

APPENDIX A

Glossary

A-1. Accuracy.

Accuracy refers to *closeness* to the *true value*. The *true value* typically refers to the expected or prepared spike concentration. For statistical applications, the *true value* typically refers to the population mean. Accuracy is a conceptualization and cannot be known with complete certainty. Accuracy is evaluated in a variety of ways. For laboratory analyses, accuracy is commonly inferred from the percent recoveries of spike samples (matrix spikes, laboratory control samples, surrogate spikes, performance evaluation samples, etc.).

The terms “accuracy” and “bias” are commonly used interchangeably, but, strictly speaking, these terms are not synonymous. Accuracy is generally a function of both “random error” and “systematic error.” “Random error” is characterized by unpredictable variations for the measured results of a parameter of interest, cannot be corrected directly, but can be reduced by increasing the number of measurements. (It should be noted that “random error” is distinguished from “spurious error,” which is also unpredictable, but arises from factors such as human blunder and gross instrument malfunction.) The term “bias” refers to systematic directional error from the “true value.” Unlike random error, “bias” or “systematic error” remains constant or varies in a predictable manner, but is independent of the number of measurements. The mean spike recovery for the LCS is a measure of method bias and the standard deviation for the LCS recoveries is a measure of method precision. The mean LCS recovery with the standard deviation essentially constitutes a measure of accuracy.

A-2. Analyte.

See “Target Analyte.”

A-3. Batch.

See “Preparation Batch.”

A-4. Batch Quality Control (QC) Sample.

See “Quality Control (QC) Sample.”

A-5. Bias.

Bias refers “systematic error.” Bias is a directional error that arises from a constant or predictable distortion of the measurement process. A measurement or estimate is said to be *unbiased* if the mean approaches the true value as the number of replicates increases. An estimate is said to possess a *low bias* if it is consistently less than the true value and is said to possess a *high bias* if it is consistently higher than the true value. The adjectives “high” and “low” are used to refer to the *direction* rather than the magnitude of the deviation from the true

value. Adjectives such as “small,” “slight,” “marginal,” “large,” and “gross” will be used to refer to the *magnitude* of the deviation. For chemical analyses, *consistently* low or high recoveries for batch QC samples (e.g., laboratory control samples and matrix spikes) are indicative of bias.

A-6. Chain-Of-Custody (COC).

Chain-Of-Custody (COC) procedures and forms primarily document the possession of the samples from collection to storage, analysis, reporting, and, ultimately, disposal. Each cooler sent from the field to a laboratory is accompanied by a unique COC record. (The COC form is typically sealed in a Ziploc-type bag and is taped to the inside of the cooler lid.) COC forms must become part of the permanent record of all sample handling and shipment. The COC form lists the samples in a cooler, and includes the following information: project identification, unique project-specific sample identifications, dates and times of sample collection, number of containers, general testing procedures, and any special remarks. Couriers’ shipping documents should also be included.

A-7. Characteristic Peaks.

For multi component target analytes (e.g., Aroclors), *characteristic peaks* are those peaks that are at least 25% of the height of the largest peak in chromatogram for the pure multi-component standard.

A-8. Comparability.

Comparability refers to the equivalency of two sets of data. This goal is achieved through the use of standard or similar techniques to collect and analyze representative samples. Comparable data sets must contain the same variables of interest and must possess values that can be converted to a common unit of measurement. *Comparability* is normally a qualitative parameter that is dependent upon the other data quality elements. For example, if the detection limits for a target analyte were significantly different for two different methods, the two methods would not be comparable.

A-9. Completeness.

Completeness refers to the percentage of data that is *valid* or usable; that is, which satisfies project-specific DQOs. The highest degree of completeness that can be achieved is normally desired. Completeness acceptance criteria would normally be defined for both field and laboratory activities. A typical acceptance criterion for completeness is 80% to 90%. A higher completeness acceptance criterion may be required for critical samples. In general, when calculating percent completeness, R-qualified and X-qualified data must not be included in the set of valid data.

A-10. Comprehensive Blank.

See “Hierarchy of Blanks.”

A-11. Comprehensive Data Package.

A *comprehensive data package* is defined as a package of “definitive” or “effective” chemical data that satisfies the minimum data reporting requirements of this document and contains sufficient information to completely reconstruct the chemical analyses that were performed. Comprehensive data packages include all **batch, method, and instrument QC** results as well as raw data (e.g., run logs, sample preparation logs, standard preparation logs, and printed instrumental output such as chromatograms).

A-12. Continuing Calibration Verification (CCV).

