



Standard Practice for Referencing Test Methods for Chemical Analysis of Metals and Related Materials¹

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1. Scope

1.1 This practice outlines procedures for relating results from test methods to a practical basis, that is, analytical traceability. It explores strategies to ensure the accuracy of a test method and to document reliability of results obtained in individual laboratories.

2. Referenced Documents

2.1 ASTM Standards:

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory²

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method²

E 2054 Practice for Performance-Based Description of Instruments in Chemical Analysis Methods²

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *analytical traceability, n*—a process relating a measurement or result to a defined chemical basis.

3.1.2 *pure substance, n*—of known purity such that the uncertainty of the sum of impurities has no observable effect on the accuracy of calibration.

4. Significance and Use

4.1 Practice E 1601 covers error to be expected in results obtained from two or more laboratories. Practice E 2054 covers variability expected in results obtained within an individual laboratory. This practice deals with the accuracy of a test method as used within an individual laboratory.

4.2 The information in this practice is to be used to identify suitable reference materials. A standard test method requires reference materials for calibrating instruments or for standardizing reagents. In writing an analytical test method, reference materials are described to emphasize required characteristics, and identify at least one source for uncommon materials. Analysts shall use reference materials specified in test methods in accordance with this practice.

4.3 Procedures from this practice are to be used to verify

that the test method produces acceptable results.

5. Types of Reference Materials

5.1 *Analytical Techniques*—Choice of optimum materials for calibration or standardization depends primarily on the characteristics of the analytical system.

5.1.1 Reference materials of three classes are generally recognized. In nominal order of decreasing quality they are:

5.1.1.1 Certified reference materials, CRMs, having the content of one or more analytes certified by a recognized standardization agency or group,

5.1.1.2 Reference materials, RMs, having the content of one or more analytes accepted for use in calibrating instruments, and

5.1.1.3 Analyzed materials, AMs, having the content of one or more analytes determined by a test method referenced to a pure substance.

5.1.2 This hierarchy often reflects the resources employed in preparing the materials and in establishing their reported values.

5.1.3 For test methods in which samples are presented for measurement as solutions, refer to 5.2. For solid-sample methods, refer to 5.3.

5.2 *Solution-Based Test Methods*—Prepare solutions for calibration of test methods from the analyte, if available as a stable material having a purity of at least 99.9 %. For example, metallic zinc of nominal 99.99 % purity is a preferred reference material for a zinc test method. Metals unaffected by atmospheric oxygen normally require no special preparation, but must be protected from corrosive vapors. For other analytes, use stable compounds of known stoichiometry. For example, reagent grade NaCl is an acceptable reference material for determining sodium or chloride. Reference compounds normally require preparation before use; dry them in air at 100 °C for 1 h, cool in a desiccator, and maintain in a water-vapor-free environment until weighed. Results of test methods of chemical analysis shall be traceable to pure substances that are purchased or prepared in the laboratory. Except for isotopically enriched analytes, calibration materials are expected to be, or be composed of, elements having commonly occurring isotopic ratios.

5.3 *Solids-Based Test Methods*—If possible, prepare solid reference materials for calibration in the same manner and under the same conditions as specified for test specimens. Note

¹ This practice is under the jurisdiction of Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.

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² *Annual Book of ASTM Standards*, Vol 03.06.

the uncertainty in reported results and determine that CRMs and RMs match the compositions of samples specified in the test method. Select those that best provide required analyte levels. In most cases, available materials do not adequately cover all analytes and concentration ranges required for accurate calibration of a test method. In this case, acquire or prepare AMs to fill voids in the calibration ranges. Results for AMs shall be traceable directly to pure substances through solution-based test methods.

5.4 Traceability of Metrology—Report analytical measurements in units that are traceable through a discernable path back to national standards (in the United States, these standards are maintained by the National Institute of Standards and Technology (NIST)). The original steps in this process are the responsibility of manufacturers of analytical instruments and equipment. Users shall ensure that weight- and volume-measuring equipment continues to demonstrate precision and accuracy equal to or exceeding performance stated in analytical test methods employed.

