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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, health, and environmental practices and determine the applicability of regulatory 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

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

[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.

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, 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.

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 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

[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.

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 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.