any pesticide/PCB compound is present in a method blank at a concentration greater than the method detection limit (MDL) for that compound, all positive data for that compound in all associated samples are qualified (J).

If method blank pesticide/PCB results were subtracted from associated sample results, add the method blank results to the sample results. The laboratory must be notified of the data reporting error and a revised data report package must be submitted.

If the chromatogram contains an unstable baseline, professional judgement may be utilized to determine the effect on the data.

Field Blanks

If the field blanks contain analytes not attributable to laboratory contamination, the field blanks must be compared against the associated samples.

If the concentration of a given analyte in a sample is less than five times the concentration of that analyte in the associated field blank, the presence of that analyte in the sample is negated due to introduced contamination as indicated by the field blank. Flag associated positive hits non-detect (U).

3.7 Surrogate Spike Analysis

3.7.1 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 demanding of analytical experience and professional judgement.

3.7.2 Requirements

Volatile Analyses

Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to purging or extraction. The surrogate spiking compounds shown below are used to fortify each sample, matrix spike, matrix spike duplicates, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Compounds	Amount in Sample/Extract		
	Fraction	Water	Soil
Toluene-d_8	VOA	50 µg/L	50 µg/L
4-Bromofluorobenzene	VOA	50 µg/L	50 µg/L
1,2-Dichloroethane-d_4	VOA	50 µg/L	50 µg/L

Upper and lower percent recovery limits have been established. These limits are listed below. Surrogate recoveries for volatile samples, blanks, and MS/MSD must all be within the control limits.

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

If sample surrogate recoveries do not meet criteria, the affected sample will be repurged, reinjected, or re-extracted to establish whether the nonconformance was due to the sample matrix or to a laboratory problem.

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

Semivolatile Analysis

Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown below are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Amount added to sample before extraction:

Fraction	Surrogate Compound	Water	Soil
Base-Neutral	Nitrobenzene-d_5	50 µg	50 µg
Base-Neutral	2-Fluorobiphenyl	50 µg	50 µg
Base-Neutral	Terphenyl-d_{14}	50 µg	50 µg
Acid	Phenol-d_5	100 µg	100 µg
Acid	2-Fluorophenol	100 µg	100 µg
Acid	2,4,6-Tribromophenol	100 µg	100 µg

Upper and lower percent recovery limits have been established. These limits are listed below.

Fraction	Surrogate Compound	Water	Low/ Medium Soil
Base-Neutral	Nitrobenzene-d_5	35-114	23-120
Base-Neutral	2-Fluorobiphenyl	43-116	30-115
Base-Neutral	Terphenyl-d_{14}	33-141	18-137
Acid	Phenol-d_5	10-110	24-113
Acid	2-Fluorophenol	21-110	25-121
Acid	2,4,6-Tribromophenol	10-123	19-122

If more than one semivolatile surrogate recovery of each fraction does not meet criteria and in the opinion of the GC/MS analyst, matrix interference is not present, the affected fraction should be reinjected or re-extracted to establish whether the nonconformance was due to the sample matrix or to a laboratory problem.

If more than one surrogate in each fraction does not meet criteria, reinjection or re-extraction of all affected samples is required to establish the existence of matrix effects.

Pesticide/PCB Analyses

Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown below are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Amount added to sample before extraction:

Fraction	Surrogate Compound	Water	Soil
Pest	Decachlorobiphenyl (DCBP)	1 µg	1 µg
Pest	Tetrachloro-m-xylene (TCMX)	1 µg	1 µg

Upper and lower percent recovery limits have been established.

Fraction	Surrogate Compound	Water
Pest	Decachlorobiphenyl	60-150
Pest	Tetrachloro-m-xylene	60-150

The limits for the surrogates are for advisory purposes only. They are not used to determine if a sample should be reanalyzed.

3.7.3 Evaluation Procedure

Volatile Analyses

Verify that all samples, blanks, matrix spikes and matrix spike duplicates have been spiked with the appropriate surrogate compounds.

Review surrogate Summary Form (EPA CLP SOW, 3/90 Edition, Form II or equivalent) and verify that outliers are marked correctly with an asterisk.

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

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

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

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

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

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

- Verify that no blanks have surrogates outside the criteria.

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:

- Surrogate recovery (marginal versus gross deviation).

- Technical holding times.

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

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

Semivolatile Analysis

Verify that all samples, blanks, matrix spikes and matrix spike duplicates have been spiked

with the appropriate surrogate compounds.

Review surrogate Summary Form (EPA CLP SOW, 3/90 Edition, Form II or equivalent) and verify that outliers are marked correctly with an asterisk.

Check raw data (e.g., chromatograms and quantitation reports) to verify the surrogate spike recoveries on the Surrogate Recovery Form (EPA CLP SOW, 3/90 Edition, Form II or equivalent). Check for any transcription or calculation errors.

Check that the surrogate spike recoveries were calculated correctly by the equation listed above.

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

- 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 samples matrix effects rather than laboratory deficiencies.

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

- 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).

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

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:

- Surrogate recovery (marginal versus gross deviation).

- Technical holding times.

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

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

Pesticide/PCB Analyses

Verify that all samples, blanks, matrix spikes, and matrix spike duplicates have been spiked with DCBP and TCMX.

Review surrogate Summary Form (EPA CLP SOW, 3/90 Edition, Form II or equivalent) and verify that all outliers are marked correctly with an asterisk.

Check raw data (i.e., chromatograms, quantitation reports, etc.) to verify the recoveries were calculated correctly.

3.7.4 Action

Volatile Analyses

If any samples, blanks, matrix spikes or matrix spike duplicates were not spiked with surrogate compounds or were spiked with incorrect surrogate compounds, all data are unusable (R). In addition, all data for samples, matrix spikes and matrix spike duplicates associated with a method blank that does not contain any surrogates are unusable (R).

If Surrogate Spike Recoveries are out of specification and the laboratory failed to repurge, reinject, or re-extract and reanalyze as required, the laboratory failed to perform satisfactorily and the following actions are taken:

- Samples, matrix spikes, matrix spike duplicates - If one surrogate compound is out of specification, all affected data are qualified (J). If two or more surrogate compounds are out of specification, all affected positive hits are qualified (J) and all non-detects are unusable (R).