6. Strategies for Calibration of Instruments

6.1 General Requirements—Calibrate every analyte at a minimum of three concentration levels, that is, at the top and bottom of the desired concentration range and at an intermediate level. If the relationship between analyte concentration and instrument response is known to be non-linear, provide additional calibration levels. A suite of calibration solutions or materials consisting of one blank (or zero-level) plus 4 or 5 at analyte levels approximately evenly distributed over the range to be calibrated is typical of properly developed test methods.

6.2 Single-Analyte Test Methods—If results from a test method are unaffected by other sample components within the scope of the test method, only calibration in accordance with 6.1 is required. Otherwise, develop inter-element corrections in accordance with the test method prior to performing calibration.

6.3 Multi-Analyte Test Methods—The concepts of 6.2 apply equally well to multi-element methods, however, the complexity of preparations for calibration (and of the calibration itself) increases as the number of analytes and interfering components increases. Avoid incompatible concentrations of analytes and associated counter-ions in the preparation of calibration solutions. If possible, avoid combinations of elements that are mutually immiscible, form immiscible inter-metallic phases, or cause migration of components to grain boundaries when melted alloy mixtures are cast to prepare solid calibration materials.

6.4 Preparation of Calibration Solutions—Calibration solutions with accurately known compositions can be prepared with relative ease if quantitative principles are followed.

6.4.1 Plan the calibration process. For a single-analyte method in which other sample components have no influence, plan to pipet volumes (for example, 5-, 10-, 15-, 20-, and 25-mL) of a solution of known high analyte concentration into identical volumetric flasks, and dilute to form a calibration series. For more complex test methods with many analytes and inter-element influences, plan a high-analyte standard solution for each analyte or influential component and the volumes and ultimate dilutions required to form a limited series of multi-

element calibration solutions.

6.4.2 Weigh the calculated quantities of pure starting materials on an analytical balance. The maximum uncertainty in the purity of a material shall be less than one-fifth the test method's relative reproducibility index for the analyte. For example, if the minimum relative reproducibility index is 1 %, the relative uncertainty in the analyte content of the base material shall be less than 0.2 %.

6.4.3 Proper quantitative techniques for dissolving materials and transferring solutions contributes uncertainty approximating 1 part per thousand if carefully performed.

6.4.3.1 Keep volumetric glassware clean to ensure proper drainage during delivery of solutions and to avoid contamination.

6.4.3.2 Prevent loss of analyte by avoiding vigorous boiling and evolution of gasses during dissolutions, carrying out these operations in covered beakers with a volume above the liquid of 3 to 4 times the liquid volume, and rinsing the lower surface of each cover glass into its beaker before discarding the cover.

6.4.3.3 Transfer solutions quantitatively from one vessel to another. Carefully pour the liquid; if a drop remains on the pour-lip, touch off inside the receiving container. Rinse the inner surface of the original container into the receiving container with 3 separate small volumes.

6.4.4 Determine trace element contents of pure materials if they are to be used for preparation of multielement calibration solutions. Each analyte concentration in a calibration solution is the sum of the significant contributions from all sources. At high analyte levels, significant contributions are unlikely. Where possible, avoid planning for low levels of analytes in any solution containing high levels of other analytes.

7. Characteristics of Calibration Types

7.1 Solution Calibrations—Solution calibrations are limited to solution-based test methods. In practice, solution calibrated test methods are the most accurate test methods available because they are referenced directly to pure substances, they provide flexibility in the number of analytes and their levels, they provide calibration solutions that simulate test materials when necessary, and, they are homogeneous.

7.1.1 Referenced Directly to Pure Substances—In general, pure substances have a smaller relative uncertainty in analyte content than solid-form AMs, RMs, and SRMs. For this reason, and because the resulting solutions retain fixed ratios among analytes on dilution, do not use the latter to prepare calibration solutions.

