National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 3169

Zirconium (Zr) Standard Solution

Lot No. 130920

This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of zirconium. A unit of SRM 3169 consists of 50 mL of an aqueous solution in a high-density polyethylene bottle sealed in an aluminized bag. The solution was prepared gravimetrically to contain a known mass fraction of zirconium. The solution contains nitric and hydrofluoric acids at volume fractions of approximately 10 % and 2 %, respectively, equivalent to amount-of-substance concentration (molarity) values of approximately 1.6 mol/L and 0.6 mol/L, respectively.

Certified Value of Zirconium: 10.000 mg/g ± 0.020 mg/g

The certified value was calculated as the weighted mean of the mass fraction values obtained through (1) gravimetric preparation using high-purity zirconium metal assayed by NIST and (2) analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) calibrated using four primary standards independently prepared from high-purity zirconium metal assayed by NIST [1,2].

The uncertainty associated with the certified value, stated as a symmetric interval with a level of confidence of 95 %, was evaluated in accordance with Supplement 1 to the ISO/JCGM Guide [3]. The uncertainty can be expressed as:

$$U = ku_c$$

where $k = 1.962$ is the coverage factor for a 95 % confidence interval and 968 effective degrees of freedom. The quantity u_c is the combined standard uncertainty, which represents, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, the ICP-OES determination, any difference between the methods' results, and stability of the zirconium mass fraction.

Expiration of Certification: The certification of **SRM 3169 Lot No. 130920** is valid, within the measurement uncertainty specified, until **30 November 2016**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of the technical measurements leading to the certification of SRM 3169 was provided by M.R. Winchester of the NIST Chemical Sciences Division.

This SRM was prepared by T.A. Butler of the NIST Chemical Sciences Division. The ICP-OES analysis was performed by T.A. Butler and M.R. Winchester using primary standards for calibration prepared by T.A. Butler.

Statistical consultation was provided by A.M. Possolo of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 16 April 2014

Robert L. Watters, Jr., Director
Office of Reference Materials

METROLOGICAL TRACEABILITY

Metrological traceability of measurement results to a given reference must be established through an unbroken chain of calibrations and/or comparisons, each having stated uncertainties [4], using measurement standards that are appropriate for the physical or chemical property being measured. Comparisons may include validation measurements using various spectroscopic, chromatographic, or classical methods of analysis. Gravimetric or volumetric dilution is also a method of comparison, where the mass or volume of a solution before and after dilution is measured.

This SRM can be used to establish traceability of the results of zirconium measurements to NIST measurement results and standards. One approach is to calibrate analytical instruments or procedures for the determination of zirconium using standards whose values are traceable to the certified value of zirconium in this SRM. When the traceable values of such standards are assigned using this SRM for calibration, the uncertainties assigned to those values must include the uncertainty of the certified value of this SRM, appropriately combined with the uncertainties of all calibration measurements.

The measurand of this SRM is the mass fraction of zirconium in solution. The certified value is metrologically traceable to the SI unit of mass, expressed as milligrams per gram.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

CAUTION: This SRM is a solution containing nitric and hydrofluoric acids. All appropriate safety precautions, including use of gloves during handling, should be taken. Consult the Safety Data Sheet for details on safe handling, storage, and use.

This SRM can be used to prepare working standard solutions in the range of 10 mg/kg to 100 mg/kg, from which more dilute standards can be prepared. The user should establish internal laboratory procedures that specify a maximum shelf-life for a working standard solution. Two procedures for the preparation of working standard solutions follow.

Preparation of Working Standard Solutions by Mass: Each working standard solution should be prepared by transferring an aliquot of the SRM into an empty, dry, preweighed polyethylene bottle and then reweighing the bottle. An appropriate dilute acid must be added by mass to bring the solution to the desired dilution. The dilution need not be exact since the mass of the empty bottle, mass of the bottle plus the SRM aliquot, and final diluted mass of the solution will permit calculation of the exact mass fraction (i.e., mass of zirconium per mass of solution) of the working standard solution. Dilutions prepared gravimetrically as described will need no correction for temperature and no further correction for true mass fraction in vacuum.

Preparation of Working Standard Solutions by Volume: Volumetric dilutions are **NOT** recommended due to uncertainties in volume calibrations and variations in density. However, for user convenience, a procedure for volumetric preparation that will minimize the major sources of error is given. Each working standard solution should be prepared by transferring an aliquot of the SRM to an empty, dry polyethylene bottle and then weighing the bottle. The solution must then be transferred to a Class A volumetric flask and the polyethylene bottle reweighed to determine the exact mass of SRM solution transferred. The solution in the flask is then diluted to 99 % + volume using an appropriate dilute acid, mixed thoroughly, and the remaining few drops needed to dilute to exact volume carefully added. The concentration (in milligrams per milliliter) of the resulting working standard solution can then be calculated by multiplying the mass (in grams) of the SRM solution amount by the SRM certified value (in milligrams per gram) and dividing the numerical product by the calibrated volume (in milliliters) of the flask used for dilution. Thus, no correction for density is needed. Although the concentration of the resulting working standard solution may be an uneven fraction of the original SRM concentration, it will be known as accurately as a volumetric dilution permits.

Transpiration: While stored in the aluminized bag, transpiration of this SRM is negligible. After the SRM has been removed from the aluminized bag, transpiration will occur at a solution mass loss rate of approximately 0.2 % relative per year, resulting in a gradual increase in the element mass fraction. It is the responsibility of the user to account for this effect. The recommended way to reduce the effects of transpiration is to deliver all of the SRM as aliquots weighed into appropriate vessels as soon as the SRM is removed from the aluminized bag. The aliquots may be stored and can be diluted to known mass or volume at a later date. Storage of a partially used SRM bottle is **NOT** recommended; however, if such storage is necessary, the cap should be tightly sealed and the SRM bottle kept in an airtight container to slow the rate of transpiration. When the bottle is weighed both before and after being placed in storage, the mass difference observed will be a measure of transpiration mass loss. The user should set a maximum shelf-life *for a partially used SRM bottle* commensurate with accuracy requirements.

REFERENCES

[1] Rukhin, A.L.; *Weighted Means Statistics in Interlaboratory Studies*; Metrologia, Vol. 46, pp. 323–331 (2009).

[2] DerSimonian, R.; Laird, N.; *Meta-Analysis in Clinical Trials*; Control. Clin. Trials, Vol. 7, pp. 177–188 (1986).

[3] JCGM 101:2008; *Evaluation of Measurement Data — Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" — Propagation of Distributions using a Monte Carlo Method*; Joint Committee for Guides in Metrology (JCGM) (2008) available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Feb 2013).

[4] JCGM 200.2012; *International Vocabulary of Metrology - Basic and General Concepts and Associated Terms*, 3rd ed. (2008 version with minor corrections); Joint Committee for Guides in Metrology (JCGM) (2012); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf (accessed Feb 2013).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.