- Method blanks - If one or more surrogate compounds are out of specification, all method blank data and associated sample data are qualified unusable (R).

If surrogate spike recoveries are out of specification on the initial analysis, but meet criteria on reanalysis, the laboratory must report results based on results of the reanalysis. A full data validation review must be conducted on the reanalysis data.

If surrogate spike recoveries are out of specification of initial analysis and are also out of specification on reanalysis, the sample is most likely exhibiting a matrix effect. The laboratory does not have to perform any additional analyses on the particular sample. The data from either analyses may be submitted by the laboratory.

If one or more surrogates in a fraction are out of specification, but have recoveries greater than 10%:

- Positive results for that fraction are flagged as estimated (J).
- Negative results for that fraction are flagged as estimated (UJ).

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

- Positive results for that fraction are flagged as estimated (J).
- Negative results for that fraction are flagged as unusable (R).

Semivolatiles Analysis

If any samples, blanks, matrix spikes or matrix spike duplicates were not spiked with surrogate compounds or were spiked with incorrect surrogate compounds, all data are considered unusable (R). In addition, all data for samples, matrix spikes and matrix spike duplicates associated with a rejected method blank are considered unusable (R).

If Surrogate Spike Recoveries are out of specification and the laboratory failed to reinject, or re-extract and reanalyze as required, the laboratory failed to perform satisfactorily and the following actions are taken:

- Samples, matrix spikes, matrix spike duplicates, method blanks - If one surrogate compound for a given analytical fraction (i.e., acid extractable and/or base neutral) is out of specification, all affected analytical fraction data are qualified (J). If two or more surrogate compounds for a given analytical fraction are out of specification, all affected analytical fraction data are considered unusable (R).

If surrogate spike recoveries are out of specification on initial analysis and are also out of specification on reanalysis, the sample is most likely exhibiting a matrix effect. The laboratory does not have to perform any additional analyses on the particular sample. The data from either analyses maybe submitted by the laboratory.

If two or more surrogates in a fraction are out of specification, but have recoveries greater than 10%:

- Positive results for that fraction are flagged as estimated (J).
- Negative results for that fraction are flagged as estimated (UJ).

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

- Positive results for that fraction are flagged as estimated (J).
- Negative results for that fraction are flagged as unusable (R).

The only exception to these qualities is for diluted samples or for those samples which exhibit obvious matrix interference. Samples which are diluted prior to injection must have the surrogate recoveries flagged as (D) diluted out. Samples which exhibit obvious matrix interference as shown by the presence of large target and/or non-target compounds are noted as such in the case narrative and do not require re-injection or re-extraction. Verify the dilution on the injection log and/or extraction log.

Pesticide/PCB Analysis

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

- If low recoveries are obtained, flag associated positive results and quantitation limits as estimated (J).
- If high recoveries are obtained, professional judgement should be used to determine appropriate action. A high bias may be due to co-eluting interferences.
- 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) and all positive results (J).

3.8 Matrix Spike/Matrix Spike Duplicate Analysis

3.8.1 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.

3.8.2 Requirements

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

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

Advisory limits for spike recoveries are listed below:

Volatiles

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

Semivolatiles

Matrix Spike Compound	Percent Recovery Limits Water	Soil/ Sediment
1,2,4-Trichlorobenzene	39-98	38-107
Acenapthene	46-118	31-137
2,4-Dinitrotoluene	24-96	28-89
Pyrene	26-127	35-142
N-Nitroso-Di-n-Propylamine	41-116	41-126
1,4-dichlorobenzene	36-97	28-104
Pentachlorophenol	9-103	17-109
Phenol	12-110	26-90
2-Chlorophenol	27-123	25-102

4-Chloro-3-Methylphenol	23-97	26-103
4-Nitrophenol	10-80	11-114

Pesticide/PCB Analyses

Matrix Spike Compound	Percent Recovery Limits Water	Soil/ Sediment
Heptachlor	40-131	35-130
Dieldrin	52-126	31-134
Endrin	56-121	42-139
DDT	38-127	23-134

Advisory limits for relative percent difference (RPD) between matrix spike and matrix spike duplicate recoveries are listed below:

Volatiles

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

Semivolatiles

Matrix Spike Compound	Maximum Acceptable RPD Water	Soil/ Sediment
1,2,4-Trichlorobenzene	28	23
Acenaphthene	31	19
2,4-Dinitrotoluene	38	47
Pyrene	31	36
N-Nitroso-di-n-propylamine	38	38
1,4-Dichlorobenzene	28	27
Pentachlorophenol	50	47
Phenol	42	35
2-Chlorophenol	40	50
4-Chloro-3-methylphenol	42	33

4-Nitrophenol	50	50

Pesticide/PCBs

Matrix Spike Compound	Maximum Acceptable RPD Water	Soil/ Sediment
Heptachlor	20	31
Dieldrin	18	38
Endrin	21	45
DDT	27	50

3.8.3 Evaluation Procedure

Determine if the proper number of matrix spike and matrix spike duplicate samples were analyzed.

Review the matrix spike/matrix spike duplicate recovery forms (EPA CLP SOW, 3/90 Edition, Form II or equivalent), MS/MSD chromatograms and MS/MSD quantitation reports to verify reported matrix spike recoveries and the relative percent difference between the matrix spike and matrix spike duplicate.

Individual compound recoveries of the matrix spike are calculated as follows:

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

where:

SSR = Spike sample results

SR = Sample result
SA = Spike added from spiking mix

Relative percent differences for each compound are calculated as follows:

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

where:

RPD = Relative percent difference
D_1 = First sample value
D_2 = Second sample value (duplicate)

3.8.4 Action

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

The results of the matrix spike and matrix spike duplicate can be used in conjunction with other QC criteria to aid the reviewer in applying more informed professional judgement when necessary.

If both matrix spike and matrix spike duplicate have 0% Recovery, then flag the compound in the associated sample (J) for positive results and (R) for non-detects.

3.9 Field Duplicates

3.9.1 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.

