

NIST Special Publication 260-136

Standard Reference Materials

Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements

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Issued January 2000

National Institute of Standards and Technology Special Publication 260-136
Natl. Inst. Stand. Technol. Spec. Publ. 260-136, 16 pages (Jan. 2000)
CODEN: NSPUE2

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 2000

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402-9325

FOREWORD

The National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, was established by the U.S. Congress in 1901 and charged with the responsibility for establishing a measurement foundation to facilitate both U.S. and international commerce. This charge was purposely stated in broad terms to provide NIST with the ability to establish and implement its programs in response to changes in national needs and priorities.

Increased requirements for quality systems documentation for trade and effective decision-making regarding the health and safety of the U.S. population have increased the need for demonstrating “traceability-to-NIST” and establishing a more formal means for documenting measurement comparability with standards laboratories of other nations and/or regions. Standard Reference Materials (SRMs) are certified reference materials (CRMs) issued under NIST trademark that are well-characterized using state-of-the-art measurement methods for the determination of chemical composition and/or physical properties. SRMs are used to ensure the accuracy, traceability, and comparability of measurement results in many diverse fields of science, industry, and technology, both within the United States and throughout the world. The NIST Special Publication 260 Series is designed to provide details concerning the procedures and philosophy used at NIST to produce and certify SRMs and their appropriate use. A list of these publications can be accessed through the Internet at <http://ts.nist.gov/srm>.

This document provides definitions of the terms and a description of NIST’s current practices for value-assigning SRMs and reference materials (RMs) used for calibrating and/or validating instrumentation and/or methods and procedures used for chemical measurements.

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Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurement

I. Introduction

Standard Reference Materials (SRMs) are certified reference materials (CRMs), issued under the National Institute of Standards and Technology (NIST) trademark that are well-characterized using state-of-the-art measurement methods and/or technologies for the determination of chemical composition and/or physical properties. Traditionally, SRMs have been the primary tools that NIST (formerly National Bureau of Standards) provides to the user community for achieving chemical measurement quality assurance and traceability to national standards.

This publication provides definitions of the terms and descriptions of NIST's current practices for value-assigning SRMs and reference materials (RMs) used for calibrating and/or validating instrumentation and/or methods and procedures used for chemical measurements. The terms and modes as described in this document are applicable for reference materials that support chemical measurements issued by NIST as of October 1, 1998.

Table 1 lists the seven modes used at NIST for value-assigning SRMs and RMs for chemical measurements and links the modes to three possible data quality descriptors: NIST Certified Values, NIST Reference Values, and NIST Information Values. A **NIST Certified Value** represents data for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or accounted for by NIST. A **NIST Reference Value** is a best estimate of the true value provided by NIST where all known or suspected sources of bias have not been fully investigated by NIST. A **NIST Information Value** is a value that will be of interest and use to the SRM/RM user, but insufficient information is available to assess the uncertainty associated with the value. Definitions of these modes are given in section IV.

Table 1. Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements

		NIST Certified Value	NIST Reference Value	NIST Information Value
1.	Certification at NIST Using a Single Primary Method with Confirmation by Other Method(s)	Y		
2.	Certification at NIST Using Two Independent Critically-Evaluated Methods	Y	Y	
3.	Certification/Value-Assignment Using One Method at NIST and Different Methods by Outside Collaborating Laboratories	Y	Y	
4.	Value-Assignment Based On Measurements by Two or More Laboratories Using Different Methods in Collaboration with NIST		Y	Y
5.	Value-Assignment Based on a Method-Specific Protocol		Y	Y
6.	Value-Assignment Based on NIST Measurements Using a Single Method or Measurements by an Outside Collaborating Laboratory Using a Single Method		Y	Y
7.	Value-Assignment Based on Selected Data from Interlaboratory Studies		Y	Y

The choice of mode(s) to be used in the value-assignment for any SRM for chemical measurements is based on our previous experiences and knowledge of the specific matrix, analyte(s) of interest, current measurement capabilities, the quality of the analytical methods results, and the intended use of the material.

The final designation of an assigned-value for an SRM as a NIST Certified Value, NIST Reference Value, or NIST Information Value is based on the specific value-assignment mode used and the assessed quality of the resulting data relative to the intended use of the material.

II. NIST Practices for Value-Assignment of SRMs and RMs for Chemical Measurements

Generally, NIST does not make or fabricate the materials from which SRMs are produced. Rather, U.S. industry, scientific groups, or companies on contract to NIST provide materials that meet NIST specifications.