A continuing calibration verification (CCV) refers to the use of a mid- to low-level instrumental standard to *check* rather than to alter instrument calibration. CCVs are typically analyzed on a continuing basis (e.g., at the beginning, middle, and end of an analytical sequence) and are evaluated to determine whether the instrument was within acceptable calibration throughout the period of time samples were instrumentally analyzed. The CCV is usually (but necessarily) prepared from a standard that is from the same source as the initial calibration standards.

A-13. 2-D and 3-D Detectors.

A “3-D” detector differs from a “2-D” detector in that the former furnishes quantitative and comprehensive qualitative information for definitive compound identification, while the latter primarily furnishes only quantitative information. Detectors such as PIDs, ECDs, and FIDs are referred to as “2-D” or “two-dimensional” detectors since they essentially yield a two-dimensional plot of gross instrumental response versus time (i.e., “single-channel” time-versus-response data). Two-dimensional detectors cannot provide sufficient qualitative information for analyte identification. Detectors such as mass selective and infrared (IR) detectors are examples of “3-D” or “three dimensional” detectors since they provide time-versus-response data for multiple mass ions and wavelengths, respectively.

A-14. Data Quality Indicators.

See “PARCCS.”

A-15. Data Quality Objectives (DQOs).

Data quality objectives (DQOs) are perhaps more appropriately referred to as data objectives. DQOs refer to the quantitative and qualitative statements that identify the goals, decision strategies, and boundaries for a particular study (e.g., acceptable levels of uncertainty); in addition, DQOs define the type, quality, and quantity of data required to support project decisions by the data users. The DQOs are developed during the planning stages of a project based upon the scientific method of inquiry. With respect to the chemical testing, DQOs are developed prior to sample collection and analysis, in order to determine appropriate analytical methodology, quality control acceptance limits (i.e., specifications for *data quality indicators*), and corrective actions.

A-16. Detection.

A detection typically refers to a reported measured concentration of a target analyte that is greater than the detection limit or the reporting limit.

A-17. Definitive Data.

The distinction between *definitive* and *screening data* is rather subjective. Definitive data are typically produced using “rigorous” analytical methods, such as EPA reference methods. The analytical results are frequently evaluated with respect to relatively stringent quality control specifications and PARCCS criteria are well defined. Recently, the term “effective” data (versus “definitive” data) has been used to describe data of sufficient quality to support project decisions. Screening data are essentially data that are not “fully effective”--data that cannot be used to support project decisions without higher quality data.

For example, since screening methods often lack specificity, they tend to give rise to false positives. Therefore, screening data are usually confirmed by testing a percentage of the environmental samples (e.g., 10%) with *definitive* methods or “more effective” methods of analysis. Quantitative data from screening methods also tend to be less precise and accurate than that from definitive methods. Screening data are typically generated by methods of analysis that are relatively rapid (typically involving minimal sample preparation) and performed in the field (as opposed to an off-site laboratory). However, real-time data generated in the field is not necessarily of inferior quality to fixed laboratory data.

A-18. External Calibration.

The *external calibration* technique is primary used for organic chromatographic analyses involving detectors other than MS detectors (e.g., FID, PID, ECLD, ECD and NPD). A **calibration factor** is calculated for each analyte and surrogate in each initial calibration standard using the equation:

$$CF = \frac{\text{Peak Area or Height of analyte in calibration standard}}{\text{Amount of the Compound Injected (e.g., mass in nanograms)}}$$

For multi component analytes, the numerator is the sum of the area or heights of several peaks. In other words, the calibration factor is the ratio of detector response to the amount of analyte in the calibration standard. The amount of analyte in an environmental sample is calculated by dividing the instrumental response for the analyte by the mean calibration factor for all the initial calibration standards.

A-19. Field Duplicates.

Field Duplicates are similar to “matrix duplicates.” They differ in that the former are prepared in the field while the latter are prepared in the laboratory. A field duplicate is an environmental sample that is homogenized and split into two separate aliquots in the field rather than at the

laboratory. This document distinguishes between field duplicates and collocated samples. Collocated samples are field samples that are collected “near” each another during a single sampling event but which are not homogenized. However, for simplicity, field duplicates and collocated samples are not distinguished from laboratory duplicates when homogenization cannot be performed because of the nature of the analyte or the methodology. For example, samples collected for low-level VOC analysis by closed-system purge-and-trap cannot be homogenized. Hence, for these type of analyses, the term “matrix duplicate” refers to collocated samples.

A-20. Field QC Samples.

