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Standard Guide for Demonstrating and Assessing Whether a Chemical Analytical Measurement System Provides Analytical Results Consistent with Their Intended Use[1]

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1. Scope

1.1 This guide describes an approach for demonstrating the quality of analytical chemical measurement results from the application of a measurement system (that is, method or sequence of methods) to the analysis of environmental samples of soil, water, air, or waste. The purpose of such measurements can include demonstrating compliance with a regulatory limit, determining whether a site is contaminated above some specified level, or determining treatment process efficacy.

1.2 This guide describes a procedure that can be used to assess a measurement system used to generate analytical results for a specific purpose. Users and reviewers of the analytical results can determine, with a known level of confidence, if they meet the quality requirements and are suitable for the intended use.

1.3 This protocol does not address the general components of laboratory quality systems necessary to ensure the overall quality of laboratory operations. For such systems, the user is referred to International Standards Organization (ISO) Standard 17025 or the National Environmental Laboratory Accreditation Conference (NELAC) laboratory accreditation standards.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory requirements prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 4687 Guide for General Planning of Waste Sampling

D 5283 Practice for Generation of Environmental Data Related to Waste Management Activities: Quality Assurance and Quality Control Planning and Implementation

D 5792 Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives

D 5956 Guide for Sampling Strategies for Heterogeneous Wastes

D 6044 Guide for Representative Sampling for Management of Waste and Contaminated Media

D 6233 Guide for Data Assessment for Environmental Waste Management Activities

D 6250 Practice for Derivation of Decision Point and Confidence Limit for Statistical Testing of Mean Concentration in Waste Management Decisions

D 6311 Guide for Generation of Environmental Data Related to Waste Management Activities: Selection and Optimization of Sampling Design

D 6582 Guide for Ranked Set Sampling: Efficient Estimation of a Mean Concentration in Environmental Sampling

D 6597 Practice for Assessment of Attaining Clean Up Level for Site Closure

2.2 *Other Documents:*

Guidelines for Evaluating and Expressing Uncertainty of NIST Measurement Results, National Institute of Standard Technology Technical Note 1297, 1994 [3]

ISO/IEC 17025:1999 General Requirements for the Competence of Testing and Calibration Laboratories[4]

Quantifying Uncertainty in Analytical Measurement, EURACHEM/ CITAC Guide, second edition, 2000

3. Terminology

3.1 *Definitions:*

3.1.1 *action level (AL)*—the level above or below which will lead to the adoption of one of two alternative actions.

3.1.2 *analyte*—the constituent to be measured.

3.1.3 *bias*—the difference between the value determined using the measurement protocol in question and the true value; operationally the difference between the expected mean of the

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899–3460.

[4] Available from the American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

sample test results and an accepted true value. **D 5792**

3.1.4 *data quality objective (DQO)*—qualitative and quantitative statements of the overall level of uncertainty that a decision-maker is willing to accept in results or decisions derived from environmental measurements, includes uncertainties in sampling location, sample handling, and sample analysis.

3.1.5 *laboratory control sample*—an aliquot of the sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes, or a material containing known and verified amounts of analytes.

3.1.6 *matrix spike*—an aliquot of the sample spiked with known levels of the target analytes.

3.1.7 *measurement quality objectives (MQOs)*—quantitative statements of the acceptable level of selectivity, sensitivity, bias, and precision for measurements of the analyte of interest in the matrix of concern.

3.1.8 *measurement system*—all elements of the analytical process including laboratory subsampling, sample preparation and cleanup, and analyte detection and quantitation, including the analysts.

3.1.9 *method of standard additions*—the addition of a series of known amounts of the analytes of interest to more than one aliquot of the sample as a means of correcting for interferences.

3.1.10 *reference material (RM)*—the generic term referring to a certified material.

3.1.11 *selectivity*—the ability to accurately measure the analyte in the presence of other sample matrix components or analytical process contaminants.

3.1.12 *surrogate* —a substance with properties that mimic the performance of the analyte of interest in the measurement system, but which is not normally found in the sample of concern and is added for quality control purposes.

4. Significance and Use

4.1 This guide is intended for use by both generators and users of analytical results. It is intended to promote consistent demonstration and documentation of the quality of the measurement results and facilitate determination of the validity of measurements for their intended use.

4.2 This guide specifies documentation that a laboratory should supply with the analytical results to establish that the resulting measurements: (*1*) meet measurement quality requirements; (*2*) are suitable for their intended use; and (*3*) are technically defensible.

4.3 While the guide describes information that the measurement results provider needs to give the user/decision maker, in order for measurement providers to supply data users with appropriate data, information is needed from the data user. Examples of information that the user should provide to the laboratory, in addition to the analytes of concern (including the form of the analyte that is to be determined, for example, total lead, dissolved lead, organic lead, inorganic lead), include but are not limited to:

4.3.1 Type of material (that is, matrix—fresh or salt water, coal fly ash, sandy loam soil, wastewater treatment sludge),

4.3.2 Maximum sample holding time,

4.3.3 Projected sampling date and delivery date to the laboratory,

4.3.4 Method of chemical preservation (for example, not preserved, chemical used),

4.3.5 Chain-of-custody requirements, if any,

4.3.6 Analytical methods that must be used, if any,

4.3.7 Measurement quality requirements expressed as DQOs or MQOs and action limits,

4.3.8 Allowable interferences as described in 10.4,

4.3.9 Documentation requirement, and

4.3.10 Subcontracting restrictions/requirements.

4.4 Users/decision makers should consult with the laboratory about these issues during the analytical design stage. This will allow the design of sample collection process and project schedule to accommodate the laboratory activities necessary to determine the desired level of measurement quality. The number of samples, budgets, and schedules should also be discussed.

5. Limitations and Assumptions

5.1 This guide deals only with samples from the time the laboratory receives the samples until the time the analytical results are provided to the user including necessary documentation.

5.2 Aspects of environmental measurements that are within the control of the laboratory are normally specified by the project stakeholders in the form of MQOs. MQOs are a subset of the data quality objectives (DQOs). The DQOs describe the overall measurement quality and tolerable error of the decision for the project while the MQOs describe the uncertainty of the analytical process only. The DQO overall level of uncertainty includes uncertainty from both sampling and environmental laboratory measurement operations. Additional information on the DQO process and establishing the level of analytical uncertainty can be found in the references provided in Section 2.

5.3 This guide applies whether the measurements are performed in a fixed location or in the field (on-site).

5.4 This guide assumes that the laboratory is operating with all administrative and analytical systems functioning within the quality assurance and quality control protocols and procedures described in their quality system documents (quality assurance plan and standard operating procedures).

