



Certificate of Analysis

Standard Reference Material[®] 3037

Arsenous Acid (AsIII) Standard Solution

This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of the arsenic species arsenous acid (AsIII). This SRM can be used for quality assurance when assigning values to in-house control materials. A unit of SRM 3037 consists of two 10 mL sealed borosilicate glass amber ampoules of an acidified aqueous solution prepared gravimetrically to contain a known mass fraction of arsenous acid. The solution contains hydrochloric acid at a volume fraction of approximately 1 %, which is equivalent to a concentration (molarity) of approximately 0.12 mol/L. Due to digestion of the starting material, arsenic trioxide, with sodium hydroxide, sodium is present in the ampoules at approximately 1000 mg/kg.

Certified Mass Fraction Value of AsIII: 1.0442 mg/g \pm 0.0020 mg/g

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 expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty, at the level of one standard deviation, due to material variability and measurement uncertainty following the ISO/JCGM guide [3] and reference 4. Analyses for value assignment were performed by NIST using gravimetric titrimetry. The associated uncertainty is expressed at an approximately 95 % level of confidence with a coverage factor of $k = 2.086$. The certified value is metrologically traceable to the derived SI unit for mass fraction, expressed as milligrams per gram.

Information Mass Fraction Value: The information value for the impurity arsenic acid, AsV, is listed in Table 1. This information value may be of interest to the SRM user [2] and is given to provide additional characterization of the material only. The value should not be used for calibration or to monitor or assess analytical performance. The information value cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 3037** is valid, within the measurement uncertainty specified, until **30 September 2027**, 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 S.A. Rabb of the NIST Chemical Sciences Division.

Analytical measurements at NIST were performed by W.C. Davis, K.W. Pratt, and L.L. Yu of the NIST Chemical Sciences Division.

Statistical analysis was provided by N.A. Heckert of the NIST Statistical Engineering Division.

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

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NOTICE TO USERS: SRM 3037 IS INTENDED FOR RESEARCH USE, NOT FOR HUMAN CONSUMPTION.

NIST strives to maintain the SRM inventory supply, but NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of this SRM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As such, the SRM should be used to validate the more routinely used reference materials in a laboratory. Comparisons between the SRM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the SRM and the stability of relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

INSTRUCTIONS FOR STORAGE AND USE

Storage and Use: The SRM is an acid solution contained in tip-sealed borosilicate glass ampoules with pre-scored stems. Therefore, all appropriate safety precautions, including use of gloves during handling, should be taken. Prior to opening, any liquid inside the tip of the ampoule should be drained, the area of the stem where the pre-scored band is located (≈ 5 mm below the encircling metallic band) should be wiped with a clean, damp cloth, and the body of the ampoule wrapped in absorbent material. To open, 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 from the ampoule should be cleaned off before emptying contents into another container for further processing or storage. Unopened ampoules should be stored at $21\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ in an upright position inside the original container supplied by NIST.

SOURCE AND PREPARATION⁽¹⁾

Source and Preparation: High purity arsenic trioxide was purchased from a commercial vendor to produce the SRM. This material was dissolved at NIST using sodium hydroxide and then stabilized with hydrochloric acid to prevent oxidation of the AsIII to AsV. Aliquots of the SRM were later dispensed into ampoules.

ANALYSIS

The certification of AsIII was based on the NIST gravimetric titrimetry primary method. In addition, the impurity arsenic species were measured by ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS) and liquid chromatography (LC) ICP-MS.

Gravimetric Titrimetry method: Aliquots of 2.8 g of solution from the SRM 3037 ampoules were dispensed using a syringe into a bottle. A drop of phenolphthalein was added and, then subsequently, 1 mol/kg NaOH was added dropwise until the endpoint was reached. A phosphate solution (10 mL) was used to buffer the solution. A slight excess of I₂ titrant was added to the solution, changing the solution from colorless to light amber. The excess I₂ was back-titrated with dilute As₂O₃ standard solution to the starch endpoint.

IC-ICP-MS method [5]: Aliquots of 0.5 g of solution from the SRM 3037 ampoules were diluted with 25 g of DI H₂O 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), arsenocholine (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.

LC-ICP-MS method [5]: Aliquots of 0.1 g of solution from the SRM 3037 ampoules were diluted with 100 g of sub-boiling distilled H₂O 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.

⁽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.

Table 1. Information Mass Fraction Value for Arsenic Acid in SRM 3037

	Mass Fraction ($\mu\text{g}/\text{kg}$)
Arsenic acid (AsV) ^(a,b)	171
^(a) IC-ICP-MS	
^(b) LC-ICP-MS	

REFERENCES

- [1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (2008); available at <https://www.nist.gov/pml/pubs/> (accessed Feb 2018).
- [2] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC (2000); available at <https://www.nist.gov/srm/upload/SP260-136.PDF> (accessed Feb 2018).
- [3] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Feb 2018); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at <https://www.nist.gov/pml/pubs/index.cfm> (accessed Feb 2018).
- [4] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.-K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; *An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM*; J. Res. Natl. Inst. Stand. Technol., Vol. 105, pp. 571–579 (2000).
- [5] 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; email srminfo@nist.gov; or via the Internet at <https://www.nist.gov/srm>.