Field QC samples are *QC samples* that are prepared in the field or that are impacted by field activities. Examples of field QC samples include trip blanks, rinsate (equipment) blanks, and field duplicates. Matrix spike samples may or may not be field QC samples. For example, if an environmental sample were homogenized in the field and subsequently split into three aliquots for MS and MSD analyses, then the MS and MSD samples would be considered to be field QC samples.

A-21. Hierarchy of Blanks.

When environmental (field) samples are subjected to multiple handling, preparatory and analytical procedures, blanks may be introduced in a sequential manner to measure the level of contamination arising from each procedure or from select sets of procedures. For example, assume that a sample is sequentially processed using two distinct preparatory techniques, which will be referred to as “technique 1” and “technique 2.” The sample and a blank, BLK(1,2), are processed using technique 1. The sample, the blank BLK(1,2), and a second blank, BLK(2), are then processed using technique 2. When blanks are processed in this manner, they can be used to evaluate the contamination associated with each stage of the preparatory process. For example, assume that contaminants are detected in BLK(1,2), but none are detected in BLK(2). It would be assumed that the contamination resulted from the first preparatory technique. Furthermore, since BLK(1,2) accounts for the contamination introduced from the entire preparatory process, only BLK(1,2) would minimally be required to evaluate environmental samples for contamination. For example, if BLK(2) were not processed, then the samples would be evaluated using BLK(1,2) alone.

A blank that measures contamination for a set of handling, preparatory, or analytical procedures is said to possess a *higher hierarchy* than a blank that measures contamination for only a subset of the procedures. In the example cited above, the blank BLK(1,2) possesses the highest hierarchy because it measures contamination from all of the preparatory techniques. The highest hierarchy blank will be referred to as a **comprehensive blank** if it accounts for contamination from all sample handling, preparatory, and analytical procedures. In general, a blank with a higher hierarchy is more critical than one with a lower hierarchy. In particular, when a blank is missing for a set of environmental samples, the samples may be qualified for contamination using a blank that possesses a higher hierarchy than the missing blank. Blanks for environmental analyses are listed in order of increasing hierarchy below:

Calibration/Instrument Blanks < Storage/Holding Blanks < Method Blanks

< Trip Blanks < Rinsate/Equipment Blanks

Note that trip blanks are collected only for VOC analyses. Furthermore, a rinsate blank may be substituted for a trip blank only when the rinsate blank is stored and shipped in the same cooler as the field samples. Under these circumstances, the rinsate blank would account for contamination arising from cleaning procedures, cross contamination in the sample coolers, and laboratory contamination.

A-22. Holding Time.

The **preparation holding time** (e.g., the **extraction** or **digestion holding time**) is defined as the period of time from the date an environmental sample is collected in the field to the date the sample is processed with the preparatory method (e.g., the date the sample is first exposed to the extraction or digestion solvent). The **analysis holding time** is defined as the period of time from the date of sample preparation (e.g., extraction or digestion) to the date of sample analysis using some determinative (i.e., instrumental) method.

A-23. Holding Time Limit.

The *holding time limit* is defined as the maximum acceptable holding time for sample preparation or analysis.

A-24. Initial Calibration.

Initial calibration refers to the establishment of a quantitative relationship between instrumental response and analyte concentration (or amount) prior to the analysis of samples. The correlation between instrumental response and analyte concentration is established via the analysis of a set of standards of known concentration and is demonstrated using quantitative performance specifications (e.g., linear correlation coefficients). The initial calibration must demonstrate that, over some concentration range of interest, a change in analyte concentration is associated with a predictable change in instrumental response and vice versa (i.e., there is a continuous functional and inverse functional relationship between instrumental response and concentration).

A-25. Initial Calibration Verification (ICV).

An *initial calibration verification (ICV)* refers to the use of a mid-level, second-source, instrumental standard to verify the accuracy of the standards used to perform the initial calibration. The ICV is typically performed immediately after the initial calibration. The acceptance limits for ICV recoveries should be similar to the acceptance limits for other instrumental QC samples such as CCVs.

A-26. Instrument Quality Control (QC) Sample.

See "Quality Control (QC) Sample."

A-27. Internal Calibration.