5.5 This guide does not address multi-laboratory approaches to demonstrating acceptable laboratory performance such as collaborative testing, inter-laboratory studies, or round-robin types of studies.

6. Outline of Approach

6.1 This guide uses the concepts of bias and precision to describe uncertainty in a measurement system. The approach set forth in this guide employs two fundamental properties of measurement systems: bias and precision to determine the quality of the analytical results. The guide singles out selectivity, a component of bias, for special emphasis. Sensitivity is also discussed since, unless a measurement system is sensitive enough to measure the analytes of interest at the level of interest, it is not capable of being used for the purpose at hand. Both areas are frequently highlighted for demonstration in acceptable environmental measurement collection efforts.

6.2 This guide provides examples of approaches that determine bias, precision, selectivity, and sensitivity of a measurement system used to analyze a set of samples. It also provides examples of factors laboratories should consider in designing the demonstration.

6.3 This guide describes, in general terms, the rigor of the demonstration of bias, precision, selectivity, and sensitivity that should be conducted for a set of samples. It describes the appropriate use of public literature and historical laboratory performance information to minimize the need to collect additional experimental measurements.

6.4 When analytical performance results are already available on the measurement system's response to the type of sample to be analyzed (for example, historical results from the laboratory conducting the demonstration, method developer information), such information may be used to determine one or more of the measurement properties (that is, bias, precision, selectivity, sensitivity). Only very limited amounts of new measurements would then be necessary to support the conclusions drawn from the existing information.

6.5 This guide is intended to offer users a technically defensible strategy to determine the applicability of an analytical technique to a set of environmental samples. The complexity of the problem, the available resources (trained staff, equipment, and time), and the intended use of the analytical results require the application of professional judgment in selecting the best available option to meet the project-specific needs. The following sections present the user with a variety of options to determine bias, precision, selectivity, and sensitivity. The discussion of these options does not recommend one over another. However, there are general principles that can assist the user in selecting an appropriate option.

6.6 The laboratory should select the available option that will provide the information needed to determine if the measurements meet the required level of quality (as defined by the user/decision maker). The necessary level of quality should be available from the project data quality requirements, DQOs or MQOs. This guide assumes that the laboratory and users have sufficient familiarity (or access to qualified individuals) that can balance the trade-offs associated with the MQOs, such that rigid standards are not applied but rather the pooled effect (overall analytical uncertainty) of all items affecting measurement usability (bias, precision, selectivity, sensitivity) are considered. The following options are ranked from the most reliable (Option 1) to the least reliable (Option 4) and should be considered in light of the overall project goals. This guide does not purpose a specific set of procedural steps because each case is different and must be addressed by a consensus process involving appropriate representatives from the stakeholders.

6.6.1 *Option 1*—The most certainty in showing that a measurement system is free of unacceptable bias is obtained when the measurement system is shown to yield the same results as another system that employs a fundamentally different measurement principle. The likelihood is small that two analytical techniques will experience the same systematic errors and will be subject to the same types of chemical and physical interferences. If two such analytical techniques agree, the possibility of unknown systematic errors is substantially decreased. Therefore, showing that a different measurement technique yields the same results as the subject technique serves to validate the ability of the subject system to yield valid measurements. If the two techniques disagree, there is a possibility of systematic or random error in one or both techniques.

6.6.2 *Option 2*—The next lower level of certainty is obtained by determining the bias, precision, sensitivity, and selectivity of the candidate measurement system using reference materials provided by NIST, or some other appropriate national certifying authority (for example, Standards Canada, DIN). Such reference materials would have been confirmed by the use of multiple methods, each using a different analytical principle. Comparison of the test results from new methods with published reference values on such materials can be used to determine measurement system bias. Commercially produced reference materials may also be used, but the true values are usually developed using only one (sometimes two) analytical technique(s). The reliable use of reference standards is extremely sensitive to the degree that the reference materials have the same matrix/analyte physical properties and chemistry as the project samples. If the match of the properties between the project samples and the reference materials is poor, the study results can be misleading.

6.6.3 *Option 3*—The lack of availability of more than one analytical method (no alternative technology or resources) or of appropriate reference materials will prevent use of the techniques mentioned above. When this is the case, the use of matrix spikes and surrogates becomes the "best available technology" and can be a reliable option. As in all analytical studies, the analyst must support conclusions with scientific rationale, including the statistical basis of the number of samples analyzed, the evaluation of experimental measurements, and the limitations of the study.

6.6.3.1 *Inorganic Matrix Spikes*—While matrix spikes can be a valuable tool in demonstrating the validity of the measurement, the uncertainty associated with the chemical form of metals in the sample and the mechanism by which it is incorporated into the sample matrix diminishes the value of this technique compared to the previous two mentioned above. In general, matrix spikes are made from known amounts of the compounds or elements (most often in solution) added to the project sample. The form of the target metal in the sample matrix is unlikely to be the same as the form of the target metal in the spiking material. This may lead to a high recovery of the spiked material (because it's in a readily soluble form) compared to the recovery of the target metal originally present in the matrix. This could lead to the erroneous conclusion that the proposed method is efficient in recovering and quantitating the target analytes in the sample.

6.6.3.2 *Organic Matrix Spikes*—Matrix spikes of organic compounds suffer from similar limitations based on the degree and type of association between the target organic analyte and the sample matrix. In addition, the spiking vehicle (for example, solvent) must be compatible with the matrix to get the spike distributed properly into the matrix. Most field samples are "aged" and the analytes may become much more intimately associated with the matrix than the spiking compounds which

are only in contact with the matrix for very short periods of time prior to extraction and isolation for analysis.

6.6.3.3 *Surrogates*—The use of surrogates (used as a measure of analyte recovery of an analytical process) is a reliable means of demonstrating that the analytical technique is being performed correctly when their recoveries are high and within the statistically defined variance normally associated with their use. Calculation of surrogate recovery can be performed using either the reported concentration of the surrogate or the total response (peak area or height) of the analytical signal. This technique suffers from the same limitations as discussed above with matrix spikes. Additionally, more uncertainty is introduced if materials selected as surrogates do not perform in the same manner as the target analyte in the sample matrix. The use of compounds outside the list of those normally used in the determination of the target analytes must be preceded by studies demonstrating that the chosen compounds have a clearly defined correlation with the target analytes. The use of surrogates determines method performance compared to historical levels (developed from statistically derived acceptance criteria). This option does not determine the ability of a method to return the true value of analyte in the matrix since it does not involve the target analytes.

