



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 1640a

#### Trace Elements in Natural Water

This Standard Reference Material (SRM) is intended for use in evaluating methods used in the determination of trace elements in fresh water. SRM 1640a consists of acidified spring water with mass fractions and mass concentrations assigned for 29 elements, 22 of which were gravimetrically added. The solution contains nitric acid at a volume fraction of approximately 2 %. A unit of SRM 1640a consists of 250 mL of solution in a high-density polyethylene (HDPE) bottle sealed inside an aluminized Mylar pouch.

**Certified Values and Uncertainties:** The certified values for 22 elements in SRM 1640a are given expressed in mass fraction units and mass concentration units in Tables 1 and 2, respectively. A NIST certified value is a value in which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been fully investigated or taken into account [1].

Each certified mass fraction value given in Table 1 is the average of the value calculated from the gravimetric preparation and the value determined using either inductively-coupled plasma optical emission spectroscopy (ICP-OES) or inductively-coupled plasma mass spectrometry (ICP-MS), adjusted upward for transpiration that may occur over the certification period while the SRM bottle remains sealed inside the aluminized Mylar pouch. (NOTE: *No correction has been applied for transpiration that will occur after the pouch seal has been broken.* See “Instructions for Use” for more information regarding transpiration.) The magnitude of the transpiration adjustment (0.11 %) is based upon the results of unpublished NIST studies of transpiration rates of similar HDPE bottles sealed inside similar aluminized Mylar pouches, and is such that the actual mass fraction is expected to be equal to the certified mass fraction value approximately halfway through the certification period. Each expanded uncertainty,  $U$ , in Table 1 is calculated as  $U = ku_c$ , where  $k$  is the coverage factor for the appropriate degrees of freedom ( $df$ ) and a 95 % level of confidence ( $k$  and  $df$  are also given in Table 1) and  $u_c$  is the combined standard uncertainty calculated according to the ISO Guide [2]. The value of  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, the ICP-OES or ICP-MS analysis, method bias [3], and the transpiration adjustment.

Each certified mass concentration value given in Table 2 is calculated from the corresponding certified mass fraction value in Table 1 through multiplication by the density of the SRM 1640a solution. Each expanded uncertainty,  $U$ , in Table 2 is calculated as  $U = ku_c$ , where  $k$  is the coverage factor for the appropriate degrees of freedom ( $df$ ) and a 95 % level of confidence ( $k$  and  $df$  are also given in Table 2) and  $u_c$  is the combined standard uncertainty calculated according to the ISO Guide [2]. The value of  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the certified mass fraction value and the solution density.

**Expiration of Certification:** The certification of **SRM 1640a** is valid, within the measurement uncertainty specified, until **05 August 2020**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see “Instructions for 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) will facilitate notification.

Coordination of the technical measurements leading to the certification of SRM 1640a was provided by M.R. Winchester of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief  
Analytical Chemistry Division

Robert L. Watters, Jr., Chief  
Measurement Services Division

Gaithersburg, MD 20899  
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*See Certificate Revision History on Last Page*

This SRM was prepared by T.A. Butler, L.L. Yu, and M.R. Winchester of the NIST Analytical Chemistry Division. The ICP-OES analyses were performed by T.A. Butler, J.L. Molloy, and M.R. Winchester of the NIST Analytical Chemistry Division. The ICP-MS analyses were performed by J.L. Molloy, T.A. Butler, L.L. Yu, and M.R. Winchester of the NIST Analytical Chemistry Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

**Reference Values and Uncertainties:** The reference values for seven elements in SRM 1640a are given expressed in mass fraction units and mass concentration units in Tables 3 and 4, respectively. Reference values are non-certified values that are best estimates of the true values. However, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [1].

The reference mass fraction values and expanded uncertainties given in Table 3 are calculated using the same approach employed for the certified mass fraction values (see explanation above), including the use of the transpiration adjustment, except that each reference mass fraction value is based solely upon analysis using either ICP-OES or ICP-MS and uncertainty components are limited to those associated with the analysis and the transpiration adjustment. The reference mass concentration values and expanded uncertainties given in Table 4 are calculated using the same approach employed for the certified mass concentration values (see explanation above), except that they are calculated using the reference mass fraction values in place of the certified mass fraction values.

## NOTICE AND WARNING TO USERS

**CAUTION:** This SRM is an acidic solution. All appropriate safety precautions, including use of gloves during handling, should be taken.

## INSTRUCTIONS FOR USE

The SRM should be shaken before use to remix water that may have condensed on the inner surfaces of the bottle. To help prevent contamination, pipettes or other labware should **NOT** be inserted into the bottle. Instead, a portion of the solution should be decanted into another clean, dry container for use. Unused portions should not be returned to the SRM bottle.

The accuracy of trace element analysis is limited by contamination, especially at the microgram per kilogram (or microgram per liter) level. All apparatuses should be scrupulously clean, and only high-purity reagents should be employed. Sampling and manipulations, such as evaporations, should be done in a clean environment, such as a Class-100 clean hood.