The *internal calibration* technique is primarily used for organic chromatographic analyses involving MS detectors. An **internal standard** is added to each sample and calibration standard immediately prior to analyses. An internal standard is a substance that is similar to the target analytes in chemical behavior, which is not normally found in the environmental samples, and which is added at a fixed, known concentration to all samples and calibration standards. A **relative response factor** is calculated for each analyte and surrogate in each initial calibration standard according to the equation:

$$\text{RRF} = \frac{A_s C_{is}}{A_{is} C_s}$$

where

- A_s = Peak area or height of the analyte or surrogate
- A_{is} = Peak area or height of the internal standard
- C_s = Concentration of the analyte or surrogate (e.g., $\mu\text{g/L}$)
- C_{is} = Concentration of the internal standard (e.g., $\mu\text{g/L}$)

For multi component analytes such as dioxins, the terms A_s and A_{is} represent the sum of the integrated ion abundance of multiple quantitation ions. The calculation of the amount of analyte in an environmental sample involves dividing instrumental response for the analyte by the instrumental response for the internal standard and the mean relative response factor for the set of initial calibration standards. The internal standard technique is superior to the external standard technique because target analyte loss is taken into account for the portion of the analytical process that takes place after the internal standard is spiked into the sample (e.g., loss during sample injection). The internal standard procedure is used primarily with MS detectors because the signal intensities used for quantitation would not otherwise be adequately stable and the masses of the internal standards can be resolved from those of the target compounds even when chromatographic resolution cannot be achieved.

A-28. Laboratory Control Sample (LCS).

The *laboratory control sample* (LCS) is used to assess laboratory method performance. Laboratory control samples are analyzed to assess the ability of the laboratory to successfully recover the method's target analytes from a sample of known composition. Precision may be evaluated by analyzing an LCS and an LCSD (laboratory control sample duplicate) for each preparation batch of samples. A laboratory control sample must be chemically and physically similar to the environmental samples and must contain a known amount of each target analyte at an appropriate concentration. A laboratory control sample typically consists of a clean matrix (e.g., reagent water or purified sand) that has been spiked with the target analytes of interest. In general, an LCS must contain all single-component target analytes of interest and must be processed through the entire sample preparatory and analytical methods. The LCS usually contains only a subset of the target analytes when multi component analytes such as Aroclors are

being analyzed. Ideally, the concentrations of the target analytes in the LCS should be determined by project-specific DQOs (e.g., should be near the regulatory or risk-based decision limits), but the LCS is typically spiked between the low-level and mid-level calibration standards.

Internal LCS acceptance limits for accuracy and precision are produced by the laboratory by performing statistical calculations (using at least 30 data points). However, since duplicate precision is not as critical as accuracy, many laboratories do not generate statistical acceptance limits for duplicate precision but use “default” (e.g., method specified or arbitrary) RPD acceptance limits. Control charts and tables are maintained to establish the bias and precision of the method, and are updated periodically (typically, on a quarterly basis). A representative subset of the target analytes for each method is normally graphed to observe method trends. Unfortunately, LCS acceptance limits for environmental sampling and analysis activities are often based upon the laboratory’s internally generated control chart limits or method-specified limits rather than project-specific DQOs. Ideally, project-specific acceptance limits should be equal to or greater than the laboratory’s in-house statistical control limits.

When an LCS result falls outside of the laboratory’s internal acceptance limits, the laboratory must implement some form of corrective action. In general, the preparation batch must be reprocessed when the associated LCS recovery falls outside of the acceptance range. When an LCS RPD is out-of-control but the LCS recovery is acceptable, the laboratory must implement corrective action but the associated environmental samples would not typically be reprocessed.

A-29. Laboratory Control Sample Duplicate (LCSD).

See “Laboratory Control Sample (LCS)”.

A-30. Limit of Identification (LOI).

The *limit of identification* (LOI) is the lowest concentration of analyte that can be detected with 99% confidence; that is, the LOI is the concentration at which the probability of a false negative (Type II decision error) is 1%. The LOI is adjusted for method specific factors (e.g., sample size) and may be approximated as twice the detection limit. The LOI may be set equal to about two times the MDL (e.g., if it is assumed that the standard deviation is not strongly dependent upon concentration).

A-31. Matrix-Dependent Duplicate.

See “Matrix Spike Duplicate (MSD) and Matrix Duplicate (MD).”

A-32. Matrix Spike (MS).

The *matrix spike* (MS) is used to assess the performance of the method as applied to a particular matrix; they are analyzed to assess the ability of the method to successfully recover target analytes in the environmental population being sampled. An MS is an environmental sample to which known concentrations of all of the method target analytes have been added before it is

carried through all sample preparation, cleanup, and analytical procedures. MS results are evaluated in conjunction with other QC information (e.g., surrogate and LCS recoveries) to determine the effect of the matrix on the accuracy of the analysis.

The target analytes added to a matrix spike sample would typically be identical to those added to a laboratory control sample. The environmental sample selected for MS analysis must be representative of the environmental population being sampled and would normally be specified in the field. Control charts may be maintained for MS recoveries, but, in general, laboratories do not base batch control on the results of MS samples unless a general method failure is indicated. Matrix spikes are typically analyzed at a frequency of at least 5% but frequency requirements are project-specific.

