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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Practice for Certificates of Reference Materials for Water Analysis[1]

This standard is issued under the fixed designation D 6362; 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 practice covers the information that must be provided on certificates of analysis of reference materials designated to support ASTM methods. It provides end users of these materials with a defined set of data that is required to be on a certificate of analysis and provides information to assist the end user in evaluating the independence of the material. Similarly, it provides the suppliers of reference materials with a consistent format for the presentation of certification data.

1.2 *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 limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

E 826 Practice for Testing Homogeneity of Materials for the Development of Reference Materials[3]

2.2 *ISO Standards*

ISO Guide 30 Terms and definitions used in connection with reference materials[4]

ISO Guide 31 Contents of certificates of reference materials[4]

ISO Guide 35 Certification of reference materials—General and statistical principles[4]

ISO/REMCO N280[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D 1129 and ISO Guide 30

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *prepared value, n*—the best estimate of the concentration of a given analyte based upon the purity of raw materials and the method of preparation of the material.

4. Significance and Use

4.1 This practice is designed to assist suppliers and users of reference materials by identifying the information necessary on the certificate of analysis of materials designated for use in ASTM test methods. This practice is specifically designed to ensure that materials suitable for use as either calibration or quality control standards are available. This practice does not define a specific certification protocol, but rather provides guidance in the development of adequate data to support the use of the material as either a calibration or quality control standard. Suppliers are referred to ISO Guide 35 for guidelines on acceptable certification protocols. End users are referred to ISO Guide 31 for a more complete description of the elements of typical certificates of analysis.

5. Certificate of Analysis

5.1 The certificate of analysis is a summary of the analysis performed to support the designated use of the material. As a summary, the certificate must be brief, but it must provide sufficient information to allow the potential user of the material to assess the suitability of the material for his intended use. Therefore, reference material suppliers are encouraged to supply method information and analytical data in a summary that clearly and unambiguously allows the user to make an informed decision about the suitability of the material. The use of terms as defined by ISO or ASTM is required.

5.2 The certificate of analysis must be supported by a certification report for the material. The certification report must contain the details of the analyses performed to develop the certified values reported on the certificate of analysis. It must contain the method(s) used for analysis, details of the method of preparation, if appropriate, including gravimetric data, supporting instrumental data, and the results of supporting statistical analysis reported on the certificate of analysis. The certification report must be provided to the end user of the material if requested.

6. Certificate Headings

6.1 The following sections detail the headings to be used on the certificate of analysis. ASTM methods require the use of a diverse set of reference materials. Therefore, it is expected that all headings will not be appropriate for all materials. However, exceptions should be avoided in order to insure sufficient

[1] This practice is under the jurisdiction of ASTM Committee D–19 on Water and is the direct responsibility of Subcommittee D19.02 on General Specifications, Technical Resources, and Statistical Methods.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 03.06.

[4] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

information for evaluation of materials. Therefore, each of the following sections is designated as either mandatory or optional based upon ensuring a minimum data set. Appendix X1 contains examples of typical certificates of analysis designed to meet these requirements.

6.1.1 *Name and Address of Certifying Organization (Mandatory)*—This is the name and address of the organization that accepts responsibility for the information on the certificate. Organizations that provided analytical data or prepared the material may be provided elsewhere on the certificate.

6.1.2 *Material Identification (Mandatory)*—This section must identify the material by name, as labeled, and must include a lot or batch number that can be used to uniquely identify the material.

6.1.3 *Supplier of the Reference Material (Optional)*—If the supplier of the reference material is different from the certifying organization then this section should contain the name and address of the supplier of the material.

6.1.4 *Preparer of the Material (Optional)*—If the material was not prepared by the supplier or the certifying organization, then this section should include the name and address of the preparer of the material.

6.1.5 *Source of the Material (Mandatory)*—For a solution standard, or a matrix material, this section must identify the source of the raw materials or the source of the matrix material, used in the preparation of the material. The supplier may identify the source of the material as proprietary. If the source of the material is declared to be proprietary then the supplier must provide contact information on the certificate in order to assist end users.

6.1.6 *Description and Intended Use of the Material (Optional)*—Most reference materials are designed to be used for a specific purpose. This section should designate the intended use of the material. It should also contain a sufficiently detailed description of the material to allow the user to estimate its usability in their application.