6.7 *Option 4, Use of Historical Analytical Results*—Performing additional studies may not be necessary to show that the proposed analytical protocol is appropriate unless required by the user/decision maker. In some instances, historical analytical results alone or in combination with abbreviated studies will suffice. The user should be informed of the laboratory's plan to use historical data to support the project. The user may elect to have the actual bias, precision, or sensitivity evaluated experimentally. Proprietary information or confidential information should not be used because review and evaluation may not be possible. Examples of the use of prior studies include but are not limited to:

6.7.1 Use of an extensive database on the performance (that is, bias, precision, sensitivity) of the candidate measurement system on project samples.

6.7.2 Validation that the measurement system was rugged/robust and the bias, precision sensitivity, and selectivity of the measurement system are well documented in available literature or reports for the analyte/matrix combination of interest.

6.7.3 The sample matrix of concern (for example, clay soils) is similar to other samples that the laboratory is familiar with and has historical analytical results, requiring only abbreviated tests to verify applicability such as performing a limited number of spike additions to splits of field samples.

6.7.4 The sample matrix and analytes are relatively simple (for example, drinking water, water from a clean surface stream) and bias, precision, and sensitivity analytical results on the application of the measurement system to the analyte/matrix exist in the literature.

6.8 Many inorganic and organic analyses rely on a sample preparation method prior to the determinative method to isolate the analytes of concern from the matrix. The use of new or modified preparative techniques is a viable way to achieve project objectives. The use of any preparative steps must be fully evaluated using the above options.

6.9 The subsequent sections discuss the application of these techniques to the demonstration of the bias, precision, selectivity, and sensitivity in more detail. In many cases, the strengths and weaknesses of the techniques are explained for the individual application.

7. Bias

7.1 *Definition of Bias*—Bias is the difference between the value determined using the measurement system in question and the true value; operationally, the difference between the sample mean and an accepted true value. Bias can be negative or positive (that is, the average of the measured values can be less than or more than the true value, respectively). Bias can be expressed in two ways: absolute bias (for example, the bias is −2 mg/L), or percent bias (for example, bias is +20 %). Method selectivity is an important element of analytical bias. Because of its importance, it is discussed separately in Section 10.

7.2 *Demonstration of Bias*—Ideally, the user will define the question to be answered by the information gathering study and the level of uncertainty that is acceptable (the DQO). Alternatively, the user may specify an acceptable level or range of bias (for example, a range of 20 % of the true concentration) for the laboratory to achieve. Through the use of the techniques described below, the laboratory determines the bias (if any) of the measurement system (including both the analytical technique and the operator in the matrix representative of those encountered in the project). This performance is then compared to the project MQOs.

7.3 *Guidance on Demonstration of Bias*—Demonstration of bias may be made through the conduct of new bias studies, the use of historical analytical results, or by some combination.

7.3.1 *Conduct of New Bias Studies*—There are four generally accepted techniques available for determining the bias of a measurement system. In the order of technical defensibility, these are:

7.3.1.1 Analysis of split samples using both the method to be verified and a second method that employs a fundamentally different measurement principle,

7.3.1.2 Analysis of a reference material (RM) whose matrix is analytically representative of the samples and contains the analyte at a concentration appropriate to the study,

7.3.1.3 Analysis of split samples using the method to be verified and a different but similar method, of known variability, that has been validated for the application by a recognized methods certification organization (for example, U.S. Environmental Protection Agency [EPA], ASTM, ISO, American Public Health Association) for the analytes of concern in the matrix of concern, and

7.3.1.4 Analysis of matrix spike samples.

7.3.2 The user is cautioned that the design of the experiments and number of replicates necessary to determine bias may not be a trivial exercise. Careful consideration must be given to the estimated level of target analytes, method sensitivity, and the presence of interferences. The design of the experiments must make appropriate use of statistical techniques to ensure that project objectives are met.

7.3.3 The choice among options depends on the available RMs, the number of viable analytical techniques, the available spiking materials, and the complexity of the sample matrix and

its constituents. Each of these options is discussed in more detail in the following sections.

7.3.3.1 *Option 1, Reference Materials*—Under this approach, samples of a RM are analyzed and the results compared to the known amount of the analyte (that is, the certified amount). The difference between the average analysis results and the known analyte concentration is the bias. Performing bias studies with RMs is useful if the field samples being tested are in relatively well-defined matrices (for example, tap water, coal fly ash). When matrices become complex (for example, soils which can be combinations of clays, silts, sands, organic matter) RMs may have limited value because they may not closely resemble the field samples. Similarly, when the contaminant mix is complex (for example, numerous compounds with similar chromatographic behavior to the compound being sought) RMs may be of limited value because of interferences (see discussion on selectivity in Section 10). Performing RM and spike tests may not accurately characterize and measure the analytes in the field sample because RMs are unlikely to contain the same number and concentration of individual compounds present in the original sample. Finally, RMs are not available for many types of analyte/matrix combinations.

7.3.3.2 *Option 2, Comparison to Alternative Measurement Technique Using a Fundamentally Different Technique*—Another approach to determine bias is the comparison of the analytical results from a candidate measurement system with those of an alternative measurement system that uses a fundamentally different science. The second technique should be recognized in the available literature as being applicable to the problem. Multiple measurement systems based on different scientific principles are unlikely to be subject to the same types of interferences and other problems. Therefore, when the same results are obtained using different methods, a high degree of confidence can be attached to the results. It should be pointed out that for the alternative technique approach to be scientifically valid, it is important that not only the determinative step be changed but also any preparative steps to ensure that the preparative step is not the accuracy limiting step.

7.3.3.3 *Option 3, Comparison to a Recognized Reference Method*—Another approach to determine bias is to compare the analytic results from the candidate measurement system to those of an alternative measurement system that has been validated for the application by a recognized methods certification organization (for example, EPA, ASTM, ISO, and American Public Health Association). To use this approach, the field sample is split and the splits are analyzed using both measurement systems. Similar results using both methods can be used to determine a lack of bias on the part of the subject method. Statistical analysis should be conducted on the two sets of results to determine whether the two methods yield significantly different results. If the two methods do not give the same results (no significant difference statistically), then additional testing will be necessary to determine the lack of bias or to determine the level of bias.

