National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 606

Trace Elements in Basalt Glass

This Standard Reference Material (SRM) is intended to facilitate development of chemical methods of analysis for trace elements in a natural ferro-magnesian silicate glass intended for use with measurement techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and microbeam X-ray fluorescence (µXRF). This SRM can also be used for quality assurance when assigning values to in-house control materials. A unit of SRM 606 consists of a single piece of basalt glass mounted in epoxy. The epoxy mounted material has a cylindrical shape approximately 14 mm tall and 12.5 mm in diameter.

Certified Mass Fraction Values: Certified values for constituents of SRM 606 and their corresponding standard uncertainties (u_c) and 95 % uncertainty intervals are reported in Table 1 as mass fractions. A National Institute of Standards and Technology (NIST) certified value 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 considered [1]. A certified value is a best estimate of the true value based on the results of analyses performed at NIST and collaborating laboratories. The certified values in this material are the unweighted means of the individual sets of NIST results and results from the U.S. Geological Survey (USGS) Reference Materials Project. The standard uncertainty and corresponding 95 % uncertainty intervals were computed using the NIST Consensus Builder [2]. The uncertainty intervals are asymmetric about the consensus value in this case [3]. The combined standard uncertainty u_c incorporates the observed difference between the results from the methods and their respective uncertainties, and an uncertainty component for homogeneity, consistently with the ISO/JCGM Guide and its Supplement 1 [4,5]. The certified mass fraction values in Table 1 are metrologically traceable to the International System of Units (SI) derived unit of milligrams per kilogram on a dry-mass basis.

Reference Mass Fraction Values: A reference value for Ce is reported in Table 2 as a mass fraction. A NIST reference value is a noncertified value that is a best estimate of the true value based on available data; however, the value does not meet the NIST criteria for certification and is provided with associated uncertainties that may not include all sources of uncertainty [1]. The reference mass fraction values were derived from results reported by NIST and collaborating laboratories. The reference values are the unweighted means of the individual sets of NIST and collaborator results. The uncertainty intervals are asymentric about the consensus value in their respective uncertainties, and an uncertainty component for homogeneity, consistent with the ISO/JCGM Guide and its Supplement [4,5], and k is a coverage factor corresponding to approximately 95 % confidence [4,5]. The reference mass fraction values in Table 2 are metrologically traceable to calibration procedures and standards used by experienced measurement community.

Expiration of Certification: The certification of **SRM 606** is valid indefinitely, within the measurement uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Use"). However, the certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Project development and coordination of the SRM material was performed by R.D. Vocke and S.E. Long of the NIST Chemical Sciences Division and S.A. Wilson of USGS.

Coordination of the technical measurements leading to the certification of this SRM was performed by W.C. Davis of the NIST Chemical Sciences Division.

Analyses at NIST were performed by W.C. Davis, and J.L. Molloy of the NIST Chemical Sciences Division.

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Certificate Issue Date: 04 May 2018

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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.

Statistical analyses for determining consensus values and corresponding uncertainty intervals were provided by H. Iyer of the NIST Statistical Engineering Division.

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

Table 1. Certified Mass Fraction Values for Elements in SRM 606

Element	Mass Fraction (mg/kg)	Standard Uncertainty, u_c (mg/kg)	95 % Coverage Interval[(a)] (mg/kg)
Barium (Ba)[(b,c,d)]	174	5	166 – 186
Cobalt (Co)[(b,c,d)]	48.3	1.3	45.3 – 50.7
Chromium (Cr)[(b,c,d)]	315	9	302 – 336
Copper (Cu)[(b,c,d)]	86.5	2.3	83.2 – 92.1
Lanthanum (La)[(b,c,d)]	5.45	0.78	4.61 – 7.14
Lead (Pb)[(b,c)]	4.26	0.60	3.55 – 5.43
Scandium (Sc)[(b,c,d)]	33.6	4.8	23.7 – 39.6
Strontium (Sr)[(b,c,d)]	169	5	160 – 178
Vanadium (V)[(b,c,d)]	266	10	251 – 288
Yttrium (Y)[(b,c,d)]	17.1	1.8	13 – 19.4
Zinc (Zn)[(b,c,d)]	79.2	3.8	73.1 – 86.3