A-33. Matrix Duplicate (MD) and Matrix Spike Duplicate (MSD).

The *matrix duplicate* (MD) and *matrix spike duplicate* (MSD) are used to assess the precision of a method in an actual matrix. A MSD is a duplicate of an MS. An MSD is also used to evaluate the accuracy of a method in a particular matrix and is evaluated using the same criteria for the MS. An MD is an environmental sample that is divided into two separate aliquots. (Care must be taken to ensure that the sample is properly divided into homogeneous fractions.) Both the MD and MSD are carried through the complete sample preparation, cleanup, and analytical procedures. For brevity, MS/MSD and matrix duplicate pairs are referred to as **matrix-dependent duplicates**.

Frequency requirements for MDs and MSDs are normally established on a project-specific basis. An MD is normally processed with each preparation batch when target analytes are expected to be present. A MSD is normally processed with each preparation batch when method target analytes are not expected to be present. As a “rule of thumb,” a MSD is used for organic methods and a MD is used for inorganic methods. The results of the MD or MSD are evaluated, in conjunction with other QC information, to determine the effect of the matrix on the precision of the analysis. Control charts, or tables, may be maintained for these samples to monitor the precision of the method for each particular matrix and may be required by certain projects.

A-34. Matrix Interference.

As used in this document, the term “matrix interference” typically refers to an effect that arises from the native physical or chemical composition of an environmental sample that produces a negative or positive bias in the results.

For example, high concentrations of non-target analytes that coelute with the analytes of interest in the instrumental portion of a chromatographic method may give rise to a positive interference (i.e., high bias). Substances such as peat and clay may bind the target of interest and prevent complete extraction of the target analytes in the preparatory portion of an analytical procedure (especially when analyte concentrations are low), may give rise to a “negative” interference (i.e., low bias). However, sample heterogeneity is viewed as a characteristic of the matrix (e.g., the spatial variability of the environmental population being sampled) rather than as an “interference” for which the method of analysis must be optimized to reduce.

A-35. Measurement Quality Objectives (MQOs).

Measurement quality objectives are acceptance criteria for PARCCS for the various phases of the measurement process (e.g., sampling and analysis) that are established to ensure that total measurement uncertainty is within the range prescribed by project DQOs.

A-36. Method Blank (MB).

Method blanks are used to assess laboratory contamination. A method blank is defined as an interference-free matrix which is similar to the field sample matrix, lacks the target analytes of interest, and is processed with the environmental samples using the same preparatory and determinative methods. Hence, all reagents added to samples during extraction, cleanup, and analysis are also added to method blanks in the same volumes or proportions. Analyte-free reagent water is frequently used to prepare method blanks for aqueous analyses and a purified solid matrix (e.g., sand) is frequently used for solids.

Contamination may result in false positives or elevated reporting levels for target analytes. Method blanks are analyzed to assess contamination for the entire analytical process. Therefore, when a batch of samples is analyzed on separate instruments or separate analytical shifts, the method blank associated with the batch (e.g., extracted with the samples) must also be analyzed with the samples for each instrument and analytical shift.

A-37. Method Detection Limit (MDL).

The *method detection limit* (MDL) is the minimum concentration of a substance that is significantly greater than zero (an analytical blank) at the 99% limit of confidence and is determined using the procedure described in 40 CFR, Part 136, Appendix B. The standard deviation, s , is calculated for n replicate aliquots (where $n > 7$) that are spiked near (e.g., one to five times) the estimated MDL and processed (as environmental samples) through the full analytical procedure. The standard deviation for the set of replicate analyses is subsequently multiplied by the Student t value corresponding to the 99% percentile of the t -distribution with $n-1$ degrees of freedom.

Since it is not practical to establish an MDL for each specific matrix received at any given laboratory, MDLs are usually estimated in interference-free matrices (typically reagent water for aqueous analyses and a purified solid matrix such as sand for the analysis of solid matrices). However, certain projects may require the determination of method detection limits in site-specific matrices.

As defined in 40 CFR 136 Appendix B, MDLs are method, matrix and instrument specific. MDL samples must be processed using the sample determinative and preparatory methods as the environmental samples (e.g., using the same extraction and cleanup procedures) and must be adjusted for method-specific procedures such as dilutions. When multiple instruments are used to perform the same method, MDLs may be *demonstrated* on individual instruments (including individual chromatographic columns and detectors) via the analysis of *MDL check samples*.