7.3.3.4 *Option 4, Matrix Spikes*—In this approach, known quantities of the analyte of concern are added to one or more aliquots of the field samples, the samples are analyzed, and the results are compared to the amount of added spike. The level of the spike should be close to the concentration of analyte anticipated to be in the field sample (for example, if the field sample is analyzed at 10 mg/L of the analyte of concern, then the spike should ideally also be near 10 mg/L). If too little of the analyte is used for the spiking, its presence may be masked. Masking occurs when the difference between the amount of added spike and its measured response is within normal analytical variance of the amount present in the original sample. If too much is used, the spike can mask the effect of interfering compounds originally present because the analytical variance of the measured response of the spiked sample exceeds the signal of the analyte in the original sample. For these reasons, it is important that the amount of added spike should be based on the estimated value of the target analyte after the field sample has been diluted to fall within the calibration range of the analytical method. When dilution of the field sample is required, the correct amount of spike should be added after the sample has been diluted to the correct range. Each of the spiked samples is then analyzed using the candidate measurement system. The average of the results of such analysis (for example, 22 mg/L) is compared with the results of measurement of an unspiked sample (that is, 10 mg/L). The arithmetic differences between the unspiked and the spiked sample average (22−10 or 12 mg/L) are compared to the known amount of the spike (10 mg/L). The amount of the spike that is recovered ($^{12}/_{10}$ or 120 %) indicates the bias is a positive 20 %. Where spiking is done properly and the physical and chemical properties of the sample are simple, the matrix spiking technique can produce an accurate measure of bias. For spiking to be valid, it should be performed using the actual sample matrix and mix of target analytes.

8. Precision

8.1 *Definition of Precision*—A measure of the scatter of measurement system test results obtained from samples that are ostensibly the same (for example, taken at the same time and location or from the same container).

8.2 *Demonstration of Precision*—Precision is determined by measuring the scatter or variability of the measurements resulting from replicate measurements of the same material. The desired level of precision should be specified by the user. It usually takes the form of an acceptable measurement system variability, for example, 10 % relative standard deviation (RSD) or the range of the average that equates to a specified degree of confidence (for example, true value lies within the range $\overline{X} \pm 3\sigma$ where σ is the standard deviation and the desired level of confidence is 99 %). It is important that the demonstration of precision be determined at the project action level (AL). The precision of most analytical techniques decreases when the concentration of the analyte decreases in the samples. Failure to match the demonstration to the action level will lead to an incorrect estimate of precision where it is most important, the action level.

8.3 *Guidance on Demonstration of Precision*—Precision may be determined by new precision studies, the use of historical analytical results from prior studies, the measured variability of the project samples, or analysis of laboratory

control samples that are representative of the analyte concentration and matrix of concern. The following are examples of approaches that may be used to determine and document precision.

8.3.1 *Project Samples*—Analysis of multiple samples of project material (for example, a series of effluent or waste samples taken over a period of time, a collection of soil samples taken from various points at a site, a series of hourly air samples) containing the analyte of interest will determine overall project-specific precision. Additionally, when the analytical results are obtained under a statistical design, the data can be analyzed using analysis of variance techniques to decompose the total variance into components due to sample variability and the variability (precision) of the measurement system. Sample variability may be composed of variance between field samples, subsampling variance, and differences in sample preparation. Note that this approach cannot be used to determine the precision of the measurement system alone (see 8.3.4) since it measures the total variability, which consists of the variance of the field sampling procedure (if one was necessary), and the variance of the measurement system. A major benefit of this approach is that it may eliminate the need to determine measurement system precision if the overall variability (sample preparation + measurement system + sample) is low enough to meet the study MQO/DQO. The use of this technique assumes that the samples submitted for evaluation adequately represent the variability of the actual materials being evaluated.

8.3.2 *Matrix Spikes*—Measurement system precision can be determined by the analysis of replicate matrix spike samples. The matrix spike is composed of analytes added to samples in known quantities and analyzed to assess the variability in recovery of the analyte due to the sample preparation and analytical steps. The matrix spike is added as early in the process as possible to ensure that as many sources of variability as possible can be evaluated. This means that matrix spikes should be added prior to any sample preparation and cleanup steps. While this approach accounts for matrix specific effects, problems associated with spiking can lead to the measured precision being better (that is, lower RSD) than it actually is. See discussion on problems associated with spiking in 6.6.3 for further information. One benefit of this approach is that precision can often be assessed without having to conduct additional analyses when spiked samples are also being used to determine analytical bias (see Section 6).

8.3.3 *Surrogates*—Surrogates are compounds that perform in a similar manner to the analytes of interest in the analytical procedure but are not naturally present in the samples analyzed. Surrogates are added to each sample prior to sample preparation (or when specified in the method). The percentage recovery monitors the extraction efficiency and any unusual matrix effects. The variability of surrogate recovery from multiple samples measures the precision of the measurement system at the surrogate concentration being used. This approach can be used if the analyte of interest is not commercially available or is too dangerous, toxic, or is unstable (that is, has a poor shelf life).

8.3.4 *Reference Materials or Laboratory Control Samples (LCS)*—These materials, normally used to ensure that the laboratory is operating in control, can also be used to assess measurement system precision. Such materials should be selected to provide a sample with analytically similar properties to that of the actual samples to be analyzed (matrix and concentrations similar to project samples). Reference materials and LCSs evaluate the precision of the entire measurement system including the sample preparation, cleanup, and determinative steps. If needed, this approach can be used to determine the precision of the determinative step alone as long as no preparation or other steps are required before the determinative step. When using reference materials whose certified analyte values and precision were obtained using a method that is different from the subject method, the precision obtained from the candidate method may be different from the certified precision. This difference indicates bias (see Section 7) between the two methods. The use of laboratory control samples as an indicator of laboratory precision is inappropriate if the sample matrix is much more complex than the matrix of the LCS.

8.4 *Use of Prior Studies*—Performing actual precision studies may not always be necessary, unless required by the user. Analytical results from historical files can be used if they cover the matrix of concern and are available for review and evaluation. In many instances, historical precision demonstrations alone or in combination with abbreviated studies will suffice.

9. Sensitivity

9.1 *Definition of Sensitivity*—Ability of the measurement system to yield valid measurements at the level of interest in the samples of concern.

9.2 *Demonstration of Sensitivity*—Sensitivity is determined by showing that the measurement system can measure the substance of interest at the level of interest in the matrix of concern.

9.3 *Guidance on Demonstration of Sensitivity*—Demonstration of adequate measurement system sensitivity may be made through the conduct of new sensitivity determinations or through the evaluation of historical analytical results combined with a verification of the test. Adequate sensitivity can be determined in a number of ways. The most valid approach is to analyze a matrix spike or reference material that contains the analyte of interest at a level 0.2 to 0.5 times the level of interest and confirm the measurement sensitivity. If the objective of the analysis is to determine if the samples contain 10 ppm or more of a particular analyte, then demonstrating acceptable measurement system accuracy at a concentration of 2 to 5 ppm in the matrix of concern determines that the measurement system has adequate sensitivity for the purpose at hand.