> This material is designed to be used in D XXXX as a calibration standard. The material was prepared in Type I water to contain 1 mg/ml of the certified components.

6.1.7 *Stability, Transportation, and Storage Conditions (Mandatory)*—Any known temperature, storage, or transportation factors that could influence the stability of the material must be identified. It is required that the supplier identify proper storage and handling conditions that are necessary to insure usability for the expected life of the material. Similarly, the supplier should identify the period of time for which they will assume responsibility for the validity of the certified values.

6.1.8 *Instructions for Use (Mandatory)*—If the material requires special handling, dilution, drying, or any other specific manipulation in order to achieve the certified values, these procedures must be clearly identified in this section.

6.1.9 *Method of Preparation (Optional)*—If the method of preparation gives the user an idea of the care taken by the supplier, significant details of the preparation procedure may be included in this section.

6.1.10 *State of Homogeneity (Mandatory)*—As it relates to the certification of reference materials, homogeneity refers to the analysis and demonstration of uniformity of final packaged units. Every certificate must contain a homogeneity statement. This section must include the sampling, analytical method(s), and procedure used to evaluate the homogeneity of the material. Appendix X2 provides a suggested procedure for homogeneity testing and references to alternative internationally accepted homogeneity testing procedures. If the homogeneity of the material has not been determined, then this must be stated on the certificate.

6.1.11 *Certified Property Values and Their Associated Uncertainties (Mandatory)*—The information in this section should be given in tabular form with appropriate subsection headings. The minimum information to be provided includes the property, the certified value of the property, the associated uncertainty, and the method of analysis. Since the certificate is a synopsis of the certification report, suppliers are encouraged to identify the method of analysis by appropriate standard method number. Modifications or exceptions to the given method may be annotated in another section of the certificate. Likewise, if the values certified are dependent upon certain conditions, for example temperature, these can be identified in footnotes to the table. Values for properties that are not certified should be included in a separate table.

NOTE 1—Several different procedures can be used to certify reference materials. These depend upon the nature of the material to be certified and the technical capability of the supplier and certifying body. The three most common procedures for certification are detailed in Section 7. The procedure used to certify property values must be provided under the heading of statistical estimators and uncertainty referenced below.

6.1.12 *Uncertified Properties (Optional)*—Many times properties of the material are known but without sufficient accuracy or precision to support certification. These values may be reported by the supplier in this section to assist the user in the selection of appropriate materials.

6.1.13 *Values Obtained by Individual Laboratories or Methods (Optional)*—Many times materials are certified based upon interlaboratory studies or by using several different methods of analysis. In these cases, this section can be used to report individual data by laboratory or method where appropriate. If the supporting data are too voluminous to report in this section, a reference to the certification report may be made here to identify the source and availability of supporting data.

6.1.14 *Statistical Estimator and Uncertainty (Mandatory)*—The meaning and nature of the certified values must be given, that is, the statistical estimator must be named. Where the estimator cannot be named then the mathematical expression used in calculation must be presented.

> The certified values are based upon the unweighted mean of nine independent measurements by each method reported.

> The certified values are based upon a biweight estimate of the mean of the center 50 % of the reported data using the Tukey Bisquare Procedure with a tuning constant of 3.97. Details of the procedure may be obtained from the certifier.

NOTE 2—The method used to estimate the uncertainty associated with the certified value of the property is important. Therefore, the supplier must identify the factors considered in estimation of uncertainty and the method used for calculation. If the uncertainty is estimated by a coverage factor, such as $2s/\sqrt{n}$, then the formula and the values for each variable

in the formula must be provided on the certificate.

6.1.15 *Measurement Methods Used for Certification (Optional)*—This section should provide the exceptions to, or modifications of, the standard or reported method(s) used for certification. Sufficient details of the analysis must be provided in the certification report to allow independent verification of the analytical values. However, only those details which are essential to reproducibility need to be reported.

6.1.16 *Identification of Analysts or Laboratories (Optional)*—This section may be used to identify the contribution of individual analysts or laboratories to the certification effort. The identification of analysts or laboratories may assist the user in establishing the quality of the certification data.

6.1.17 *Legal Notice (Optional)*—Disclaimers or legal limitations of liability for the information on the certificate should appear in this section.