3.9.2 Requirements

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

3.9.3 Evaluation Procedures

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

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

where:

RPD	=	Relative percent difference
D_1	=	First sample value
D_2	=	Second sample value (duplicate)

3.9.4 Action

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

3.10 Internal Standard Area Evaluation

3.10.1 Objective

The assessment of changes in the absolute area of internal standards is for the purpose of determining the existence of inferior GC performance and/or loss of instrument sensitivity resulting in an adverse effect on compound quantitation. The criteria for evaluating internal standards areas applies to all samples, blanks and matrix spike/matrix duplicates.

3.10.2 Requirements

Volatile and Semivolatile Analysis

The internal standards shall be the ones specified in the EPA CLP SOW, 3/90 Edition.

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

If samples, blanks or matrix spike/spike duplicates are analyzed immediately following an initial calibration but before another GC/MS tune and a continuing calibration, evaluation will be conducted on the basis of the internal standard areas of the 50 µg/L initial calibration standard for volatiles, and the 50-ng initial calibration standard for semivolatiles.

If samples, blanks, or matrix spike/spike duplicates are analyzed immediately following a GC/MS tune and a continuing calibration, evaluation will be conducted on the basis of the internal standard areas in the volatile and semivolatile continuing calibration standards.

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

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

3.10.3 Evaluation Procedure

Review Internal Standard Area Summary Form (EPA CLP SOW, 3/90 Edition, Forms III-VOA and VIII-SV or equivalent) and verify that outliers are noted by the laboratory.

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

3.10.4 Action

If internal standard EICP areas are out of specification and the laboratory failed to reanalyze the affected sample(s), the laboratory failed to perform satisfactorily. The following action must be taken:

- For each internal standard that does not meet criteria, all positive results for those compounds associated with the particular internal standard (i.e., those compounds that are quantified using the particular internal standard) are quantitatively qualified (J). Nondetects for those compounds associated with the particular internal standard (i.e., those compounds that are quantified using the particular internal standard) are qualified (UJ) or (R) if there is a severe loss of sensitivity.

If internal standard EICP areas are out of specification on initial analysis, but meet criteria on reanalysis, the laboratory must report results based on the results of the reanalysis. A full data validation review must be conducted on the reanalysis data.

If internal standard EICP areas are out of specification on initial analysis and also out of specification on reanalysis, the sample may be exhibiting a matrix effect.

The laboratory does not have to perform any additional analyses of the particular sample. The data for either analysis may be submitted by the laboratory. A full data validation review

may be conducted on either set of data. For each internal standard that does not meet criteria, all positive results for those compound associated with the particular internal standard (i.e., those compounds that are quantified using the particular internal standard) are quantitatively qualified (J).

If an internal standard retention time varies by more than 0.5 minutes:
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.

3.11 Compound Identification and Sample Evaluation

3.11.1 Objective

The objective of the criteria for qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (finding a compound present when in actuality it is not) or a false negative (not finding a compound that is actually present). The objective of the criteria for sample evaluation is to assess the impact of sample dependent (i.e., surrogate compound analysis, internal standard area evaluation) and independent (i.e., system tuning, calibration, blanks) variables on the individual sample according to the required standards.

3.11.2 Requirements

Volatiles and Semivolatiles (GC/MS Analysis)

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

Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds at 200 µg/L for VOA compounds nor at 160 ng for semivolatile compounds.

If any compound in any sample exceeds the initial calibration range, that sample must be

diluted, the internal standard concentration readjusted, and the sample reinjected, as described in the specific methodologies. Secondary ion quantitation is only allowed when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, the laboratory must document the reasons in the case narrative.

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

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

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

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

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

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

- The relative intensities of ions specified in the above paragraph must agree within ±20% between the standard and sample spectra.

- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated.

If a compound cannot be verified by all of the criteria above, but in the technical judgement of the mass spectral interpretation specialist the identification is correct, the laboratory shall report the identification and proceed with the quantitation.

The comparison of sample and standard mass spectra must be made for all compounds tentatively identified in a sample at a concentration of 10% of the closest internal standard or greater based on the GC analysis. Sample and standard mass spectra must be provided for both positive identifications as well as negated identifications.

A library search shall be executed for nonsurrogate and sample components for the purpose of tentative identification.

Guidelines for making tentative identification:

Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

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

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

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

Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

If in the technical judgement of the analyst, no valid tentative identification can be made, the compound should be reported as unknown. The analyst should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

Components identified shall be quantitated by the associated internal standard method. The internal standards used shall be the ones used in the U.S. EPA CLP methodology. The EICP area of characteristic ions of analytes are used. Compounds are calculated as follows:

Volatiles:

Water

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

where:

A_X	=	Area of the characteristic ion for the compound to be measured
I_S	=	Amount of internal standard added in nanograms (ng)
DF	=	Dilution factor
A_{IS}	=	Area of the characteristic ion for the specific internal standard associated with the compound to be measured
RRF	=	Relative response factor for the compound being measured
V_O	=	Volume of water purged in milliliters (mL)

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

where:

A_X	=	Area of the characteristic ion for the compound to be measured
C_{IS}	=	Concentration of the internal standard
A_{IS}	=	Area of the characteristic ion for the specific internal standard associated with the compound to be measured
C_X	=	Concentration of the compound to be measured

Sediment/Soil (low level)

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

where:

A_X	=	Area of the characteristic ion for the compound to be measured
I_S	=	Amount of internal standard injected in nanograms (ng)
V_T	=	Volume of total extract (µL)
DF	=	Dilution factor
A_{IS}	=	Area of the characteristic ion for the internal standard associated with the compound to be measured
RRF	=	Relative response factor
V_I	=	Volume of extract added (µL) for purging
W_S	=	Weight of sample extracted (g) or purged
D	=	(100-% moisture)/100

Sediment/Soil (medium level)

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

Semivolatiles

where:

A_X	=	Area of the characteristic ion for the compound to be measured
I_S	=	Amount of internal standard injected in nanograms (ng)
V_T	=	Volume of total extract (µL)
DF	=	Dilution factor
A_{IS}	=	Area of the characteristic ion for the internal standard associated with the compound to be measured
RRF	=	Relative response factor
V_I	=	Volume of extract added (µL) for purging
W_S	=	Weight of sample extracted (g) or purged
D	=	(100-% moisture)/100

Water

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

where:

A_X	=	Area of the characteristic ion for the compound to be measured

I_S	=	Amount of internal standard injected in nanograms (ng)
V_T	=	Volume of total extract
DF	=	Dilution factor
A_{IS}	=	Area of the characteristic ion for the internal standard associated with the compound to be measured
RRF	=	Relative response factor
V_O	=	Volume of water extracted in milliliters (mL)
V_I	=	Volume of extract injected (µL)
RRF	=	Relative response factor for the compound being measured

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

where:

A_X	=	Area of the characteristic ion for the compound to be measured
C_{IS}	=	Concentration of this internal standard
A_{IS}	=	Area of the characteristic ion for the internal standard associated with the compound to be measured
C_X	=	Concentration of the compound to be measured

Soil/Sediment

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

where:

A_X	=	Area of the characteristic ion for the compound to be measured
I_S	=	Amount of internal standard injected in nanograms (ng)
V_T	=	Volume of low level total extract or volume of medium level extract
DF	=	Dilution factor
A_{IS}	=	Area of the characteristic ion for the internal standard associated with the compound to be measured
RRF	=	Relative response factor
V_I	=	Volume of extract injected (µL)

W_S = Weight of sample extracted (grams)
D = (100 - % moisture)/100

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

The formula for calculating non-target concentrations are the same as those above. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

The method detection limit (MDL) must be corrected for dilution and for percent moisture. For example, 10 for phenol in water if the sample final volume is the protocol-specified final volume. If a 1 to 10 dilution of extract is necessary, the reported limit is 100. For a soil sample, the value must also be adjusted for percent moisture. For example, if the sample had 24% moisture and a 1 of 10 dilution factor, the sample method detection limit for phenol (330) would be corrected to:

$$\frac{(330)}{D} \times DF \quad where\ D = (100 - \%\ moisture)/100$$

$$DF = dilution\ factor$$

$$at\ 24\%\ moisture,\ D = (100 - 24)/100$$

$$\frac{(330)}{(.76)} \times 10 = 4300$$ rounded to the appropriate number of significant figures

Specific qualifiers are to be used when reporting results. The qualifier symbols are J, B, and E and are defined as below.

J Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed, or when the mass spectral data indicate the presence of a compound that meets the identification criteria but the result is less than the sample quantitation limit but greater than zero. For example, if the sample quantitation limit is 10 µg/L, but a concentration of 3 µg/L is calculated, report it as 3J.

B This flag is used when the analyte is found in the associated blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action. This flag must be used for a non-target as well as for a positively identified target compound.

E This flag identifies compounds whose concentrations exceed the calibration range of the instrument for that specific analysis. If one or more compounds have a response greater than the linear range, the sample or extract must be diluted and reanalyzed according to the specifications of the method. All such compounds with a response factor greater than the linear range should have the concentration flagged with an "E".

Pesticide/PCBs (GC/ECD Analysis)

Primary Column Analysis

Determine if any target pesticides/PCBs are present. Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 24-hour period.

Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds and toxaphene compounds.

If the response for any of these compounds is within the calibration range, the extract is ready for confirmation and quantitation.

If the response for any compound is greater than the calibration range, the extract is diluted so that the peak will be between 50 and 100% the calibration and reanalyzed range on the both columns. This dilution is also used for confirmation and quantitation.

If a sample extract is diluted 10 fold or more prior to analysis, a more concentrated extract (at least 10 fold more concentrated than the diluted extract analyzed) must also be analyzed to determine if other compounds of interest are present at lower concentrations.

Consider the sample negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the detection limit. The sample quantitation is complete at this point. Confirmation is not required.

If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident, Sulfur Cleanup must be conducted. If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup be applied.

Confirmation Column Analysis

Separation should be greater than 25% resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

A compound tentatively identified in the primary analysis is confirmed if the retention time from the confirmation analysis falls within the retention time window of corresponding standards that were chromatographed on the confirmation column within a 24-hour period.

Computer reproductions of chromatograms that are attenuated to ensure all peaks are on scale over a 100 fold range are acceptable. However, this can be no greater than a 100 fold range. This is to prevent retention time shifts by column or detector overload. Also, peak response must be greater than 25% of full scale deflection to allow visual pattern recognition of multicomponent compounds, and individual compounds must be visible.

If identification of compounds of interest is prevented by the presence of interferences, further cleanup is required. If sulfur is evident, Sulfur Cleanup should be conducted. If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup be applied.

Calculate the concentration of target compounds in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

Water

$$Concentration\ (\mu g/L) = \frac{(A_X)(I_S)(V_T)(DF)}{(A_S)(V_I)(V_S)}$$

where:

A_X	=	Response for the parameter to be measured
I_S	=	Amount of standard injected in nanograms (ng)
V_T	=	Volume of total extract (μL) (take into account any dilutions)
DF	=	Dilution factor

A_S = Response for the external standard
V_I = Volume of extract injected (µL)
V_S = Volume of water extracted (mL)

Sediment/Soil

$$Concentration\ (\mu g/kg) = \frac{(A_X)(I_S)(V_T)(DF)}{(A_S)(V_I)(W_S)(D)}$$

where:

A_X = Response for the parameter to be measured
I_S = Amount of standard injected in nanograms (ng)
V_T = Volume of low level total extract or volume of medium level extract
DF = Dilution factor
A_S = Response for the external standard
V_I = Volume of extract injected (µL)
W_S = Weight of sample extracted
D = (100 - % moisture)/100

For multicomponent mixtures (toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate the pattern using a minimum of three dominant peaks (greater than 50% of the total area must be used) unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

Specific qualifiers are to be used by the laboratory when reporting results. These qualifiers have been defined in the volatiles and semivolatiles (GC/MS Analyses) above.

3.11.3 Evaluation Procedure

Volatiles and Semivolatiles (GC/MS Analysis)

Verify that all required deliverables for each sample have been delivered (i.e., EPA CLP SOW, 3/90 Edition, Form I (or equivalent) for both target and nontarget compounds, sample chromatograms, quantitation reports and mass spectra, and standard reference mass spectra).

Check each sample chromatogram for system saturation. Verify that for any analysis that

resulted in system saturation, a diluted sample analysis was also conducted and both sets of data were presented.

Verify that the RRT of reported compounds is within ±0.06 RRT units of the reference standard.