7.1.2 Provide Flexibility in the Number of Analytes and Their Levels—A solution-based test method shall specify the analyte levels necessary to ensure proper calibration.

7.1.3 Provide Calibration Solutions that Simulate Test Materials When Necessary—Simplify calibration solutions of test methods in which the analyte response is not affected by the presence of non-analyte components by omitting them. Otherwise, ensure that test methods use calibration solutions that contain those components at appropriate levels.

7.1.4 Homogeneous—By their chemical nature, calibration solutions do not change composition for a specified time if they are protected from evaporation and are handled and stored as directed in the test method.

7.2 *Solid Calibrations*—Solid-based test methods require solid calibration specimens similar in form, and often also in metallurgical history, to test specimens. In general, solid calibration materials are not perfectly homogeneous. They frequently vary in composition within individual specimens (limiting use to specific exposed areas) and from specimen to specimen of the same material. Unlike calibration solutions, most calibration solids are not prepared to specification by mixing weighed portions of pure substances. Analyte contents are assigned by careful chemical analysis of the prepared specimens. These “certified” or accepted values thus reflect both material variability and variability inherent in the analytical test methods.

8. Verification

8.1 *Reference Materials*—Obtain one or more CRMs, if available, to match sample types and analyte contents of analytical interest. Use CRMs when a test method is first applied in a laboratory to demonstrate that calibration is performed without gross error. If results from CRMs do not fall within the reproducibility index confidence interval of the test

method (see Section 6 of Practice E 1601), determine and correct the cause. If a CRM is not available, analyze several test materials by a reliable independent test method to demonstrate that comparable results are obtained by both test methods. The acceptance criterion is the reproducibility index or the accuracy required by the process being controlled, whichever is larger. Possible sources of apparent error include: one or more defective calibration solutions or specimens; improper implementation of calibration or inter-element correction procedures; insufficiently homogeneous CRMs; or, inaccurate certified values. (**Warning**—Under no circumstances are calibrations to be corrected based upon verification data.)

8.2 *Control Materials*—Periodically verify test methods used in a laboratory on a continual basis under a quality control program (see Guide E 882). Although CRMs can be used for control purposes, a large quantity of homogeneous control material selected to represent as exactly as possible the type of material routinely being tested is greatly preferred. Evaluate the homogeneity of the bulk control material during the period preliminary control data is generated.

APPENDIX

(Nonmandatory Information)

X1. RATIONALE

X1.1 Chemical analysis poses the simple question: what fraction of the total sample weight is the weight of pure analyte it contains? Classical analytical chemistry first answered the question by separating a pure substance containing a theoretical fraction of the analyte. The weight of analyte was calculated from the weight of the separated substance. A second answer to the analysis question was provided by measuring the quantity of a substance needed to react completely with the analyte. In this process, the weight of analyte was calculated directly from the weight of pure reactant in accordance with an equivalence shown by the equation of the chemical reaction. A useful, accurate variation of the second process does not require a pure or accurately weighed reacting substance. Instead, an equivalence ratio between analyte and reactant is established by standardization experiments in which the quantity of reactant needed to react completely with weighed portions of pure analyte is determined. This concept is method calibration, that is, establishing equivalence between response of a test method and the fraction of analyte in a sample.

X1.2 Within the last 100 years, test method calibration has been transformed from an approximate procedure suitable only for routine process control to a preferred practical approach to most analytical problems. This change was driven by commercial production of reasonably priced pure metals and compounds suitable for calibration and of sensitive, selective, and reliable analytical instrumentation.

X1.3 The concept of calibration is simple, but successful applications depend upon detailed understanding of the chemi-

cal and physical principles involved in each test method. Two distinct processes are available: direct calibration from pure substances (primarily used in test methods with analytes in solution), and indirect calibration from analyzed materials (primarily used in test methods for analyzing solid specimens).