6.1.18 *Reference to Certification Report (Mandatory)*—The certification report supporting the summary provided on the certificate must be unambiguously identified in this section. Instructions for obtaining the full certification report must be provided in this section.

6.1.19 *Signature of Certifying Officer (Mandatory)*—It is required that the officer of the certifying body who accepts responsibility for the information on the certificate sign the certificate.

6.1.20 *Annex (Optional)*—The annex may be used by the supplier to supply additional information about the material or its certification. It may contain graphical presentations or other information not appropriate in the body of the certificate.

7. Certification Procedures

7.1 The certification procedure is the protocol used to develop certification data. It is independent of the method(s) used for certification and is usually dependent upon the nature of the material to be certified. The procedure used to certify the reference material is usually dependent upon the nature of the material and the property to be certified. In the case of a pure or neat compound to be used for preparation of calibration materials, the properties of interest are confirmation of identity and an accurate assay of the material. In the case of a prepared calibration solution, the property of interest is the best estimate of the concentration of the analyte in the solvent. In the case of a quality control material, the property of interest is the performance of the material in a particular method.

7.1.1 Most reference materials, and properties of interest, are certified by one of the following three procedures: 1) direct comparison method, most frequently used for assay work, or analysis of calibration materials where a suitable NIST standard reference material (SRM) exists; 2) verification of the prepared value, used to certify the prepared value of a material if an SRM is not available for direct comparison; and, 3) interlaboratory certification procedure, used to establish typical method performance values or an assigned value for matrix materials.

7.1.2 In the case of the direct comparison method, the certified value is based upon analysis to a known calibrant prepared from an SRM or other national standard. In the second case, where an SRM calibrant does not exist, the value certified is the prepared value. In the case of interlaboratory studies, the certified value is a best estimate of typical performance.

7.2 *Direct Comparison Method*—In cases where an SRM or other national standard exists and well defined methods are available, a material should be certified by direct comparison to the SRM or other national standard. If the reference material is used as the calibrant in the analytical system, then the certified values are linked to the SRM or other national standard. The value certified in this procedure is usually the mean of replicate analyses. The appropriate number of samples to be analyzed is dependent upon the material, the precision of the method, and the desired level of uncertainty.

7.2.1 In cases where multiple methods are used in the certification procedure, it is important to identify the analytical results from each method, and to explain how results were combined to establish the values certified. This information must be reported under 6.1.15.

7.2.2 Suitable procedures for the certification of reference materials using a direct comparison method may be found in ISO Guide 35.

7.3 *Verification of the Prepared Value*—Where a suitable SRM or other national standard does not exist for direct comparison, it is often the prepared value of the material that best estimates the property value of interest. In this case, the prepared value may be certified by comparison of the prepared value to the mean of replicate analyses based upon an independently prepared calibration material. If the prepared value falls within the 95 % confidence interval of the mean of the analytical values, then the prepared value is consistent with the analytical data and may be certified. However, since an SRM was not used for comparison, it is important that the supplier provide the user with sufficient data to estimate the quality of the analyses. Therefore, the supplier must provide the mean, confidence limits, and number of independent samples analyzed to support the certification of the property value. These must be reported in 6.1.11. since they are essential for evaluation of the material.

7.4 *Interlaboratory Certification Procedure*—Interlaboratory certification procedures are most commonly used to develop data on naturally occurring materials that allow them to be used for quality control or instrument calibration. Often, interlaboratory studies involve multiple methods as well as multiple laboratories in order to establish the best available estimate for the property to be certified.

7.4.1 In most cases, the most suitable estimate for the property of interest is the grand mean of the interlaboratory data. However, many other types of data analysis systems exist and may be more appropriate for particular materials, methods, or industries. Therefore, it is important that the supplier provide sufficient data to the user of the material to allow them to estimate the suitability of the property values. This must include the mean, standard deviation, and number of data points included in the estimation of the certified value. It is also important that the user understand if the original data set was censored, and by what procedure. If the certified property values are not based upon the mean, a detailed explanation of the method of data evaluation must be provided in 6.1.14.

7.4.2 Detailed procedures for the certification of reference

materials based upon interlaboratory studies can be found in ISO Guide 35.

8. Suitability for Use

8.1 It is the responsibility of the user of the reference material to evaluate the suitability of the given material for their application. This can be done by comparing the information available on the certificate of analysis to their analytical needs. Particular attention should be given to the uncertainty of the certified property values as it relates to the required precision of the analysis.