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

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

Verify that all nontarget peaks on the sample chromatogram (up to a maximum of 20 peaks each for volatiles, base neutrals, acid extractables) that have peak heights/area that are greater than 10% of the nearest internal standard have undergone a nontarget library search.

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

Verify target and nontarget compound quantitations by recalculating the quantitation of a percentage (up to 5%) of compounds.

Check all QA/QC parameters (i.e., sample holding time, GC/MS tuning, calibration, blanks, surrogate compound analysis, matrix spike/spike duplicate analysis, internal standard area, etc.) to determine if any or all of the sample data are qualified and/or rejected.

Verify that the laboratory has properly used the data qualifier symbols on EPA CLP SOW, 3/90 Edition, Form I (or equivalent).

Verify that the laboratory reported the proper method detection limits including any adjustments for sample dilution, change in sample size and/or percent moisture content.

Pesticides/PCBs (GC/ECD Analysis)

Verify that all required deliverables for each sample have been included (i.e., EPA CLP SOW, 3/90 Edition, Forms I and X (or equivalent), sample chromatograms and sample quantitation reports for all GC columns used.

Check each sample chromatogram (including primary and confirmation columns) for system

saturation. Verify that for any analysis that resulted in system saturation, a diluted sample analysis was also conducted and both sets of data were presented.

Verify all target compound qualitative identifications by comparing sample retention times with target compound retention times windows for both the primary and confirmation columns.

Verify target compound quantitation by recalculating the quantitation of a percentage (up to 5%) of compounds.

Check all QA/QC parameters (i.e., sample holding time, calibration, DDT/Endrin breakdown, surrogate retention time shift, blanks, surrogate compound analysis, matrix spike/spike duplicate analysis and any QA/QC parameters associated with GC/MS pesticide/PCB confirmation) to determine if any or all of the sample data are qualified and/or rejected.

Verify that the laboratory has properly used the data qualifier symbols on EPA CLP SOW, 3/90 Edition, Form I (or equivalent).

Verify that the laboratory reported the proper method detection limits including any adjustments for sample dilution, change in sample size and/or percent moisture content.

3.11.4 Action

Volatiles and Semivolatiles (GC/MS Analysis)

If any required deliverables are missing (i.e., sample chromatograms, sample mass spectra, etc.), the laboratory must be contacted for delivery of the missing information.

If a sample chromatogram reveals system saturation and a dilution analyses was not conducted, the chromatogram and associated quantitation report must be closely examined. All target compounds whose quantitation value exceeds the upper concentration of the calibration curve must be quantitatively qualified (J).

If the relative retention time (RRT) of a reported target compound is not within ±0.06 RRT units of the reference standard, the mass spectrum of the affected sample must be closely examined. If the sample mass spectrum matches the reference standard mass spectrum, the qualitative identification is confirmed. The excessive RRT shift, however, must be noted in the data validation report.

If it is determined that incorrect identifications of target compounds were made all such data

is to be corrected by the data validator and noted in the data validation report. This must also include the reasons for making a change in the qualitative identification.

If a nontarget compound is identified as a compound which is a target compound in another analytical fraction (i.e., a volatiles target compound which is identified as such but as a nontarget compound in the semivolatile fraction), the following actions are taken:

- If the identified nontarget compound is present as the target compound in the sample, its presence in the "inappropriate" fraction is ignored.

- If the identified nontarget compound is not present as a target compound in the appropriate fraction of the sample, its presence in the sample is probably due to laboratory contamination. This must be noted in the data validation report.

If the laboratory failed to conduct a nontarget library search for all applicable nontarget peaks on a chromatogram, no action is taken except that said deficiency must be noted in the data validation report.

If it is determined that incorrect identifications of nontarget compounds were made all such data are to be corrected by the data validator and noted in the data validation report. This must include the reasons for making a change in the qualitative identification.

If spot check calculations of compound quantitation do not match the concentrations reported by the laboratory, the laboratory must be contacted in order to resolve the quantitation problem.

Based on the review of all QA/QC parameters (i.e., sample holding time, GC/MS tuning, calibration, blanks, surrogate compound analysis, internal standard areas, etc.), any or all affected sample data must be qualified and/or rejected.

Any improperly used or missing data qualifier symbols should be noted in the data validation report along with the corrected/added qualifiers.

If the laboratory reported the incorrect method detection limits (MDLs) or reported MDLs that cannot be verified, the laboratory must be contacted in order to resolve the discrepancies in the MDLs.

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).

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

All TIC results should be qualified as tentatively identified (NJ) with approximated concentrations.

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).

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).

Pesticide/PCB Analysis

If any required deliverables are missing (i.e., sample chromatogram, sample quantitation report, etc.), the laboratory must be contacted for delivery of the missing information.

If a sample chromatogram reveals system saturation and a dilution analysis was not conducted, the chromatogram and associated quantitation report must be closely examined. Professional judgement must be used to determine the severity of the system saturation and any resultant qualification or rejection of the data.

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

If spot check calculations of compound quantitation do not match the concentrations reported by the laboratory, the laboratory must be contacted in order to resolve the quantitation problem.

Based on the review of all QA/QC parameters (i.e., sample holding time, DDT/Endrin breakdown, blanks, surrogate compound analyses, etc.) any or all affected sample data must be qualified and/or considered unusable (R).

If the laboratory reported the incorrect method detection limits or reported method detection limits that cannot be verified, the laboratory must be contacted in order to resolve the discrepancies in the method detection limits.

4.0 RESPONSIBILITIES

4.1 QA/QC Data Reviewer

The Data Reviewer is responsible for a working knowledge of the method used to obtain the data and to insure that all documents are included and complete (see Appendices D, E and F), that the lab is in compliance with the method and that all requested analysis were performed.

The Data Reviewer is responsible for checklists, data assessment forms and a written report of anomalies.

The Data Reviewer is responsible for informing the Data Validation and Report Writing Group Leader of any major non-compliance of the method that may affect the usability of the data.

The Data Reviewer will prepare any written communication to the laboratories detailing anomalies of the method.

4.2 Data Validation and Report Writing Group Leader

The Data Validation and Report Writing Group Leader is responsible for the accurate updating of data validation SOP as requirements change.

The Data Validation and Report Writing Group Leader audits the review process to ensure compliance with review requirements.