The mass concentration values and uncertainties given in Tables 2 and 4 were calculated from the mass fraction values and uncertainties in Tables 1 and 3, respectively, taking into account the anticipated range of density values of the SRM solution in the temperature range 17 °C to 27 °C. Therefore, the mass concentration values and uncertainties given in the tables are valid when the SRM solution is used within a temperature range of 22 °C ± 5 °C. A more precise estimate of the mass concentration for a given temperature can be obtained by multiplying the mass fraction value by the accurately measured density of the solution at that temperature. The uncertainty associated with a mass concentration value calculated in this way can be estimated by combining the uncertainty components for the mass fraction value and the measured density following the ISO Guide [2].

**Transpiration:** The certified and reference values given in Tables 1 through 4 account for the effects of transpiration that may occur *prior to the first opening of the sealed pouch by the SRM user*. After the SRM bottle has been removed from the pouch, the rate of transpiration will rise, resulting in gradual increases in the mass fractions (and concentrations) of the elements. *It is the responsibility of the user of this SRM to account for this effect*. One approach is to weigh the SRM bottle both before and after each use. Mass loss observed during storage can be utilized to correct for transpiration. In order to minimize transpiration, the SRM bottle should be stored tightly closed and sealed inside an airtight container. The user should set a maximum shelf-life for a partially used SRM bottle commensurate with accuracy requirements.

## PREPARATION OF MATERIAL

SRM 1640a was prepared at NIST using only high-purity reagents. An acid-cleaned HDPE tank of 2 kL capacity was filled with a known mass of commercially available spring water and enough concentrated nitric acid to adjust the acid volume fraction to approximately 2 %. After thorough mixing with a precleaned recirculating pump, a preliminary ICP-MS analysis was performed to determine the levels of the 29 elements of interest. The levels of the 22 elements to be certified were gravimetrically adjusted to target values by additions of aliquots of known masses of the SRMs in the SRM 3100 series of single-element standard solutions. For each of these elements, the target value was approximately 80 % of the Maximum Contaminant Level (MCL) listed in either the National Primary Drinking Water Regulations or the National Secondary Drinking Water Regulations maintained by the United States Environmental Protection Agency (EPA) [4], or approximately the mass fraction that was present in SRM 1640 Trace Elements in Natural Water, whichever was less. After addition of the aliquots and thorough mixing, the SRM solution was packaged in acid-cleaned HDPE bottles of 250 mL capacity and sealed inside aluminized Mylar pouches.

Table 1. Certified Values for Elements in SRM 1640a Expressed in Mass Fraction Units<sup>(a)</sup>

Element	Mass Fraction ( $\mu\text{g/kg}$ )			$k$	$df$
Aluminum	52.6	$\pm$	1.8	2.069	23
Antimony	5.064	$\pm$	0.045	2.365	7
Arsenic	8.010	$\pm$	0.067	1.980	120
Barium	150.60	$\pm$	0.74	1.984	98
Beryllium	3.002	$\pm$	0.027	2.060	25
Boron	300.7	$\pm$	3.1	2.365	7
Cadmium	3.961	$\pm$	0.072	2.365	7
Chromium	40.22	$\pm$	0.28	2.021	40
Cobalt	20.08	$\pm$	0.24	2.447	6
Copper	85.07	$\pm$	0.48	2.228	10
Iron	36.5	$\pm$	1.7	2.447	6
Lead	12.005	$\pm$	0.040	1.970	227
Manganese	40.07	$\pm$	0.35	2.201	11
Molybdenum	45.24	$\pm$	0.59	2.017	43
Nickel	25.12	$\pm$	0.12	2.026	37
Selenium	19.97	$\pm$	0.16	2.228	10
Silver	8.017	$\pm$	0.042	2.086	20
Strontium	125.03	$\pm$	0.86	2.179	12
Thallium	1.606	$\pm$	0.015	2.365	7
Uranium	25.15	$\pm$	0.26	2.145	14
Vanadium	14.93	$\pm$	0.21	2.447	6
Zinc	55.20	$\pm$	0.32	2.010	49

<sup>(a)</sup> Certified mass fraction values are the equally weighted means of results from gravimetry and ICP-OES or ICP-MS, adjusted upward for transpiration that may occur over the certification period while the SRM bottle remains sealed inside the aluminized Mylar pouch. (NOTE: *No correction has been applied for transpiration that will occur after the pouch seal has been broken.* See "Instructions for Use" for more information.) The magnitude of the transpiration adjustment (0.11 %) was selected so that the actual mass fractions are expected to be equal to the corresponding certified values approximately halfway through the certification period. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as  $U = ku_c$ , where  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, the ICP-OES or ICP-MS analysis, method bias [3], and the transpiration adjustment. The coverage factor ( $k$ ) for each analyte is determined from the Student's  $t$ -distribution corresponding to the degrees of freedom ( $df$ ) and a 95 % level of confidence.