9.3.1 Alternative approaches to demonstrating sensitivity by either identifying the presence or determining the concentration of the analyte of concern (whichever is germane to the situation at hand) include the following, if they are conducted in the matrix of interest.

9.3.1.1 Level of detection determination:

(1) Critical Level Approach (Currie, 1968),

(2) Detection Limit Approach (Hubaux and Vos, 1970),

(3) Decision Limit Approach using Noncentral *t*-Distribution (Clayton et al., 1987),

(4) U.S. EPA Method Detection Limit Approach (40 CFR 136, Appendix B), and

(5) Weighted Least Squares Approach (Gibbons et al., 1997).

9.3.1.2 Level of quantitation determination.

9.3.2 Results from bias studies conducted at the concentration of interest can also be used to determine adequate system sensitivity if a response significantly above the baseline is noted.

9.4 The level of effort that should be used to determine adequate sensitivity is dependent upon several factors, including but not limited to:

9.4.1 The closeness that the estimated project sample concentration is to the known system sensitivity,

9.4.2 The variability of the sample matrix (presence of interference), and

9.4.3 Stability of the measurement system over the period of analysis.

9.4.4 For example, if the question being addressed is whether the discharge concentration is below the permit level of 1 mg/L, then the demonstration only has to show that the system can yield accurate results at a level of 1 mg/L (this usually means showing that reliable quantitation is achieved at 0.2 to 0.5 mg/L).

10. Selectivity

10.1 *Definition of Selectivity*—The ability to accurately measure the analyte in the presence of other sample matrix components or analytical process reagents. Selectivity or the lack thereof, is one aspect of bias in analytical measurements. In this guide, selectivity is discussed as a separate subject because of its importance in developing accurate analytical information to support project decisions. See Section 6 for a complete discussion of bias.

10.2 *Demonstration of Selectivity*:

10.2.1 Selectivity can usually be adequately determined by various approaches. These include the following:

10.2.1.1 Method of standard additions as found in 10.5.1,

10.2.1.2 Comparison of results of a test in the concentration range of interest of samples with and without potential interferences,

10.2.1.3 Comparison to the results of a test that uses a different measurement principle, or

10.2.1.4 Demonstrating that potential interferences do not adversely affect the decision resulting from the use of the measurements.

10.2.2 For example, a successful demonstration of selectivity might use samples of the matrix that contain the same potential interferences that are present in actual samples to determine that the measurement system is free from:

10.2.2.1 Overlapping chromatographic peaks in the region where the compound of interest elutes,

10.2.2.2 Interfering ions in mass spectrum,

10.2.2.3 Overlapping spectral peaks in emission spectrometry,

10.2.2.4 Interfering absorbances in absorption spectrometry, and

10.2.2.5 Cross sensitivity in immunoassay.

10.3 Selectivity is not an absolute. This means that interfering substances can affect the reported results while the measurement system is still considered suitable for its intended purpose. The interferences do not affect the usability of the measurements if the sum of both the target analyte and the absolute value of the interfering substance are below the action level for the project (this can happen in chromatographic methods when the interferents co-elute with the target analyte). Spectroscopic methods can have spectral inferences (emission, absorbance) in the region where the target analyte is measured. The method is suitable for its intended use if the emission lines or spectral absorbance do not cause the measured value of the target analyte to be outside the project-specific acceptability levels.

10.4 When demonstrating the effect of potential interferences, the direction of the likely interference needs to be taken into account. Negative interferences decrease the measured response of the target analyte and lead to a result that is biased low. Positive interferences increase the measured response and lead to a result that is biased high. Depending on the use of the measurements, one type of interference may be allowable while the other may not. The project stakeholders should provide the laboratory with any limitations on the allowable level of both positive and negative interferences. In the absence of such guidance, the laboratory must document the level of interference found.

10.5 *Guidance on Demonstration of Selectivity*—Demonstration of freedom from interferences may be determined in a number of ways. These include but are not limited to:

10.5.1 *Use of Method of Standard Addition*—The method of standard additions can determine selectivity for the target analytes in samples whose matrices are unknown or have not been characterized previously. After the sample matrix (believed to contain no or low levels of target analytes) has been through the sample preparation step, a series of spikes are added to the prepared matrix solution. The plot of the concentration of added analyte versus measured concentration determines the presence of bias if the slope of the linear regression best fit line deviates from the theoretical value of 1.0 for no interference. Values less than one indicate a negative bias; values greater than one indicate a positive bias. The absence of bias is indicated if the slope is 1.0. Straight line linear regression solutions occur when there is a one-to-one correlation between the biasing agent and the target analyte. Curvilinear plots occur when there are more than two interferents with different levels of influence or when the effect of a single interferent is nonlinear.

10.5.2 *Demonstrating Absence of Known Interferents*—The absence of known interferences can be determined by the direct analysis of the sample for the interferents or by spiking the sample with known amounts of the potential interferents and measuring their effect on the target analytes. The use of the second approach is restricted to cases where the quantitative correlation of bias versus interferent concentration is known.

This is necessary for the back calculation of the interferent concentration based on the amount of bias determined by the addition of the interferent spikes to sample.

10.5.3 *Verification of Results Using Fundamentally Different Measurement System*—Analytical techniques that are fundamentally different from the proposed measurement system can be used to determine that the proposed system is free from interferences. This is because fundamentally different analytical techniques have differing responses to potential interferences. If the two techniques give the same quantitative results, it is likely that the target analytes are free from interferences by both techniques. It is important that comparisons be conducted on aliquots of the same sample material as the project samples, and that appropriate statistical techniques are used to determine that the two sets of measurements give the same estimated value of the target analyte.

10.5.4 *Use of Appropriate Reference Materials*—Reference materials known to be similar to project samples can be used to determine the absence of interferents in the concentrations of the target analytes. The reference material does not need to contain the target analytes because they can be added as spikes. If spikes are necessary, they should be added prior to any required sample preparation steps. A one-to-one correlation of the spiked amount with the measured values indicates the lack of interferents.

10.6 In general, analyzing a representative sample with known analyte concentration and demonstrating acceptable results determines the lack of interferences and acceptable selectivity. The sample should be representative of the sample matrix, analyte, and concentration. Multiple samples may be necessary for complex matrices or sites where only one sample is unlikely to be representative of the analytical challenges. Judgment and knowledge of similar measurement principles, analytes, and matrix components should be used to address selectivity issues. Documentation of the reasoning in such a manner that a peer reviewer would be able to understand the process must be provided.