The Data Validation and Report Writing Group Leader is responsible for communication of any major non-compliance of the method that may affect the usability of the data to the Task Leader of the project and to the Analytical Section Leader.

The Data Validation and Report Writing Group Leader initial the checklists, data assessment forms and anomaly reports.

4.3 Analytical Section Leader

The Analytical Section Leader ensures adherence to the guidelines prior to authorizing the release on analytical deliverables.

The Analytical Section Leader initiates updating of this SOP on a timely basis.

APPENDIX A
SERAS VOA Compound List with Detection Limits
SOP #1016
October 1994

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

ANALYSIS:	SERAS VOA
Method Reference:	Modified 524.2
Extraction Procedure:	N/A
Sample Amount:	5 mL/5g

COMPOUND LIST	DL (Water) µg/L	DL (Soil) µg/K
Dichlorodifluoromethane	10	10
Chloromethane	10	10
Vinyl Chloride	10	10
Bromomethane	10	10
Chloroethane	10	10
Trichlorofluoromethane	5	5
1,1-Dichloroethene	5	5
Methylene Chloride	5	5
trans-1,2-Dichloroethene	5	5
1,1-Dichloroethane	5	5
2,2-Dichloropropane	5	5
cis-1,2-Dichloroethene	5	5
Chloroform	5	5
1,1,1-Trichloroethane	5	5
Carbon Tetrachloride	5	5
1,1-Dichloropropene	5	5
Benzene	5	5
1,2-Dichloroethane	5	5
Trichloroethene	5	5
1,2-Dichloropropane	5	5
Dibromomethane	10	10
Bromodichloromethane	5	5
trans-1,3-Dichloropropene	5	5
cis-1,3-Dichloropropene	5	5
Toluene	5	5
1,1,2-Trichloroethane	5	5
Tetrachloroethene	5	5
1,3-Dichloropropane	5	5
Dibromochloromethane	5	5
1,2-Dibromoethane	5	5
Chlorobenzene	5	5
1,1,1,2-Tetrachloroethane	5	5
Ethylbenzene	5	5
p & m Xylene	5	5

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

ANALYSES: SERAS VOA

COMPOUND LIST	DL (Water) µg/L	DL (Soil) µg/Kg
o-Xylene	5	5
Styrene	5	5
Bromoform	5	5
Isopropylbenzene	5	5
Bromobenzene	5	5
1,1,2,2-Tetrachloroethane	5	5
1,2,3-Trichloropropane	5	5
n-Propylbenzene	5	5
2-Chlorotoluene	5	5
1,3,5-Trimethylbenzene	5	5
4-Chlorotoluene	5	5
tert-Butylbenzene	5	5
1,2,4-Trimethylbenzene	5	5
sec-Butylbenzene	5	5
p-Isopropyltoluene	5	5
1,3-Dichlorobenzene	5	5
1,4-Dichlorobenzene	5	5
1,2-Dichlorobenzene	5	5
n-Butylbenzene	5	5
1,2-Dibromo-3-Chloropropane	5	5
1,2,4-Trichlorobenzene	5	5
Hexachlorobutadiene	10	10
Naphthalene	5	5
1,2,3-Trichlorobenzene	10	10
Acetone	10	10
Carbon Disulfide	5	5
2-Butanone	10	10
4-Methyl-2-Pentanone	10	10
2-Hexanone	10	10

APPENDIX B
SERAS BNA Compound List with Detection Limits
SOP #1016
October 1994

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

ANALYSIS:	SERAS/BNA
Method Reference:	EPA Method 625
Extraction Procedure:	Separatory Funnel/Sonication
Sample Amount:	1L/30g

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

COMPOUND LIST	DL (Water) µg/L	DL (Soil) µg/Kg
Phenol	10	330
bis(-2-Chloroethyl)Ether	10	330
2-Chlorophenol	10	330
1,3-Dichlorobenzene	10	330
1,4-Dichlorobenzene	10	330
Benzyl alcohol	10	330
1,2-Dichlorobenzene	10	330
2-Methylphenol	10	330
N-Nitroso-Di-n-propylamine	10	330
Hexachloroethane	10	330
Nitrobenzene	10	330
Isophorone	10	330
2-nitrophenol	10	330
2,4-Dimethylphenol	10	330
bis(2-Chloroethoxy)methane	10	330
2,4-Dichlorophenol	10	330
1,2,4-Trichlorobenzene	10	330
Naphthalene	10	330
4-Chloroaniline	10	330
Hexachlorobutadiene	10	330
2,4,6-Trichlorophenol	10	330
2,4,5-Trichlorophenol	50	1650
2-Chloronaphthalene	10	330
2-Nitoraniline	50	1650
Dimethylphthalate	10	330
Acenaphthylene	10	330
3-Nitroaniline	50	1650
Acenaphthene	10	330
2,4-Dinitrophenol	50	1650
4-Nitrophenol	50	1650
Dibenzofuran	10	330
2,6-Dinitrotoluene	10	330
2,4-Dinitrotoluene	10	330
Diethylphthalate	10	330
4-Chlorophenyl-phenylether	10	330
Fluorene	10	330
4-Nitroaniline	50	1650

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

ANALYSIS: SERAS/BNA

COMPOUND LIST	DL (Water) µg/L	DL (Soil) µg/Kg
4,6-Dinitro-2-methylphenol	50	1650
N-Nitrosodiphenylamine	10	330
4-Bromophenyl-phenylether	10	330
Hexachlorobenzene	10	330
Pentachlorophenol	50	1650
Phenanthrene	10	330
Anthracene	10	330
Carbazole	10	330
Di-n-butylphthalate	10	330
Fluoranthene	10	330
Pyrene	10	330
Butylbenzylphthalate	10	330
3,3'-Dichlorobenzidine	20	330
Benzo(a)anthracene	10	330
Bix(2-Ethylhexyl)phthalate	10	330
Chrysene	10	330
Di-n-octylphthalate	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzo(a)pyrene	10	330
Indeno(1,2,3-cd)pyrene	10	330
Dibenzo(a,h)anthracene	10	330
Benzo(g,h,i)perylene	10	330

APPENDIX C
SERAS Pesticide/PCB with Detection Limits
SOP #1016
October 1994

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

ANALYSIS: SERAS PESTICIDE/PCB

Method Reference: EPA Method 608
Extraction Procedure: Separatory Funnel/Sonication
Sample Amount: 1L/30g

