National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 3034

Arsenocholine Standard Solution

This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of arsenocholine (AC). A unit of SRM 3034 consists of two 5 mL sealed borosilicate glass amber ampoules of water solution prepared gravimetrically to contain a known mass fraction of AC.

Certified Mass Fraction Value of AC (as As): 19.77 mg/kg ± 0.27 mg/kg $k = 2.16$

A NIST certified value [1] is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [2]. The AC value is calculated by subtracting the mass fraction of arsenic impurities from the mass fraction of total arsenic as detailed below. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c represents, at the level of one standard deviation, the combined effects of the between-method and the within-method components of uncertainty. The coverage factor, k, corresponds to an approximately 95 % level of confidence. The certified value is metrologically traceable to the derived SI unit for mass fraction, expressed as milligrams per kilogram.

The NIST measurements of total arsenic were made using inductively coupled plasma optical emission spectrometry (ICP-OES) and instrumental neutron activation analysis (INAA). These measurements were combined as the weighted means of the individual sets of measurements, estimated using a Gaussian random effects model [3] and the DerSimonian-Laird procedure [4,5]. The associated measurement uncertainty was evaluated by the application of the parametric statistical bootstrap, consistent with the ISO/JCGM Guide and its Supplement 1 [6-8]. The NIST measurements of arsenic impurities were made using ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS) and liquid chromatography inductively coupled plasma mass spectrometry (LC-ICP-MS). When possible, these measurements were combined using the same approach as used for the total arsenic measurements. When arsenic impurity measurement values were observed to be below detection limits, the nonparametric Kaplan-Meier method for computing summary statistics of censored data [9] was utilized.

For convenience of unit conversion, the density measured at 23.2 °C and the expanded uncertainty at approximately 95 % confidence for SRM 3034 are provided as (0.9980 ± 0.0013) g/mL.

Expiration of Certification: The certification of **SRM 3034** is valid, within the measurement uncertainty specified, until **31 March 2028**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). The 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 or register online) will facilitate notification.

Coordination of the technical measurements leading to the certification of this SRM was performed by L.L. Yu of the NIST Chemical Sciences Division.

Analytical measurements at NIST were performed by V.M.O. Carioni, W.C. Davis, K.P. Grogan, M. Ellisor, M.D. Le, D.J. O'Kelly, K.A. Lippa, Y. Nuevo Ordonez, S.A. Rabb, T.W. Vetter, and L.L. Yu of the NIST Chemical Sciences Division.

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Certificate Issue Date: 22 August 2018

Steven J. Choquette, Director
Office of Reference Materials

Statistical analysis was provided by D.D. Leber of the NIST Statistical Engineering Division.

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

NIST encourages the use of its SRMs to establish metrological traceability for the user's measurement results, and NIST strives to maintain the SRM inventory supply. However, NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of SRMs as primary benchmarks for the quality and accuracy of the user's in-house (working) standards. As such, SRMs should be used to validate or otherwise assign values to the more routinely used standards in a laboratory. When the metrologically 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 the calibration measurements for the in-house standard. Comparisons between NIST SRMs and such working measurement standards should take place at intervals appropriate to the conservation of the SRM primary standard and the stability of relevant in-house standards. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

INSTRUCTIONS FOR STORAGE AND USE

The SRM is a water solution contained in tip-sealed borosilicate glass ampoules with pre-scored stems. All appropriate safety precautions, including use of gloves during handling, should be taken. Drain any liquid inside the tip of the ampoule before opening the ampoule. Wipe the area of the stem where the pre-scored band is located (≈ 5 mm below the encircling metallic band) with a clean, damp cloth. Wrap the body of the ampoule in absorbent material. Hold the ampoule steady while grasping the stem at the metallic band with thumb and forefinger, and then snap off the stem by applying minimal thumb pressure. The stem should break off easily and cleanly where pre-scored. Using a metal file to break off the stem is **NOT** recommended. Excess liquid or glass on the outside of the ampoule should be cleaned off before emptying contents into another container for further processing or storage. Unopened ampoules should be stored in the dark at 21 °C ± 3 °C inside the original container supplied by NIST.

SOURCE AND PREPARATION[(1)]

Arsenocholine was purchased from a commercial vendor to produce the SRM. This material was dissolved at NIST using sub-boiling distilled water and later dispensed into ampoules.

ANALYSIS

ICP-OES method: A mixture of a 2 g aliquot of SRM 3034, a 4 g aliquot of concentrated hydrochloric acid and a 3 g aliquot of water was digested in a microwave. The digest was evaporated on a hot plate. Indium was added as an internal standard, and the contents were reconstituted to 20 g in dilute nitric acid. Two 5 g aliquots of the solution were taken, one spiked with 0.5 g arsenic standard prepared by serial dilution from SRM 3103a *Arsenic (As) Standard Solution*. The spiked and the unspiked solutions were measured for arsenic by ICP-OES for quantification by the method of standard addition.