11. Assessing Measurement System Suitability

11.1 A measurement system is appropriate for its intended application if the resulting measurements are suitable for their intended use. Thus, a measurement system may be suitable for one purpose but not be appropriate for a different application. The criteria for overall suitability are expressed as the data quality objectives (DQO). DQOs establish the acceptable level of overall uncertainty in the project decision from the combined sampling and analytical operations. Measurement quality objectives (MQO) address only uncertainty of measurements from the analytical or measurement process of the laboratory. The user of this standard is cautioned that this is an important difference as illustrated in the example in Appendix X1.

11.2 *Measurement Quality Objective Criteria*—Assessing measurement system performance when a measurement quality objective has been established is a relatively straightforward exercise. The bias, precision, selectivity, and sensitivity that were determined for the measurement system are compared to the measurement quality objectives. If they are within the range of their respective MQOs, then the measurement system provides measurements suitable for its intended use. See X1.2 for an example of the application of this approach.

11.3 *Data Quality Objective Criteria*—Assessing measurement system performance when a data quality objective has been established is a multi-step process. Since the DQO establishes the overall uncertainty that is acceptable for a project, it is necessary to estimate uncertainty associated with the sampling and analysis activities. This is normally part of the DQO process and should be documented in the project records. If not, the laboratory and user should agree on the acceptable level of uncertainty that can be attributed to the sampling process.

11.4 The uncertainty in the analytical results (total uncertainty minus sampling uncertainty) can be expressed as an MQO by first estimating the concentration of the target analyte at the site. Then the uncertainty in the analytical data for this concentration is made using preliminary site survey data but if preliminary information is not available, data from similar analyte/matrix samples can be used for the concentration range of interest. Once the concentration has been estimated, the precision of the measurement system is then estimated based on actual site data.

11.5 The ultimate purpose is to compare the site concentration of an analyte to an action level (AL), after adjusting it for overall bias from the sampling and measurement process and accounting for sampling and analytical variabilities. This final adjusted concentration can be called the upper limit (UCL) and is expressed in the equation below.

$$\frac{X_e}{1 - bias_{overall}} + t\delta \leq UCL \quad (1)$$

where:

X_e = expected or specified site concentration for analyte to be measured in mg/kg,

$bias_{overall}$ = percent of material, expressed as a decimal (represents both sampling and analytical bias),

δ = variability of estimated mean sample concentration (square root of the sum of sampling variability + variability of measurement system), mg/kg, and

t = tabled *t*-value dependent on the number of samples tested and the level of confidence that is acceptable to the user.

11.5.1 The UCL can then be compared to the AL (if a separate action level has been established by the stakeholders) and, depending on the outcome of the comparison, an appropriate action can be taken.

11.5.2 Alternatively, if the stakeholders can estimate the UCL and the expected site concentration (X_e) with its associated variability, δ, the overall acceptable bias can be calculated using Eq 1. When the calculated bias, ${}^{UCL}b_{X_e,\delta}$, is greater than or equal to the bias determined using reference materials with similar matrices to the site or matrix spikes (when appropriate reference materials are not available), then the data is acceptable for its intended use. If the experimental data show that the analytical bias exceeds ${}^{UCL}b_{X_e,\delta}$, the analytical methodology is not acceptable.

11.5.3 The utility of the DQO approach to evaluating analytical acceptability has an added advantage over the MQO approach because it allows the project team to balance sampling considerations (statistical approach, number of samples) with analytical bias. The bias and precision (δ) of the sampling and measurement system can be adjusted as long as the condition given by Eq 1 is met. See X1.3 for an example.

11.6 With respect to sensitivity, the criterion for the measurement system is that it is sensitive enough to measure the property being measured at the level of interest (generally the AL). As a general rule, for most environmental applications involving very low levels of analysis, if the measurement system is sensitive enough to measure the analyte or property of interest at a value of 0.2 × AL, the system is sufficiently sensitive for the intended application. For measurement systems that determine high levels of precision at the level of concern, adequate sensitivity can approach the AL. Therefore, if a spiked sample or reference material containing the analyte at a level below the MQO or AL (in the case of a DQO based standard) has been successfully analyzed, then sensitivity will have been determined.

12. Documentation

12.1 For measurements to be of known and documented quality, the following minimum information set is needed in addition to the analytical results:

12.1.1 Bias of measurement system and how determined,

12.1.2 Sensitivity of measurement system and how determined,

12.1.3 Precision of measurement system (and how determined) or variability of measurement system + sample, and

12.1.4 Description of how adequate selectivity was determined.

12.2 If the measurement system does not achieve the requisite bias, sensitivity, and precision, the laboratory must document the actual determined bias, precision, and sensitivity and notify the user of any requirement that cannot be met. At a minimum, the inability to meet bias, precision, or sensitivity requirements should be discussed in the case narrative accompanying the final report. In the absence of user-specified levels of measurement quality, the laboratory may establish quality levels based on its internal standard operating procedures and report them along with the results of the sample testing.

APPENDIX

(Nonmandatory Information)

X1. EXAMPLES ON THE ASSESSMENT OF LABORATORY DATA

INTRODUCTION

The following example is used to illustrate the evaluation of analytical data based on site-specific quality requirements using both the MQO and DQO approaches.

X1.1 Description of the Problem

X1.1.1 A site containing a recently sandblasted house was assessed for lead contamination using a hot acid leach combined with analysis using flame atomic absorption. The objective agreed upon by the stakeholders shows the upper concentration limit (UCL) for lead is less than 400 mg/kg with 95 % confidence. The MQOs established by the data user are:

X1.1.1.1 Bias ≤ 15 % near the action level concentration,

X1.1.1.2 Precision (RSD) ≤ 10 % of the action level for concentrations near the AL, and

X1.1.1.3 Sensitivity ≤ 100 mg/kg.