Techniques and methods used at NIST for providing certified values for SRMs for chemical measurements are critically evaluated and have demonstrated accuracy in the matrix under investigation. Potential sources of error for such methods are evaluated and addressed [1,2]. Methods that are “ratio-based” (i.e., that require instrumental comparison versus calibrants of a known quantity of the measurand) use high-purity, well-characterized primary reference compounds or species as their basis for calibration (either directly or through gravimetrically prepared calibration solutions, e.g., NIST Elemental Solution SRMs).

The details of NIST methods and their testing are well documented (i.e., internal NIST Reports of Analysis) and often published in refereed technical journals. When results from outside laboratories are used in the value-assignment process, the NIST Chemical Science and Technology Laboratory (CSTL) is responsible for the selection of the laboratories and the technical evaluation of these reported data.

Appropriate control materials are concurrently analyzed in all value-assignment activities – both within NIST and by any outside collaborating laboratories. When available, appropriate SRMs or CRMs from other National Metrology Laboratories are used for this purpose.

III. Modes for Value-Assignment and/or Certification

The quality of assigned values for any CRM is based on the existence and application of sound measurement principles and practices. It is with this basic premise that we provide the following seven modes used at NIST to acquire analytical data for the value assignment of our SRMs and RMs for chemical measurements and link these modes to three data quality descriptors: NIST Certified Values, NIST Reference Values and NIST Information Values.

1. Certification at NIST Using a Single Primary Method with Confirmation by Other Method(s)

The Consultative Committee on the Quantity of Material (CCQM) [3] has described a primary method as:

“A primary method of measurement is a method having the highest metrological properties, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units.

A primary direct method: measures the value of an unknown without reference to a standard of the same quantity.

A primary ratio method: measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation.”

Certification at NIST using a single primary method is only possible when (with the exception of special cases noted below in 1.1, 1.2, and 1.3) [4]:

- All potentially significant sources of error have been evaluated explicitly for the application of the method and the matrix under investigation; a short written description is provided in the Report of Analysis for other sources of error that might reasonably be present and why they are not expected to be significant in this particular case.
- Confirmation of measurements by a primary NIST method can be accomplished by one or more of the following:
 - determination of certified constituents in other SRM(s) or CRM(s) of similar matrix and constituent concentration range;
 - a second NIST technique with appropriate controls; or
 - results of measurements from selected outside collaborating laboratories with appropriate experience.

The required level of agreement between the primary method and any confirmatory method(s) must be predetermined and specified in the experimental plan.

1.1. Certification of Gaseous Mixtures at NIST Using a Primary Method

Certification of gaseous mixture SRMs at NIST requires that:

- Primary standard suites be prepared gravimetrically from well-characterized starting materials and demonstrated to be internally consistent by a well-characterized analytical method.
- NIST primary standards be intercompared with primary standards from other National Metrology Laboratories or verified by a second NIST independent technique.
- Primary standards be documented to be stable for a minimum of two years.
- SRMs be value-assigned relative to the NIST primary standard suites.
- Uncertainty associated with the certified value includes contributions from the uncertainties associated with the primary standard suite, the analytical ratio method used to compare the SRM and primary standards, and the heterogeneity of the SRM lot.
 - The lot homogeneity is determined by NIST analysis of all samples.
- Absence of significant impurities in the SRMs be verified by NIST analyses.

1.2. Certification of NIST pH SRMs

Certification of NIST pH SRMs requires that:

- Homogeneity of the candidate material(s) for each pH SRM be evaluated by intercomparisons of randomly selected aliquots of candidate material(s) normalized to the preceding issuance of the corresponding pH SRM using a glass electrode.
- As an internal control measure, a candidate material be rejected if a significant difference is observed between the mean pH value of the current candidate material and the certified pH of the previous SRM issue (unless redetermination of the pH of the previous issue of the SRM using a Harned cell indicates a significant change from its certified pH value).
- Certification of each pH SRM be performed using cells without liquid junction (Harned cells) at each temperature of interest using at least three independently prepared buffer solutions of composite samples of the candidate SRM.
- Uncertainty associated with the certified value includes the measurement uncertainty (in potential of Harned cell), the uncertainty in standard potential of Ag, AgCl reference electrodes, the theoretical uncertainty in the conventional calculation of $-\log \gamma_{Cl}$, and the replication uncertainty for the overall pH value-assignment.