Table 2. Certified Values for Elements in SRM 1640a Expressed in Mass Concentration Units<sup>(a)</sup>

Element	Mass Concentration <sup>(b)</sup> (µg/L)			<i>k</i>	<i>df</i>
Aluminum	53.0	±	1.8	2.064	24
Antimony	5.105	±	0.046	2.262	9
Arsenic	8.075	±	0.070	1.977	142
Barium	151.80	±	0.83	1.976	151
Beryllium	3.026	±	0.028	2.045	29
Boron	303.1	±	3.1	2.306	8
Cadmium	3.992	±	0.074	2.365	7
Chromium	40.54	±	0.30	2.008	51
Cobalt	20.24	±	0.24	2.365	7
Copper	85.75	±	0.51	2.120	16
Iron	36.8	±	1.8	2.447	6
Lead	12.101	±	0.050	1.965	517
Manganese	40.39	±	0.36	2.160	13
Molybdenum	45.60	±	0.61	2.013	46
Nickel	25.32	±	0.14	2.001	59
Selenium	20.13	±	0.17	2.160	13
Silver	8.081	±	0.046	2.040	31
Strontium	126.03	±	0.91	2.120	16
Thallium	1.619	±	0.016	2.306	8
Uranium	25.35	±	0.27	2.120	16
Vanadium	15.05	±	0.25	2.365	7
Zinc	55.64	±	0.35	1.995	68

<sup>(a)</sup> Certified mass concentration values are calculated from the certified mass fraction values in Table 1 through multiplication by the density of the SRM 1640a solution. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as  $U = ku_c$ , where  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the certified mass fraction value and the solution density. The coverage factor ( $k$ ) for each analyte is determined from the Student's  $t$ -distribution corresponding to the degrees of freedom ( $df$ ) and a 95 % level of confidence.

<sup>(b)</sup> The certified mass concentration values and expanded uncertainties are valid when the SRM solution is used within the temperature range (22 °C ± 5 °C).

Table 3. Reference Values for Elements in SRM 1640a Expressed in Mass Fraction Units<sup>(a)</sup>

Element	Mass Fraction (mg/kg)			<i>k</i>	<i>df</i>
Calcium	5.570	±	0.016	2.120	16
Magnesium	1.0502	±	0.0034	2.262	9
Potassium	0.5753	±	0.0020	2.179	12
Silicon	5.169	±	0.017	2.074	22
Sodium	3.112	±	0.031	2.776	4
(µg/kg)					
Lithium	0.4034	±	0.0092	2.776	4
Rubidium	1.188	±	0.011	1.961	3204

<sup>(a)</sup> Reference mass fraction values are the ICP-OES or ICP-MS values, adjusted upward for transpiration that may occur over the certification period while the SRM bottle remains sealed inside the aluminized Mylar pouch. (NOTE: *No correction has been applied for transpiration that will occur after the pouch seal has been broken.* See “Instructions for Use” for more information.) The magnitude of the transpiration adjustment (0.11 %) was selected so that the actual mass fractions are expected to be equal to the corresponding reference values approximately halfway through the certification period. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as  $U = ku_c$ , where  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the ICP-OES or ICP-MS analysis and the transpiration adjustment. The coverage factor ( $k$ ) for each analyte is determined from the Student's  $t$ -distribution corresponding to the degrees of freedom ( $df$ ) and a 95 % level of confidence.

Table 4. Reference Values for Elements in SRM 1640a Expressed in Mass Concentration Units<sup>(a)</sup>

Element	Mass Concentration <sup>(b)</sup> (mg/L)			<i>k</i>	<i>df</i>
Calcium	5.615	±	0.021	2.005	54
Magnesium	1.0586	±	0.0041	2.045	29
Potassium	0.5799	±	0.0023	2.040	31
Silicon	5.210	±	0.021	2.005	54
Sodium	3.137	±	0.031	2.571	5
(µg/L)					
Lithium	0.4066	±	0.0094	2.776	4
Rubidium	1.198	±	0.011	1.961	3657

<sup>(a)</sup> Reference mass concentration values are calculated from the reference mass fraction values in Table 3 through multiplication by the density of the SRM 1640a solution. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as  $U = ku_c$ , where  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the reference mass fraction value and the solution density. The coverage factor ( $k$ ) for each analyte is determined from the Student's  $t$ -distribution corresponding to the degrees of freedom ( $df$ ) and a 95 % level of confidence.

<sup>(b)</sup> The reference mass concentration values and expanded uncertainties are valid when the SRM solution is used within the temperature range (22 °C ± 5 °C).

## REFERENCES

- [1] 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 (2000); available at <http://ts.nist.gov/MeasurementServices/ReferenceMaterials/PUBLICATIONS.cfm> (accessed Jun 2010).
- [2] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf) (accessed Jun 2010); 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 <http://www.nist.gov/phylab/pubs/index.cfm> (accessed Jun 2010).
- [3] 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; p. 571 (2000).
- [4] *Drinking Water Contaminants*, United States Environmental Protection Agency, available at <http://www.epa.gov/safewater/contaminants/index.html#listsec> (accessed Jun 2010).

<p><b>Certificate Revision History:</b> 08 June 2010 (This revision includes corrected lithium values in Tables 3 and 4 and minor editorial changes.); 03 December 2009 (Original certificate date).</p>
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*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) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*