X1.1.2 The measurement system was evaluated by replicate analyses on three samples randomly collected across the site and by analysis of a lead-containing soil reference material characteristic of the site soil. The reference material lead concentration was certified as 90 ± 0.8 mg/kg. The results of the analyses and statistical summary of the data are shown in Table X1.1. The data in Table X1.1 consist of three samples randomly selected at the site. Each sample was subsampled to produce three replicates, each of which was digested and analyzed separately. These data can be analyzed by analysis of variance (ANOVA) to estimate the total sampling and analytical variance, δ, as well as its components, sampling variance (σ^2_s) and analytical variance (σ^2_a). ANOVA gives an estimated sampling variance and analytical variance as follows:

TABLE X1.1 Results of Data Assessment

	Reference Material	Sample #, mg/kg			Average Site Properties
		1	2	3	
Replicate 1	85.1	26.50	50.20	48.50	
Replicate 2	88.5	28.40	50.40	43.40	
Replicate 3	86.3	30.80	55.30	55.20	
Mean	86.6	28.57	51.97	49.03	
Standard Deviation (SD)	1.41	1.76	2.36	4.83	
RSD, %	1.63	6.16	4.54	9.85	6.85
Mean Concentration					43.19
Standard Deviation of Mean Concentration					12.75

$$\sigma^2_s = 157.17$$

$$\sigma^2_a = 16.00$$

X1.1.2.1 Thus, the total standard deviation of the estimated lead concentration is:

$$\delta = \sqrt{(\sigma^2_s + \sigma^2_a)}$$

$$= \sqrt{(157.17 + 16.00)}$$

$$= 13.16 \text{ mg/kg}$$

X1.1.2.2 The degree of freedom for the residual term from the ANOVA is 6 ([3 samples − 1] [3 replicates] = 6). This degree of freedom, together with the desired confidence level, can be used to find the tabled *t*-value for future calculations of bias using Eq 1.

X1.2 Assessing Measurement System Suitability against Measurement Quality Objectives

X1.2.1 *$Bias_{mqo}$*—Using the results from analysis of the reference material, the bias of the measurement system (*$bias_{mqo}$*) is (86.6 − 90.0)/90.0 ≃ −4 %. Results indicate that the measurement system underestimated the actual concentration of lead in the reference soil by 4 % (a negative bias). The MQO for bias is ± 15 % at the 400 mg/kg level; therefore, the measurement system determines acceptable bias for the analysis because bias and precision normally improve as the sample concentration increases. Note that this assessment of bias is limited to measurement bias because it contains no sampling component. At the practical level, sample variability approaches zero ($\sigma^2_s \rightarrow 0$) for reference materials.

X1.2.2 *Precision*—The MQO for precision was established at a RSD of ≤ 10 % of the AL of 400 mg/kg. Table X1.1 shows the average measurement system RSD was 6.85 % and the maximum RSD for any site sample location was 9.85 %, both of which are less than the MQO of 10 %. Therefore, the overall system (sampling and analytical activities) determines that it is suitable for the intended application.

X1.2.3 *Sensitivity*—The MQO for sensitivity is 100 mg/kg. The reference material concentration was 90.0 mg/kg. Adequate sensitivity was determined since the analysis of reference material replicates gave a value for the mean reference material lead concentration of 86.6 mg/kg with acceptable bias.

X1.3 Assessing Measurement System Suitability against Data Quality Objectives

X1.3.1 The example given in this appendix sets the MQO for bias (*$bias_{mqo}$*) at less than 15 %. This type of specification is limited to the acceptable measurement bias. If the example were changed to establish that the DQO for the project bias (*$bias_{dqo}$*) as being less than 15 %, the evaluation of suitability must use the approach described in 11.3 as shown below. Overall project bias is the result of the summation of sampling bias and measurement bias. If they are of opposite signs (one positive and one negative) they will tend to cancel each other out.

X1.3.2 *$Bias_{dqo}$*—The maximum total *$bias_{dqo}$* that the project data could have and still determine that the project DQO has been achieved is calculated using Eq 1:

$$\frac{X_e}{1 - bias_{overall}} + t\delta \leq UCL$$

where:

X_e = estimate of the expected maximum lead concentration (60 mg/kg),
δ = standard deviation for all samples (overall variability of the site data),
t = value for t at the target confidence level with appropriate degrees of freedom, and
UCL = acceptable upper concentration limit of the samples (400 mg/kg).

X1.3.2.1 From the results of the screening analyses of the samples collected at the site in Table X1.1, the expected maximum concentration was estimated by the stakeholders to be 60 mg/kg (slightly above the highest concentration found in the test samples). The total variability in the nine sample analyses was shown to be 13.16 % and was derived using ANOVA analysis on the concentrations of three samples from the site (each analyzed in triplicate).

X1.3.2.2 Solving for acceptable *$bias_{dqo}$* at the 95 % confidence level (student-t = 1.943) set by the stakeholders gives the following result:

$$^{400}Bias_{60} = 1 - 60/(400 - 1.943 \cdot 13.16) = 0.84 \text{ or } 84\ \%$$

X1.3.2.3 The data from the reference material indicates that the bias at the 90 mg/kg level is only −4 %. Since the level of bias at the 60 mg/kg level is less than the acceptable maximum of 84 %, it results in analytical system producing data suitable for its intended use.

X1.4 Interrelationship between $Bias_{dqo}$ and Total Variability of Sampling and Analytical Activities

X1.4.1 As noted in 11.3, use of the DQO approach in specifying overall performance of both the sampling and analytical activities allows the project team the flexibility to balance sampling and measurement considerations to achieve acceptable levels of uncertainty in project decisions. As illustrated in X1.2, the evaluation of measurement bias leads to a pass/fail decision on the applicability of the measurement approach. It does not allow the project team and the laboratory to accept higher levels of bias as overall sampling and analytical variability, δ decreases (see X1.3.2), or if the estimate of the analyte concentration in the field samples is low compared to the UCL or AL (see X1.1). Conversely, as sampling and analytical variability increases (situations of increasing delta (δ) and therefore increasing RSD) as illustrated in X1.3.2 or as the actual field concentration approaches the UCL or AL (see A-3.3), the team cannot take advantage of low levels of bias in the analytical process to achieve overall acceptability of the final project decision. Simple illustrations of these points are given below.

X1.4.2 *Impact of Overall Variability,* δ*, on Acceptable Level of Bias*:

X1.4.2.1 Assume:

UCL = 400 mg/kg,

Three site samples are analyzed in triplicate, degrees of freedom = 6; therefore, t = 1.943,

X_e = 200 mg/kg, and

δ = 100 mg/kg.

X1.4.2.2 Using these assumptions, $^{UCL}b_{X_e,100}$ = 3 %

If overall variability, δ, decreases to 60 mg/kg, $^{UCL}b_{X_e,60}$ = 29 %,

If overall variability, δ, decreases to 30 mg/kg, $^{UCL}b_{X_e,30}$ = 42 %,

If overall variability, δ, decreases to 10 mg/kg, $^{UCL}b_{X_e,10}$ = 48 %, and

At zero variability, δ = 0 and $^{UCL}b_{X_e,0}$ = 50 %.

