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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]

This standard is issued under the fixed designation D6956; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory ~~requirements~~limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4687 Guide for General Planning of Waste Sampling

D5283 Practice for Generation of Environmental Data Related to Waste Management Activities: Quality Assurance and Quality Control Planning and Implementation

D5681 Terminology for Waste and Waste Management

D5792 Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives

D5956 Guide for Sampling Strategies for Heterogeneous Wastes

D6044 Guide for Representative Sampling for Management of Waste and Contaminated Media

D6233 Guide for Data Assessment for Environmental Waste Management Activities (Withdrawn 2016)[3]

D6250 Practice for Derivation of Decision Point and Confidence Limit for Statistical Testing of Mean Concentration in Waste Management Decisions

[1] This guide is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.01 on Planning for Sampling.

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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] The last approved version of this historical standard is referenced on www.astm.org.

D6311 Guide for Generation of Environmental Data Related to Waste Management Activities: Selection and Optimization of Sampling Design
D6582 Guide for Ranked Set Sampling: Efficient Estimation of a Mean Concentration in Environmental Sampling (Withdrawn 2012)[3]
D6597 Practice for Assessment of Attaining Clean Up Level for Site Closure (Withdrawn 2016)[3]

2.2 *Other Documents:*

Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, National Institute of Standard Technology Technical Note 1297, 1994 [4]

ISO/IEC 17025:1999 General Requirements for the Competence of Testing and Calibration Laboratories[5]

Quantifying Uncertainty in Analytical Measurement, EURACHEM/ CITAC Guide, ~~second edition,~~Second Edition, 2000[6]

3. Terminology

3.1 For definitions of terms used in this guide, refer to Terminology D5681.

3.2 *Definitions:*

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

3.2.2 *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.

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

3.2.4 *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.

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

3.2.6 *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.

[4] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.
[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.
[6] Available from http://www.citac.cc/QUAM2000–1.pdf.

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~~propose 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],~~(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).~~ 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~~10 mg ~~mg/L).~~ 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 $\bar{X} \pm 3\sigma$ 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