COMPOUND LIST	DL (Water) µg/L	DL (Soil) µg/Kg
alpha-BHC	.05	1.7
beta-BHC	.05	1.7
delta-BHC	.05	1.7
gamma-BHC (Lindane)	.05	1.7
Heptachlor	.05	1.7
Aldrin	.05	1.7
Heptachlor epoxide	.05	1.7
Endosulfan I	.05	1.7
Dieldrin	.10	3.3
p,p'-DDE	.10	3.3
Endrin	.10	3.3
Endosulfan II	.10	3.3
p,p'-DDD	.10	3.3
Endosulfan sulfate	.10	3.3
p,p'-DDT	.10	3.3
Methoxychlor	.50	17.0
Endrin ketone	.10	3.3
Endrin aldehyde	.10	3.3
alpha-Chlordane	.05	1.7
gamma-Chlordane	.05	1.7
Toxaphene	5.0	170.0
Aroclor-1016	1.0	33.0
Aroclor-1221	2.0	67.0
Aroclor-1232	1.0	33.0
Aroclor-1242	1.0	33.0
Aroclor-1248	1.0	33.0
Aroclor-1254	1.0	33.0
Aroclor-1260	1.0	33.0

APPENDIX D
Deliverable Checklist for GC/Analyses
SOP #1016
October 1994

Rev. 2/3/92

FOR WESTON/SERAS USE ONLY			
Project Name:	WA#:	Data Pkg #	Date:

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

_____ Case narrative (indicating columns used for analyses and quantification)

_____ Chain of custody (signed with date of receipt)

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

_____ Compositions of surrogate and matrix spike solutions and the volumes used

_____ Worksheet of % solid or % moisture

_____ Analysis logs for all columns used for analyses

_____ Method numbers and any modifications

Initial Calibration Data (for all columns)

_____ Analysis logs

_____ Degradation check summary table, if applicable

_____ Summary of the calibration results

_____ Chromatograms for all calibration standards (At least one representative chromatogram should be labeled with elution order)

_____ Quantitation reports for all calibration standards (For toxaphene, chlordane,PCBs, peaks chosen for identification/quantitation must be clearly labeled)

Continuing Calibration Data (for all columns)

_____ Degradation check summary table, if applicable

_____ Summary of % difference of response (or calibration) factors

_____ Chromatograms labeled with elution order

_____ Quantitation reports (For toxaphene, chlordane, PCBs, peaks chosen for identification/quantitation must be clearly labeled)

Rev. 2/3/92

GC deliverable check list (cont'd)

Sample Data (including Method Blank)

_____ Result summary table (including detection limits)

_____ Surrogate recovery table

_____ Chromatograms (for all columns, all dilutions)

_____ Labelled with retention time and identified compound(s)

_____ Quantitation reports (for all columns, all dilutions)

_____ Positive identification must be clearly labeled right next to the retention time

_____ Peaks chosen for toxaphene, chlordane, PCBs identification/quantitation must be clearly labeled

Matrix Spike/Matrix Spike Duplicate Data

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

_____ Chromatograms (see requirements under sample data section)

_____ Quantitation reports (see requirements under sample data section)

_____ _____
Signature Date

APPENDIX E
Deliverable Checklist for GC/MS Analyses
SOP #1016
October 1994

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

Rev.: 2/3/92

FOR WESTON/SERAS USE ONLY			
Project Name:	WA#:	Data Pkg#	Date:

Deliverable Checklist for GC/MS Analyses

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

_____ Case narrative
_____ Chain of custody (signed with date of receipt)
____ All sample preparation logs (initial and re-extractions), if applicable
_____ Compositions of the spike solutions (surrogate,calibration standards, matrix spike and internal standard) and the volumes used on the extraction log and injection log
_____ Worksheet of % solid or % moisture
_____ Analysis logs for all instruments used for analyses
(For VOA analysis, the sample size used for analysis must be clearly documented)
_____ Method numbers and any modifications

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

_____ Summary table
_____ Spectrum
_____ Ion chromatogram
_____ Mass listing

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

_____ Analysis logs
_____ Summary table of calibration results

_____ Chromatograms for all calibration standards
_____ Quantitation reports for all calibration standards

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

_____ Summary table of % difference of relative response factors

_____ Ion chromatograms

_____ Quantitation reports

_____ Internal standard area summary table, if applicable
(for all Method Blanks, sample and dilution analyses, and MS/MSDs)

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

_____ Result summary table (including detection limits)

_____ Surrogate recovery table

_____ Ion Chromatograms

_____ Quantitation reports

_____ Target compound spectra, which should include

_____ Raw target compound spectra

_____ Enhanced or background subtracted spectra

_____ Laboratory generated target compound standard spectra

_____ Tabulated results for Tentatively Identified Compounds, if applicable

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

Matrix Spike/Matrix Spike Duplicate Data

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

_____ Ion Chromatograms

_____ Quantitation reports

Rev. 2/3/92

Sample Data

_____ Result summary table (including detection limits)

_____ Surrogate recovery table

_____ Ion Chromatograms (including dilutions)

_____ Quantitation reports (including dilutions)

_____ Target compound spectra, which should include

_____ Raw target compound spectra

_____ Enhanced or background subtracted spectra

_____ Laboratory generated target compound standard spectra

_____ Tabulated results for Tentatively Identified Compounds, if applicable

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

_____ _____

Signature Date

APPENDIX F
Data Assessment Forms
SOP #1016
October 1994

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

TOTAL REVIEW

CLP DATA ASSESSMENT

Functional Guidelines for Evaluating Organics Analysis

CASE NO._____SDG NO._____LABORATORY_____SITE_____

DATA ASSESSMENT:

The current functional guidelines (1988) for evaluating organic data have been applied.

All data are valid and acceptable except those analytes which have been qualified with a "J" (estimated), "U" (non-detects), "R" (unusable), or "JN" (presumptive evidence for the presence of the material at an estimated value). All action is detailed on the attached sheets.

Two facts should be noted by all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems the analysis is invalid and provides no information as to whether the compound is present or not. "R" values should not appear on data tables because they cannot be relied upon, even as a last resort. The second fact to keep in mind is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data but any value potentially contains error.