X1.3.1 *Direct Calibration*—In this standard “pure” means: of known purity such that the uncertainty of the sum of impurities has no observable effect on the accuracy of calibration.

X1.3.1.1 Pure substances are produced by minimizing impurities during initial production, or by final purification steps, or both. They are often sold with certification of principal impurity components. If no information is given or the reliability of the information is questionable, obtain estimates of trace constituents by sensitive test methods, sum the results obtained, and subtract from 100 %. Highly precise determinations are not required; relatively large trace element errors translate into insignificant errors for the main constituent.

X1.3.1.2 Nominal 99.5 % pure materials usually have a calculated purity with an uncertainty of about ± 0.1 % and are satisfactory for test methods having a relative reproducibility index, $R_{rel\%}$, of 1 % or greater. Materials with a nominal purity of 99.99 % are considered 100 % pure for most test methods of commercial importance. (**Warning**—Low-level impurity elements may contribute significant errors if the impurity elements are specified in mixed solutions.)

X1.3.1.3 Calibration is performed directly from a weighed quantity of the pure substance or from measured volumes of a standard solution prepared by dissolving a weighed quantity

and diluting it to a specified volume. For mixed-analyte calibration, the number of analytes included and the level of each is under the direct control of the user.

X1.3.2 Indirect Calibration—The quantity of analyte is not measured directly, but is calculated from the weight of a calibration material times the weight fraction of analyte it contains. This procedure allows a user to calibrate with a selected quantity of analyte by weighing a quantity of material calculated to contain the desired weight of analyte. This procedure has its limitations. Many test methods restrict the user to a sample size established by the equipment (for example, arc/spark AES) and, even when different sample weights may be taken, the weight ratios between analyte and each other constituent remain unchanged.

X1.3.2.1 Materials suitable for calibrating test methods are solids containing a matrix and at least one analyte component at a known concentration. Practical reference materials are analyzed samples containing a number of analytes at levels of analytical interest, with concentration values determined by chemical analysis. A certificate identifies the batch or lot of material from which the specific sample was selected and states the analyte concentrations. The uncertainty of certified values is the statistical sum of uncertainties associated with production and analysis of the reference material.

X1.3.2.2 The factors in the uncertainty of certified reference values are: (1) uncertainty in the purity of the substance used to reference the certifying analytical test method; (2) uncertainty contributed by analytical methods used in certification; and, (3) inhomogeneity in distribution of analyte among the pieces comprising the reference material and within the specific piece used for calibration. Unlike the minimal influence on purity determinations of high purity materials, analytical

inaccuracy and imprecision directly affect the uncertainty of analyte determinations in analyzed samples. Pure materials do not suffer from inhomogeneity in the major component, but analyzed samples are highly impure materials and must be prepared with care to minimize inhomogeneity of analytes. The problem is aggravated by metallurgical complexities when molten metal mixtures solidify. For test methods in which samples are used in solid form, compositional inhomogeneity is often the major cause of uncertainty in analyte content. Factors (2) and (3) together create uncertainty in the analyte content of solid reference materials that is many times greater than the uncertainty in the purity of pure substances. This uncertainty is often large enough to affect the accuracy of test methods calibrated with solid reference materials.

X1.4 Some private and statutory regulatory organizations have established regulations requiring calibrations of analytical test methods to be traceable to national standards. This concept appears to be modeled upon a defensible metrology requirement that the ultimate definition of physical measurement units lies with the one agency in the country that possesses or determines physical artifacts defining length, mass, and time. This discussion suggests that the concept cannot be defended if applied to results of chemical analysis; no national or international agency possesses unique artifacts defining chemical composition with ultimate accuracy. If CRMs are offered as definitive artifacts, this discussion reveals that, compared with pure substances, they are second-class reference materials. The conclusion is that requiring traceability of chemical analysis results to national standards leads to poorer analytical performance than the normal requirement that, to the extent possible, results be traceable to pure materials.

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