9. Keywords

9.1 calibration; certified reference material; laboratory control standard; quality control standard; reference material; standard

APPENDIXES

(Nonmandatory Information)

X1. EXAMPLE CERTIFICATES

X1.1 Certification Based Upon Comparison to NIST SRM

Certificate of Analysis

Material—Iron ICP Standard 1000 µg/ml
Matrix—2 % v/v Nitric Acid
Lot Number—12345
Expiration—12/1/00

Preparation—This standard was prepared from iron wire having a purity of 99.99 % (Aldrich Lot Number KFBC67H), trace metals grade nitric acid (Fisher Lot Number 94067), and deionized water that met ASTM Type I specifications. All glassware used in the preparation of the material was certified to meet ASTM Class A specifications.

This material was prepared, analyzed, and certified by ABC Reference Materials Company, 2891 South Main St., Golden, Colorado 27865.

Intended Use—This material is designed to be used for the calibration of instruments for the analysis of iron by ICP such as Test Method D 1237.

Stability—This material is guaranteed to be within ±0.5 % of the certified value for iron for one year from the date of purchase, or until the expiration date shown above.

Homogeneity—This material was found to be homogeneous at the 95 % confidence level based upon the analysis of 15 independent samples tested in duplicate. Samples were randomly selected throughout the packaging of the material.

Certified Value

Property	Prepared Value	Certified Value	Method	SRM
Iron	1002 µg/ml	1001 ± 1.1 µg/ml	ICP	3101a

Statistical Estimators and Uncertainty—The certified value reported is the mean of 15 independent samples analyzed against the reported NIST SRM. The reported uncertainty in the certified value is based upon $2s/\sqrt{n}$, where $n = 15$ and s = sample standard deviation, 1.35 µg/ml.

Certification Report—All data developed in the preparation and certification of this material are contained in Certification Report CR12345. Copies of the report are available from the supplier.

John Doe, Quality Assurance Officer

X1.2 Certification of the Prepared Value of a Material

Certificate of Analysis

Material—2,4 Dinitrophenol 1000 µg/ml
Matrix—Acetone
Lot Number—12345
Expiration—12/1/00

Preparation—This standard was prepared from 2,4 dinitrophenol having a purity of 98.6 % (Aldrich Lot Number KFBC67H) and GC grade acetone (Fisher Lot Number 94067). All glassware used in the preparation of the material was certified to meet ASTM Class A specifications.

This material was prepared by AMOCO Products, 776 High St., Columbus OH 45961. It was analyzed and certified by ABC Reference Materials Company, 2891 South Main St., Golden, Colorado 27865.

Intended Use—This material is designed to be used for the calibration of instruments for the analysis of 2,4 dinitrophenol by gas chromatography, such as Test Method D 1237.

Stability—This material is guaranteed to be within ±2 % of the certified value for 2,4 dinitrophenol for one year from the date of purchase, or until the expiration date shown above.

Homogeneity—Based upon the analysis of 15 independent samples tested in duplicate. The 95 % confidence interval of a single analytical result can be expected to be between 980 and 1020. The samples tested were randomly selected throughout the packaging of the material.

Certified Value

	Certified Prepared	Analytical Data Based Upon GC Analysis		
Property	Value	Mean	95 % CI	n
2,4 Dinitrophenol	1002 ± 6 µg/ml	1004 µg/ml	990-1010 µg/ml	6

Statistical Estimators and Uncertainty—The certified value reported is the prepared value based upon the method of preparation of the material. This value was verified by the analysis of six random samples against an independently prepared calibration solution (Aldrich Lot Number: JTY987). All analyses were performed by gas chromatography. The uncertainty in the prepared value is estimated based upon the volumetric method of preparation.

Certification Report—All data developed in the preparation and certification of this material are contained in and are available from ABC Reference Materials Company, 2891 South Main St., Golden, Colorado 27865 as Certification ReportJR12345.

John Doe, Quality Assurance Officer

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X1.3 Certification Using Interlaboratory Data

Certificate of Analysis

Material—Iron ICP Standard 420 µg/ml Lot Number—12345
Matrix—2 % v/v Nitric Acid Expiration—12/1/00

Preparation—This standard was prepared from iron wire having a purity of 99.99 % (Aldrich Lot Number KFBC67H), trace metals grade nitric acid (Fisher Lot Number 94067), and deionized water that met ASTM Type I specifications. All glassware used in the preparation of the material was certified to meet ASTM Class A specifications.