X1.4.2.3 For a fixed number of degrees of freedom ([number of samples − 1] [number of replicate analyses]), this relationship is governed by two limiting conditions: (*1*) the situation at which overall variability approaches zero as in the case of a perfectly mixed material collected and analyzed with no sampling or analytical variability, and (*2*) the concentration level at which no further improvements in ${}^{UCL}b_{X_e,\delta}$ can be realized by further reduction of the overall variability. The first situation is given by solving equation 1 for bias to result in Eq X1.1.

$$ {}^{UCL}b_{X_e,\delta} = 1 - \left(\frac{X_e}{UCL - t\delta}\right) \quad \text{(X1.1)} $$

X1.4.2.4 When overall variability, δ is 0, the equation reduces to:

$$ {}^{UCL}b_{X_e,0} = 1 - \left(\frac{X_e}{UCL}\right) \quad \text{(X1.2)} $$

X1.4.2.5 This is a general equation and can be used for any combination of UCL (or AL), X_e, and degrees of freedom (because the delta (δ) term in Eq X1.1 is 0). This equation allows the determination of the maximum allowable bias for any measurement system applied to samples with no variability between samples for any action level and estimated site concentration.

X1.4.2.6 For the other case, one in which no further improvement in ${}^{UCL}b_{X_e,\delta}$ can be realized by improvements (Δδ) in overall sampling and analysis variability is given by Eq X1.3:

$$ 1 - \left(\frac{X_e}{UCL - \Delta(t\delta)}\right) = 0 \quad \text{(X1.3)} $$

X1.4.2.7 At the unique value of $t\delta$ at which no further improvement in bias occurs the equation becomes:

$$ \left(\frac{X_e}{UCL - t\delta}\right) = 1 \quad \text{(X1.4)} $$

or

$$ t\delta = UCL - X_e $$

X1.4.2.8 This value of $t\delta$ will vary with changes in the UCL and X_e. However, if the project team can accurately estimate X_e and the UCL (or AL) is known, Eq X1.4 can be used to estimate the minimum number of samples and replicates that will yield an acceptable $bias_{dqo}$ based on a known or estimated value of overall variability, δ, as shown in the following paragraph.

X1.4.2.9 Using the situation described in X1.1, the maximum allowable variability in the analytical data is 40 mg/kg (10 % of the action level of 400 mg/kg). For an estimated site concentration of 60 mg/kg, the student-*t* value, which determines an acceptable level of bias is 8.5 ([400 − 60]/40) which corresponds to less than one degree of freedom or less than one sample. At estimated site concentrations near 60 mg/kg and an action level of 400 mg/kg, bias is trivial and does not need to be evaluated as part of the DQO evaluation process. If the estimated site concentration is 300 mg/kg, the student-*t* value which determines an acceptable level of bias, is 2.5 ([400 − 300]/40) which corresponds to four degrees of freedom that can be reached with five samples analyzed once ([5 − 1] [1] = 4) or three samples analyzed in duplicate ([3 − 1] [2] = 4). The choice of which scenario to employ depends on the relative cost between sampling and analysis. This method of estimating the total number of samples and replicates holds as long as the RSD among all the samples is less than the 40 mg/kg used in the calculations (this assumes that the DQO for precision is 40 mg/kg). If the actual site RSD from the collected samples is greater than 40 mg/kg the underlying assumption of the calculation was not met and the number of samples is inadequate to establish if acceptable bias was achieved. This indicates that the initial DQO will have to be revised or more samples collected until the new $t\delta$ term is less than UCL − X_e.

X1.4.3 *Impact of the Estimate of Mean Concentration, X_e, Approaching the UCL (or AL)*:

X1.4.3.1 As the estimate of the mean concentration of the target analyte, X_e, approaches the level at which project decisions are made (UCL or AL), the acceptability of the measurement system bias becomes more important. In the limiting case where the UCL approaches the actual estimated site concentration, Eq X1.1 indicates that acceptable bias approaches 0.

X1.4.3.2 An increase in the number of samples collected from the site will cause a decrease in the student-*t* once the numbers of degrees of freedom are increased. In the example discussed above, three samples were analyzed in triplicate, therefore the degrees of freedom are (3 − 1) (3) = 6. At the 95 % confidence level, t = 1.943. If the number of samples is increased to 7, the degrees of freedom increases to 18 and the student-*t* decreases to 1.734. An increase in the number of samples from the site will also lead to a lower value of sampling variability which is a component of the total variability, δ. Both of these conditions will decrease the value of the $t\delta$ term and will cause a decrease in the overall bias as determined in Eq X1.1.

X1.4.3.3 It is reasonable to determine at what point does the difference between the UCL and X_e become so large that improving measurement bias makes no significant impact on the usability of environmental data? Table X1.2 shows the impact of varying the ratio of X_e to the UCL from 1 to 100 for different values of the $t\delta$ term, where t = the student t value for n-degrees of freedom (number of samples − 1) (number of replicates of each sample analyzed). The total variability of the

TABLE X1.2 Variation of Acceptable Bias %, with Different Combinations of UCL, X_e, and $t\delta$[A]

X_e	UCL	$t\delta$ Term				
		0	5	10	15	25
		Acceptable Bias, %				
1	100	99	99	99	99	99
10	100	90	89	89	88	87
20	100	80	79	78	76	73
30	100	70	68	67	65	60
40	100	60	58	56	53	47
50	100	50	47	44	41	33
60	100	40	37	33	29	20
70	100	30	26	22	18	7
80	100	20	16	11	[B]	[B]
90	100	10	[B]	[B]	[B]	[B]
100	100	[B]	[B]	[B]	[B]	[B]

[A] t = student-*t* value for n-degrees of freedom ([number of samples − 1] [number of replicates]); δ = total variability of analytical results.
[B] No level of acceptable bias.

analytical results, δ, is determined from preliminary screening data or estimated from similar target analyte/matrix data.

X1.4.3.4 Table X1.2 shows that for any given ratio of X_e to UCL, the decrease in the bias achieved by reducing the size of the $t\delta$ term by an increased level of sampling is small at low ratios of X_e to the UCL (up to 50/50). However, as X_e approaches the UCL, this reduction can lead to a two-fold to fourfold increase in the level of acceptable bias (at the 60/100 and 70/100 ratios, respectively). Therefore, an increased number of samples may allow the project to reach the level of acceptable bias specified by the stakeholders for a given level if uncertainty in their final decision.