Reviewer's
Signature:_____Date:____/____/19____

Verified By:_____Date:____/____/19____

DATA VALIDATION PROCEDURES FOR ROUTINE ORGANIC ANALYSIS

DATA ASSESSMENT:

1. HOLDING TIME:

The amount of an analyte in a sample can change with time due to chemical instability, degradation, volatilization, etc. If the specified holding time is exceeded, the data may not be valid. Those analytes detected in the samples whose holding time has been exceeded will be qualified as estimated, "J". The non-detects (sample quantitation limits) will be flagged as estimated, "J", or unusable, "R", if the holding times are grossly exceeded.

The following action was taken in the samples and analytes shown due to excessive holding time.

DATA ASSESSMENT:

2. BLANK CONTAMINATION:

Quality assurance (QA) blanks, i.e., method, trip, field, rinse and water blanks are prepared to identify any contamination which may have been introduced into the samples during sample preparation or field activity. Method blanks measure laboratory contamination. Trip blanks measure cross-contamination of samples during shipment. Field blanks measure cross-contamination of samples during field operations. If the concentration of the analyte is less than five times the blank contaminant level (10 times for the common contaminants), the analytes are qualified as non-detects, "U". The following analytes in the samples shown were qualified with "U" for these reasons:

A) Method blank contamination

B) Field or rinse blank contamination ("water blanks" or "distilled water blanks" are validated like any other sample)

C) Trip blank contamination

DATA ASSESSMENT:

3. MASS SPECTROMETER TUNING:

Tuning and performance criteria are established to ensure adequate mass resolution, proper identification of compounds, and to some degree, sufficient instrument sensitivity. These criteria are not sample specific. Instrument performance is determined using standard materials. Therefore, these criteria should be met in all circumstances. The tuning standard for volatile organics is bromofluorobenzene (BFB) and for semivolatiles is decafluorotriphenyl-phosphine (DFTPP).

If the mass calibration is in error, all associated data will be classified as unusable, "R".

DATA ASSESSMENT:

4. CALIBRATION:

Satisfactory instrument calibration is established to ensure that the instrument is capable of producing acceptable quantitative data. An initial calibration demonstrates that the instrument is capable of giving acceptable performance at the beginning of an experimental sequence. The continuing calibration checks document that the instrument is giving satisfactory daily performance.

A) RESPONSE FACTOR:

The response factor measures the instrument's response to specific chemical compounds. The response factor for the Target Compound List (TCL) must be $\geq$ 0.05 in both the initial and continuing calibrations. A value of < 0.05 indicates a serious detection and quantitation problem (poor sensitivity). Analytes detected in the sample will be qualified as estimated, "J". All non-detects for that compound will be rejected ("R").

DATA ASSESSMENT:

5. CALIBRATION:

B) PERCENT RELATIVE STANDARD DEVIATION (%RSD) AND PERCENT DIFFERENCE (%D):

Percent RSD is calculated from the initial calibration and is used to indicated the stability of the specific compound response factor over increasing concentration. Percent D compares the response factor of the continuing calibration check to the mean response factor (RRF) from the initial calibration. Percent D is a measure of the instrument's daily performance. Percent RSD must be <30% and %D must be <25%. A value outside of these limits indicates potential detection and quantitation errors. For these reasons, all positive results are flagged as estimated, "J" and non-detects are flagged "J" (if %D or %RSD >50%). If there is a gross deviation of %RSD and %D, the non-detects may be rejected ("R").

For the PCB/PESTICIDE fraction, %RSD for aldrin, endrin, and DDT must not exceed 25%. Percent D must be within 25% on the quantitation column.

DATA ASSESSMENT:

6. SURROGATES:

All samples are spiked with surrogate compounds prior to sample preparation to evaluate overall laboratory performance and efficiency of the analytical technique. If the measured surrogate concentrations were outside contract specifications,

qualifications were applied to the samples and analytes as shown below.

DATA ASSESSMENT:

7. INTERNAL STANDARDS PERFORMANCE:

Internal standard (IS) performance criteria ensure that the GC/MS sensitivity and response are stable during every experimental run. The internal standard area count must not vary by more than a factor of two (-50% to +100%) from the associated continuing calibration standard. The retention time of the internal standard must not vary more than ±30 seconds from the associated continuing calibration standard. If the area count is outside the (-50% to +100%) range of the associated standard, all of the positive results for compounds quantitated using that IS are qualified as estimated, "J", and all non-detects as "J", or "R" if there is a severe loss of sensitivity.

If an internal standard retention time varies by more than 30 seconds, the reviewer will use professional judgment to determine either partial or total rejection of the data for that sample fraction.

DATA ASSESSMENT:

8. COMPOUND IDENTIFICATION:

A) VOLATILE AND SEMIVOLATILE FRACTIONS:

TCL compounds are identified on the GC/MS by using the analyte's relative retention time (RRT) and by comparison to the ion spectra obtained from known standards. For the results to be a positive hit, the sample peak must be within ±0.06 RRT units of the standard compound and have an ion spectra which has a ratio of the primary and secondary m/e intensities within 20% of that in the standard compound. For the tentatively identified compounds (TIC) the ion spectra must match accurately. In the cases where there is not an adequate ion spectrum match, the laboratory may have provided false positive identifications.

B) PESTICIDE FRACTION:

The retention times of reported compounds must fall within the calculated retention time windows for the primary chromatographic columns.

DATA ASSESSMENT:

9. MATRIX SPIKE/SPIKE DUPLICATE, MS/MSD:

The MS/MSD data are generated to determine the long-term precision and accuracy of the analytical method in various matrices. The MS/MSD may be used in conjunction with other QC criteria for some additional qualification of the data.

DATA ASSESSMENT:

10. OTHER QC DATA OUT OF SPECIFICATION:

11. SYSTEM PERFORMANCE AND OVERALL ASSESSMENT (continued on next page if necessary):

12. CONTRACT PROBLEMS_____NON-COMPLIANCE:

13. This package contains re-extraction, re-analysis or dilution. Upon reviewing the QA results, the following Form I(s) are identified to be used.

DATA ASSESSMENT:

11. SYSTEM PERFORMANCE AND OVERALL ASSESSMENT (continued):