This material was prepared and certified by ABC Reference Materials Company, 2891 South Main St., Golden, Colorado 27865.

Intended Use—This material is designed to be used as a quality control material for the analysis of iron by ICP such as Test Method D 1237.

Stability—This material is guaranteed to be within ±0.5 % of the certified value for iron for one year from the date of purchase, or until the expiration date shown above.

Homogeneity—This material was found to be homogeneous at the 95 % confidence level based upon the analysis of 15 independent samples tested in duplicate. Samples were randomly selected throughout the packaging of the material.

		Certified Value		
		Certified Consensus Interlaboratory Data		
Property	Prepared Value	Mean	Std Dev	n
Iron	740 µg/L	742 ± 2.3 µg/L	18.4 µg/L	27

Statistical Estimators and Uncertainty—The certified value reported is the mean of 27 independent laboratories who tested the material as an unknown. The reported uncertainty in the certified value is based upon the standard error of the mean calculated as $2s/\sqrt{n}$.

Certification Report—All data developed in the preparation and certification of this material are contained in and are available from the manufacturer as Certification Report CR12345.

J. D. Doe, Certification Officer

X2. HOMOGENEITY TESTING

The variability in sample analysis is dependent upon the precision of the test method and the homogeneity of the material tested. As it relates to reference materials, homogeneity includes both variations in the bulk of the standard before packaging, and variation in final packaged units. However, as it relates to certification, homogeneity is limited to analysis and demonstration of uniformity of final packaged units. The homogeneity of the bulk material may be established by using a modification of Practice E 826. This procedure can be used to test the homogeneity of solid reference materials. Similarly, ISO/REMCO has developed a separate homogeneity testing procedure for the evaluation of interlaboratory test samples. This procedure is presented in ISO/REMCO N280. ISO Guide 35 also contains two separate procedures for testing homogeneity of reference materials.

The following procedure is designed to establish homogeneity based upon the analysis of replicates taken from several portions of the packaging run. If homogeneity can be established by the data analysis presented, then the uncertainty related to the certified value is due to the variability of the test method. If the material is shown to be nonhomogeneous by this procedure, then lack of homogeneity is a significant contributing factor to the uncertainty of the certified value and it must be considered in the presentation of the certified value.

X2.1 Sampling

X2.1.1 In order to perform the analysis of homogeneity random replicate samples are taken from distinct portions of the packaging run from the first to last packaged container. The number of samples taken and the number of portions of the run sampled should be selected by the supplier to maximize the amount of data available within reasonable cost constraints. However, at least three samples from at least each third of the packaging run should be analyzed. It should be noted that increasing sample sizes improve the possibility of establishing homogeneity. Samples should be analyzed in random order.

X2.2 Data Analysis

X2.2.1 The data developed is analyzed by an analysis of variance procedure to consider whether the variation between sections of the packaging run is consistent with variation within the sections of the run. The resulting F value is compared to the critical value F_0 based upon a 0.05 significance level, and (a-1), (N-a) degrees of freedom where a is the number of sections tested and N is the total number of samples taken. Typical values of F_0 are shown below for combinations of a and N:

Sections (a)	Total Samples (N)	Critical F_0(0.05)
3	9	5.15
3	15	3.89
3	30	3.35
4	12	4.07
4	20	3.27
4	40	2.87
5	15	3.48
5	25	2.87
5	50	2.58

If the calculated value of F is less than the critical value then it can be stated that the reference material is homogeneous at a 95 % confidence interval. If the calculated F value for the data set is greater than the critical value of F_0, then the standard cannot be said to be homogeneous at the 95 % level. Reference materials which fail the F test for homogeneity should be investigated by the manufacturer to determine the cause of failure, and cannot be certified as homogeneous by this procedure.

X2.3 Statement of Homogeneity

X2.3.1 If the data set shows that the standard is homogeneous based upon the F test then the certificate of analysis may state that:

> This material has been demonstrated to be homogeneous based upon analysis by the method used for certification at the 95 % confidence level.

If the data fail to show that the material is homogeneous, then no statement of homogeneity can be made using this procedure.