1.3. Certification of NIST Optical Filter SRMs

Specific requirements for the certification of NIST optical filter SRMs include:

1.3.1 Photometry

- Regular transmittance scale is maintained on the National Reference Spectrophotometer in the NIST Analytical Chemistry Division which is validated by the double-aperture method of light addition and benchmarked through international intercomparisons using optical filter artifact standards.
- Solid (neutral glass and metal-on-silica) SRMs are assigned certified values for transmittance and/or transmittance density at specified wavelengths by individual measurement of each artifact on the National Reference Spectrophotometer.
- Liquid or powder SRMs are assigned certified values for absorbance per unit pathlength or specific absorptivity at specified wavelengths by batch certification on the National Reference Spectrophotometer using a random sampling from the batch.
- The uncertainty for each assigned photometric value includes components to account for the precision and accuracy of the instrument; heterogeneity, temporal drift, and thermal characteristics of the artifact; and the geometry of sample positioning. Uncertainties are not individually evaluated but are based on pooled measurements with more than 30 degrees of freedom. Uncertainties are re-assessed annually for continuously produced solid standards or with each re-issue for batch-certified standards.
- A control filter is run with all data acquisitions, and the data are used to “control-chart” the measurement process and verify consistent performance.

1.3.2 Wavelength

- SRMs are assigned certified values for peak wavelength or wavenumber by comparison to atomic wavelengths (ultimately traceable to the standard meter) using a transfer spectrometer.
- Wavelength standards are batch certified using a random sampling from the lot. The uncertainty for each peak position in a wavelength standard includes components to account for the calibration accuracy of the transfer spectrometer, the precision in locating the standard peaks, and relevant temperature coefficients over the specified temperature range of valid certification.

2. Certification at NIST Using Two Independent Critically-Evaluated Methods

A second mode of certification for NIST SRMs involves the use of two or more critically evaluated independent methods [5,6]. Method independence is of critical importance, and while it is rare that two analytical methods have completely different sources of error and variability, they are chosen so that the most significant sources of error are different. For example, the following considerations are carefully evaluated:

- Methods are selected to minimize common steps in sample preparation and the final analytical measurement techniques.
- Methods rely on different physical, spectroscopic, or chemical phenomena that generate the analytical response.
- Methods/procedures selected are appropriate for the required precision and accuracy for measurement of the analyte(s) of interest in the matrix.
- The criteria for between-method agreement required for certification is pre-determined and documented in the experimental plan.

3. Certification/Value-Assignment Using One Method at NIST and Different Methods by Outside Collaborating Laboratories

In some cases, there does not exist a suitable second independent method at NIST. In these instances, we carefully select outside laboratories to collaborate on the certification process. Ideally this collaboration begins at the very start of the experimental design process. In this way, both NIST and outside laboratory analysts are able to coordinate the details of the measurement, data analysis, and reporting requirements for the SRM with careful attention to the following:

- The NIST method and the methods of the outside collaborating laboratories must have been critically evaluated and demonstrated to provide accurate results for the matrix under investigation.
- The method(s) used by outside collaborating laboratories should be different from the method used at NIST as required by the “Two Independent NIST Methods” mode (see Mode 2).
- Data reporting requirements for outside collaborating laboratories should be specified in the experimental plan, and reports should contain sufficient information to evaluate all significant sources of uncertainty.

4. Value-Assignment Based on Measurements by Two or More Laboratories Using Different Methods in Collaboration with NIST

This mode can be used to provide NIST Reference Values or NIST Information Values for an SRM, e.g., in instances in which there do not exist suitable methods at NIST. This mode requires that:

- The outside collaborating laboratories' methods have demonstrated accuracy in the matrix under investigation.
- Analyses provided by the outside collaborating laboratories involve at least two different methods (see Mode 2).
- Data reporting requirements for the outside collaborating laboratories be specified in the experimental plan and their report should contain sufficient information to evaluate all significant sources of uncertainty, unless a large number of labs/methods submit data, in which case the "Interlaboratory Study" criteria apply (see Mode 7).

5. Value-Assignment Based on a Method-Specific Protocol

In cases of method-defined parameters, the value of the parameters of interest result from the appropriate and validated use of a defined protocol. Appropriate implementation of this mode requires that:

- The protocol used be one that is recognized by the user community as the prescribed method for measurement of the analyte (or property) of interest in this matrix.
- Only data from experienced practitioners of the protocol be used.
- Measurements using the method-specific protocol be made by NIST, outside laboratories, or both.
- Method-specific value-assignment typically involve no fewer than three experienced practitioners of the method.

6. Value-Assignment Based on NIST Measurements Using a Single Method or Measurements by an Outside Collaborating Laboratory Using a Single Method

In some cases the intended use by the measurement community does not require a NIST Certified Value as an assigned value. This mode can be used to provide NIST Reference Values or NIST Information Values.

- The NIST method used is typically one that would be used in the "Two Independent NIST Methods" mode (see Mode 2), i.e., the method may have been used in the past as

one of several methods for SRM certification, but in this instance was the only method used.