An *MDL check sample* is prepared by spiking an interference free matrix with all target analytes of interest at about two times the estimated MDL and subsequently processing it through the entire analytical procedure. If a target analyte is not recovered in the MDL check sample, then the MDL study should be repeated for that target analyte. It is recommended that a laboratory's MDLs be verified quarterly by analyzing detection limit check samples. MDL studies should be performed at least annually and whenever the basic chemistry or instrumentation for method is changed.

It should be noted that the statistical approach described in 40 CFR 136 Appendix B does not take calibration uncertainty into account. It is implicitly assumed that the calibration curve is known with certainty. Since the variability associated with the estimate of the calibration curve is not taken into account, when samples do not undergo a significant preparatory process, it may be desirable to establish detection limits using the procedure described by Andre Hubaux and Gilbert Vos (*Decision and Detection Limits for Linear Calibration Curves*, Analytical Chemistry, Volume 42, No. 8, July 1970).

A-38. Method Quantitation Limits (MQL).

The *method quantitation limit* (MQL) is the concentration of an analyte in a sample that is equivalent to the concentration of the lowest initial calibration standard adjusted for method-specified sample weights and volumes (e.g., extraction volumes and dilutions). Typically, MQLs are equal to or greater than the lowest initial calibration standard and are at least five times greater than the MDL. MQLs must also be less than project-specific action levels. It is usually desirable for the MQL to be equal to some fraction of the project's action levels (e.g., one half or one third of the action levels).

A-39. Method Reporting Limit (MRL).

The *method reporting limit* (MRL) is the threshold or censoring limit below which target analyte concentrations are reported as "< MRL" or "MRL U," where "MRL" is the numerical value of the method reporting limit. The method reporting limit is usually established based on the laboratory's LOIs, MQLs, or project-specific action levels. The MRL for *undetected* analytes should not be less than the LOI or RDL and must not be greater than the AL.

A-40. Native Analyte.

In the context of environmental testing, the term "native analyte" refers to the analyte incorporated into the test material by natural processes or from past waste handling activities (e.g., as opposed to spike addition).

A-41. Nondetection.

A *nondetection* typically refers to a target analyte concentration that is less than the detection limit or the method reporting limit.

A-42. PARCCS.

The term “PARCCS” is an acronym for the primary elements of data quality: *Precision, accuracy, representativeness, completeness, comparability, and sensitivity*. It should be noted that *sensitivity* is often omitted and the acronym PARCC is commonly used; these five data quality elements (PARCC) are often referred to as *Data Quality Indicators* (DQIs).

A-43. Percent Difference (%D).

The percent difference of a measurement, X_o , of a variable X is defined by the equation:

$$\%D(X) = (| X_o - \langle X \rangle | / \langle X \rangle) 100$$

where

$$\langle X \rangle = \sum X_i / n$$

is the mean of a set of n replicate measurements of X (that excludes X_o). For brevity, unless otherwise specified, the term *percent difference* (%D) will refer to the percent difference for the **response factor** of a continuing calibration standard for an organic chromatographic method.

A-44. Percent Recovery (%R).

The *percent recovery* for a matrix or post-digestion spike is defined by the equation:

$$\%R = 100 (X_F - X_O) / S$$

where

X_F = Measured concentration of environmental sample after spike addition
 X_O = Measure concentration of environmental sample prior to spike addition
 S = Spike (reference) concentration

For CCVs, ICVs, and LCSs, the percent recovery is defined as:

$$\%R = 100 (X/S)$$

where

X = Measured concentration of QC sample

For brevity, the *percent recovery* is referred to as the **recovery**.

A-45. Percent Relative Standard Deviation (%RSD).

The *percent relative standard deviation* for n replicate measurements of a variable X is defined by the equation:

$$\%RSD(X) = (SD/\langle X \rangle) 100$$

where

$$\langle X \rangle = \sum X_i / n$$

is the mean of the variable. For brevity, the term *relative standard deviation* (%RSD) will refer to the percent relative standard deviation of the **response factors** for the initial calibration standards for a chromatographic method.

A-46. Performance-Based Method/Approach.

This term does not appear to be well-defined in the literature. As applied to chemical testing, the term *performance-based* implies that the methodology used to produce an analytical result is secondary to the quality of the result itself. When a performance-based approach is implemented, specifications are primarily imposed upon the data (the “end product” of the analytical process) rather than upon the process by which the data are produced. Chemical data are generated by any analytical method which can demonstrate project-specific PARCCS requirements are met. Method QC elements such as detection limits, method blanks, laboratory control samples, and matrix spikes are minimally required to demonstrate method performance.

A-47. Post Digestion Spike (PDS).