INAA method [10]: Aliquots of 0.1 g – 0.3 g of solution from the SRM 3034 ampoules were applied to filters using a plastic pipet. The filters were dried, made into 13 mm pellets, doubly sealed in polyethylene bags, and irradiated for 8 h at a neutron flux of approximately 3×10^{13} cm^{-2} s^{-1}. After 2 d decay, the samples were counted for ^{76}As gamma rays for 2 h using a high purity germanium detector with associated electronics. Calibrants were created and processed similarly to the samples using SRM 3103a *Arsenic (As) Standard Solution* for the As determination.

IC-ICP-MS method [11]: Aliquots of 0.5 g of solution from the SRM 3034 ampoules were diluted with 25 g of deionized water for the impurity analysis. Separation of the arsenic species was carried out using a gradient chromatographic method at a flow rate of 1 mL/min with a Dionex IonPac guard column (4 mm x 50 mm) and AS7 (4 mm x 250 mm) analytical column. The mobile phases were prepared with nitric acid, acetic acid, and sodium acetate. Calibrants, containing a mixture of monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine oxide (TMAO), arsenobetaine (AB), AC, arsenic acid (AsV), and arsenous acid (AsIII) from commercial vendors, were created to determine the level of As impurities. The structural formulas of arsenic species are given in the Appendix. The assigned values for all the calibrants are traceable to the derived SI unit for mass fraction.

[(1)]Certain commercial instruments, materials, or processes are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply that the instruments, materials, or processes identified are necessarily the best available for the purpose.

LC-ICP-MS method [11]: Aliquots of 0.5 g of solution from the SRM 3034 ampoules were diluted with 50 g of sub-boiling distilled water for the impurity analysis. Separation of the arsenic species was carried out using a gradient chromatographic method at a flow rate of 1 mL/min with a CC 8/4 Nucleosil 100-5 SA guard column (4 mm x 8 mm) and analytical column (4 mm x 250 mm). The mobile phases were prepared with pyridine and methanol in water. Calibrants, containing a mixture of MMA, DMA, TMAO, AB, AC, AsV, and AsIII from commercial vendors, were created to determine the level of As impurities. The assigned values for all the calibrants are traceable to the derived SI unit for mass fraction.

REFERENCES

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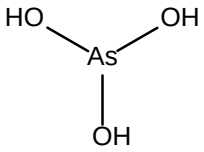
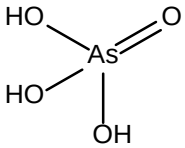
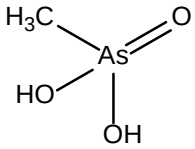
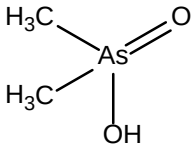
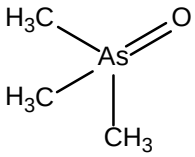
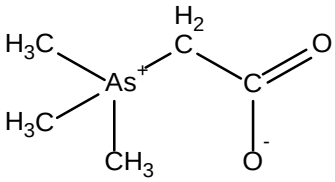
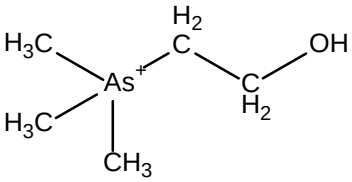
[10] Greenberg, R.R.; Bode, P.; De Nadai Fernandez, E.A; *Neutron Activation Analysis: A primary method of measurement*; Spectrochim. Acta, Part B, Vol. 66, pp. 193−207 (2011).

[11] Davis, W.C.; Zeisler, R.; Sieber, J.R.; Yu, L.L.; *Methods for the Separation and Quantification of Arsenic Species in SRM 2669 Arsenic Species in Frozen Human Urine*; Anal. Bioanal. Chem., Vol. 396, pp. 3041–3050 (2010).

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 https://www.nist.gov/srm.

APPENDIX

Structural Formulas for Arsenic Species

Name (Abbreviation)	CAS Registry Number	Structural Formula
Arsenous acid (AsIII)	13464-58-9	
Arsenic acid (AsV)	7778-39-4	
Monomethylarsonic acid (MMA)	124-58-3	
Dimethylarsinic acid (DMA)	75-60-5	
Trimethylarsine oxide (TMAO)	4964-14-1	
Arsenobetaine (AB)	64436-13-1	
Arsenocholine (AC)	39895-81-3