- The method used by the outside laboratory must have been demonstrated to provide appropriate precision and accuracy in the matrix under investigation.
- Data reporting requirements for outside collaborating laboratories are specified in the experimental plan, and their reports should contain sufficient information to permit evaluation of significant sources of uncertainty.

7. Value-Assignment Based on Selected Data from Interlaboratory Studies

This mode allows NIST to take advantage of interlaboratory studies designed for purposes other than value-assignment of reference materials. In this mode:

- The particular study must be well documented and organized by a reputable organization.
- NIST Chemical Science and Technology Laboratory is responsible for evaluating the appropriateness of analytical procedures to identify a subset of results to be selected for use in value-assignment.

IV. Definition of Terms

NIST references a number of definitions in connection with the production, certification, and use of its SRMs and RMs. The uses of the terms “certified values,” “reference values,” etc., have multiple meanings based on the intent and practices of a particular reference material supplier. Certain definitions, adopted for NIST use, are derived from international guides and standards on reference materials and measurements while others have been developed by NIST to describe those activities unique to NIST operations and philosophy. To avoid any ambiguity, this publication provides definitions of the terms as they are currently used by NIST and a description of NIST’s current practices for value-assigning SRMs and RMs that support chemical measurements. A listing of NIST-adopted and NIST-developed definitions follows.

Reference Material (RM): Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

[ISO VIM: 1993, 6.13 [7]]

Certified Reference Material (CRM): Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

[ISO VIM: 1993, 6.14]

NIST Standard Reference Material[®] (SRM[®]): A CRM issued by NIST that also meets additional NIST-specified certification criteria. NIST SRMs are issued with Certificates of Analysis or Certificates that report the results of their characterizations and provide information regarding the appropriate use(s) of the material.

NIST Traceable Reference Material[™] (NTRM[™]): A commercially-produced reference material with a well-defined traceability linkage to existing NIST standards for chemical measurements. This traceability linkage is established via criteria and protocols defined by NIST to meet the needs of the metrological community to be served.

NIST Certified Value: A value reported on an SRM Certificate/Certificate of Analysis for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or accounted for by NIST. Values are generally referred to as certified when Modes 1, 2, or 3 have been used for value-assignment and all the criteria for that mode are fulfilled. These three modes all require NIST measurements and oversight of the experimental design for the value-assignment process. The uncertainty associated with a certified value generally specifies a range within which the true value is expected to lie at a level of confidence of approximately 95 % if the sample is homogeneous. If significant sample heterogeneity is included, the uncertainty generally represents a prediction interval within which the true values of 95 % of all samples are expected to lie at a stated level of confidence.

Uncertainty of a Certified Value: An estimate attached to a certified value of a quantity which characterizes the range of values within which the “true value” is asserted to lie with a stated level of confidence. [*ISO Guide 30: 1992 3.4 [8]*]

Uncertainty of a Measurement: Parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. [*ISO VIM: 1993 3.9*]

NIST Reference Value (formerly called Noncertified Value) for Chemical Composition and Related Properties: A NIST Reference Value is a best estimate of the true value provided on a NIST Certificate/Certificate of Analysis/Report of Investigation where all known or suspected sources of bias have not been fully investigated by NIST. Reference values are generally determined using the following modes:

- Mode 2 or 3 is used when there is lack of sufficient agreement among the multiple methods.
- Modes 4, 5, or 6 are used when the intended use of the value by the measurement community does not require that it be a certified value.
- Mode 7 can be used in special cases, e.g., when results are obtained from another national metrology laboratory with whom NIST has historical comparability data for the method(s) used for the specific matrix/analyte combination.

The uncertainty associated with a NIST Reference Value may not include all sources of uncertainty and may represent only a measure of the precision of the measurement method(s).

NIST Information Value: A NIST Information Value is considered to be a value that will be of interest and use to the SRM/RM user, but insufficient information is available to assess the uncertainty associated with the value. Typically, the information value has no reported uncertainty listed on the certificate and has been derived from one of the following value-assignment modes:

- Results from modes 4, 5, 6, or 7 in which the intended use of the value by the measurement community does not require that it be a certified or reference value. (E.g., information about the composition of the matrix such as the value of “total organic carbon” of a sediment material may be useful to the user in selecting an appropriate analytical method.)
- The results from modes 4, 5, 6, or 7 lack sufficient information to assess the uncertainty.
- Results are provided from outside NIST as supplemental information on the SRM matrix and are not measurements typically made at NIST but may be of interest to the user.

V. References

- [1] Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, NIST Technical Note 1297, 1994 Edition.
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- [8] Terms and Definitions Used in Connection with Reference Materials, ISO Guide 30, International Organization for Standardization (ISO), 1992.