A *post digestion spike (PDS)* is typically analyzed for metals to assess the ability of a method to successfully recover target metals from an actual matrix after the digestion process. A PDS is an environmental sample to which known concentrations of target metals are added after the digestion process. The spiking concentration for the PDS should not be less than about two times the native analyte concentration. The same target analytes should be spiked into the LCS, MS, and PDS. A PDS should be analyzed when the MS is unacceptable. When the MS is unacceptable, an aliquot of the same environmental sample should be selected for the PDS. Alternatively, a PDS should be routinely processed with each MS so that every batch of samples contains at least one sample that is spiked *before and after* the digestion process.

A-48. Precision.

Precision refers to the repeatability of measurements. For statistical applications, *precision* refers to the spread or distribution of values about the population mean and is frequently measured by the standard deviation. For the chemical analyses of environmental samples, *precision* is commonly determined from duplicate samples (e.g., matrix spike duplicates, matrix

duplicate and laboratory control sample duplicates) and is commonly measured using either the relative percent difference (RPD) or the percent relative standard deviation (%RSD).

A-49. Preparation Batch.

A *preparation batch* is defined as a set of samples that are prepared together by the same person or group of people; using the same equipment, glassware, and lots of reagents; by performing manipulations common to each sample in the same sequence and within the same time period (usually not to exceed one analytical shift). Ideally, the samples in a preparation batch must be from the same study area and must be of similar composition. Samples taken from the same study area would normally be grouped together for batching purposes within the constraints imposed by the method holding times. However, laboratories may find it necessary to group samples from different clients into a single batch.

Environmental and QC samples must be prepared, analyzed, and reported in a manner that is traceable to individual batches. Hence, each preparation batch must be uniquely identified within the laboratory. A preparation batch is normally limited to twenty field environmental samples of a similar matrix and also contains the appropriate QC samples (e.g., a laboratory control sample and a method blank). The QC samples undergo the same preparatory procedures (e.g., using the same extraction and cleanup methods) as the environmental samples. Samples in the same preparation batch would normally be analyzed together using the same instrument.

A-50. Preservation.

The term “preservation” refers to any technique (frequently involving the addition of laboratory-grade reagents) that retards biological, chemical, or physical processes that would alter the “representativeness” of the sample relative to the environmental population of interest (e.g., alter the analyte concentration in the sample matrix being tested). The most common preservation methods include pH adjustment, dechlorination, and temperature adjustment (i.e., cooling or freezing).

A-51. Professional Judgment.

As per ISO/IEC Guide 25 (August 1996 draft), the term *professional judgment* refers to “the ability of a single person or a team to draw conclusions, give opinions and make interpretations based on measurement results, knowledge, experience, literature and other sources of information.” A “professional judgment” must be supported by appropriate documentation. The information or factors taken into account during the decision making process must be discussed.

A-52. Quality Control (QC) Sample.

This document distinguishes between *preparatory methods* (e.g., Method 3010A) and *determinative methods* (e.g., Method 6010A) of analyses. A QC (quality control) sample that is *independent of matrix effects* and analyzed *only in a determinative method* is referred to as an **instrument QC sample** (e.g., a CCV and CCB). A non-instrument QC sample that is *processed* with the same *preparatory and determinative* methods as the environmental samples (e.g., matrix

spikes and laboratory control samples) is referred to as a **method QC sample**. Note that method QC samples (e.g., MDL study samples) are not necessarily analyzed on a per batch basis. A non-instrument QC sample that is analyzed on a per batch basis is referred to as a **batch QC sample**. Hence, a batch QC sample is a method QC sample that is analyzed on a per batch basis, or is a QC sample which is analyzed in only the determinative method but which is dependent upon matrix effects (e.g., post-digestion spikes).

A-53. Recovery.

See **Percent Recovery**.

A-54. Relative Percent Difference.

The *relative percent difference* for a set of duplicate measurements of the variable X, RPD(X), is defined by the equation:

$$RPD(X) = (|X_1 - X_2| / \langle X \rangle) 100$$

where

$$\langle X \rangle = (X_1 + X_2) / 2$$

is the mean of the pair of variables. The RPD is a measure of precision. For brevity, unless otherwise specified, the term *relative percent difference* refers to the relative percent difference of duplicate spike recoveries.

A-55. Reliable Detection Limit (RDL).

The *reliable detection limit (RDL)* is the upper 95% upper confidence limit of the MDL defined in 40 CFR, Part 136, Appendix B. RDLs for the upper 100ξ% upper confidence limit are calculated as follows:

$$RDL = [(n - 1) / \chi_{n-1, (1-\xi)/2}]^{1/2} MDL$$

where the MDL is calculated by multiplying the standard deviation, *s*, by the 99th percentile point of the t-distribution with *n*-1 degrees of freedom, $t_{n-1, 0.99}$:

$$MDL = t_{n-1, 0.99} s$$

The number of replicate analyses used to compute the MDL is denoted by *n*. The 100 (1 - ξ) / 2 percentile of the Chi-Square distribution with *n* - 1 degrees of freedom is denoted by $\chi_{n-1, (1-\xi)/2}$. For *n* = 7 and ξ = 0.95

$$\chi_{n-1, (1-\xi)/2} = \chi_{6, 0.025} = 1.24$$

and

$$\text{RDL} = (6 / 1.24)^{1/2} \text{MDL} \approx 7 s \approx 2 \text{MDL}$$

A-56. Representativeness.

Representativeness refers to the degree to which a sample or set of samples estimates the characteristics of a target population. For the chemical analysis of environmental samples, representativeness is a usually a qualitative parameter that is dependent upon the design of the field sampling program and laboratory methods (e.g., subsampling techniques). An evaluation of *representativeness* would include an assessment of laboratory holding time and method blank data. For example, samples that are not properly preserved or that are analyzed beyond acceptable holding times may not provide representative data.

A-57. Response Factor.

The term “response factor” refers to the *calibration factor* or *relative response factor*. Refer to **internal calibration** and **external calibration**.

A-58. Rinsate Blank.

Equipment or *rinsate blanks* consist of reagent water passed through or over sampling equipment following sample collection and sample equipment decontamination. Contaminated equipment blanks indicate inadequate decontamination between samples and a likelihood of cross-contamination between samples.

A-59. Sample.

The term “sample” refers to non-instrument QC samples (i.e., batch QC and method QC samples) and environmental (field) samples.

A-60. Sensitivity.

Sensitivity refers to the amount of analyte necessary to produce a detector response that can be reliably detected or quantified. Detection limits (e.g., instrument and method) and quantitation limits are commonly used to measure sensitivity.

A-61. Surrogate.

In the context of environmental testing, a surrogate is a relatively pure organic compound which is added to samples prior to preparation and analysis and which is similar to the analytes of interest (in physical and chemical behavior), but which is not normally found in environmental samples. *Surrogates* are typically spiked into environmental samples as well as batch QC and instrument QC samples for chromatographic methods. Surrogate recoveries in environmental samples are primarily used to assess overall performance on a sample-specific basis. Surrogate recoveries for environmental samples measure matrix effects (e.g., and extraction efficiency for

organic analysis involving solvent extractions), are evaluated in a similar manner as matrix spikes, but are evaluated on a sample-specific rather than batch-specific basis.

Surrogate recoveries for instrument QC samples (such as continuing calibration standards) are dependent upon instrument performance. Surrogate recoveries for the LCS and MB are used to evaluate the performance of the preparatory and analytical procedure. Laboratories should maintain surrogate control charts using LCSs or MBs results to monitor method performance and to evaluate surrogate recoveries in actual environmental matrices.

A-62. Target Analyte.

A *target analyte* is an environmental compound or element that is being measured or identified in a chemical test to satisfy project-specific data objectives. Target analytes are distinguished from compounds or elements analyzed solely for the purposes of quality control (e.g., surrogates and internal standards). For brevity, target analytes are often referred to as *analytes*.

A-63. Traceability.

Traceability is formally defined as follows: “The property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties” (“International Vocabulary of basic and general standard terms in Metrology,” ISO, Geneva, Switzerland 1993, ISBN 92-67-10175-1).

A-64. Trip Blank.

Trip blanks are prepared from reagent water and accompany each shipment of aqueous samples to be analyzed for volatile organic compounds. Analysis of the trip blanks indicates whether sample cross-contamination occurred during shipment and/or storage.

A-65. Validation.

A number of definitions for the term *validation* are currently being used in the environmental testing industry. In this document, *data validation* or *validation* refers to a systematic review of **comprehensive data packages**, *performed external to the data generator*, with respect to a predefined set of technical performance criteria for precision, accuracy, representativeness, completeness, comparability, and sensitivity. Validation is an objective sample and analyte-specific evaluation process that involves the application of scientific rather than contractual criteria to determine whether requirements for a specific intended use are potentially fulfilled. Validation results in a higher level of confidence when determining whether an analyte is actually present in an environmental sample at a particular level of interest, but usually results in a qualitative evaluation of the data. Data validation occurs prior to determining whether the overall project-specific objectives have been satisfied (i.e., prior to drawing conclusions from the body of the data).