[(a)] The standard uncertainty and corresponding 95 % uncertainty intervals were computed using the NIST Consensus Builder [2]. The uncertainty intervals are asymmetric about the consensus value in this case [3]. The combined standard uncertainty, u_c, incorporates the observed difference between the results from the methods and their respective uncertainties, and an uncertainty component for homogeneity, consistent with the ISO/JCGM Guide and its Supplement 1 [4,5].
[(b)] NIST ICP-MS
[(c)] USGS ICP-MS
[(d)] USGS ICP-OES

Table 2. Reference Mass Fraction Values for Elements in SRM 606

Element	Mass Fraction (mg/kg)	Standard Uncertainty, u_c (mg/kg)	95 % Coverage Interval[(a)] (mg/kg)
Cerium (Ce)[(b,c,d)]	14.6	3.8	11 – 20.8

[(a)] The standard uncertainty and corresponding 95 % uncertainty intervals were computed using the NIST Consensus Builder [2]. The uncertainty intervals are asymmetric about the consensus value in this case [3]. The combined standard uncertainty, u_c, incorporates the observed difference between the results from the methods and their respective uncertainties, and an uncertainty component for homogeneity, consistent with the ISO/JCGM Guide and its Supplement 1 [4,5].
[(b)] NIST ICP-MS
[(c)] USGS ICP-MS
[(d)] USGS ICP-OES

INSTRUCTIONS FOR STORAGE AND USE

Each wafer surface should be cleaned before use. To prepare a wafer for analysis, wipe it clean with ethanol and then do a mild surface cleaning (not etch) in dilute (1:10) HNO_3. The material should be stored in its original container in a cool, dry location.

To use the uncertainty intervals given in this certificate in comparisons and calculations, the user must be aware that intervals are not symmetric about the assigned values. The use of the intervals depends on the context, and instructions for two common uses follow.

Direct comparison to a result of a user determination: For this case, directly compare a coverage interval calculated by the user for their result to the appropriate coverage interval provided in this certificate.

Propagation of uncertainty when using SRM 606 as a calibration standard: When a value provided in this certificate is used to calibrate a measurement process, the uncertainty associated with that value should be appropriately propagated into the user's uncertainty calculation. The asymmetric intervals in Table 1 and Table 2 cannot be interpreted as (value $\pm k u_c$), where k is an expansion factor, and u_c is a combined standard uncertainty representative of both sides of the interval around the value. The user may use a Monte Carlo method for propagation of probability distributions. This can be done using the NIST Uncertainty Machine [see reference 6 for detailed instructions].

ANALYSIS

Homogeneity Assessment: The homogeneity of representative elements was performed by micro X-ray fluorescence (µXRF) and measured in 4 mm × 4 mm areas of three different samples with an analysis point spacing of 50 µm. Microscale heterogeneity testing using µXRF resulted in an estimated minimum recommended mass of 0.3 mg. Analyses of variance and graphical analyses of the data found no detectable inhomogeneity at 95% confidence. No assessment of the microscale heterogeneity was conducted for Ba, La, Pb, and Ce.

Determination of Elements: Value assignment of the mass fractions of the elements in SRM 606 was based on measurements using inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and isotope dilution ICP-MS (ID-ICP-MS).

ICP-OES and ICP-MS methods from the USGS: For the determination of all elements 0.2 g test portions of the bulk SRM 606 material were digested with an aluminum heat block using nitric acid, perchloric, and hydrofluoric acid. Quantification for all analyses was based on standardizing with digested rock reference materials and a series of multi-element solution standards.

ICP-MS methods from NIST: For the determination of cerium, cobalt, lanthanum, lead, scandium, vanadium, and yttrium, test portions of 0.25 g of the bulk SRM 606 material were digested in a closed-vessel microwave system using a mixture of hydrofluoric acid, hydrochloric and nitric acid. Measurements were made at mass resolution of approximately 4000 using a sector-field ICP-MS by the method of standard additions.

ID-ICP-MS methods from NIST: For the determination barium, chromium, copper, strontium, and zinc, test portions of 0.25 g of the bulk SRM 606 material were digested with enriched isotopes in a closed-vessel microwave system using a mixture of hydrofluoric acid, hydrochloric acid and nitric acid. Isotopic measurements were made at mass resolution of approximately 4000 using a sector-field ICP-MS.

SOURCE AND PREPARATION

SRM 606 consists of a geological matrix produced by processing SRM 688 *Basalt Rock* into a glass material. The glass matrix was produced by heating the SRM powdered material in a platinum bowl in a furnace at ≈ 1300 °C. The molten material was removed from the furnace and mixed with a platinum rod and returned to the furnace for further heating. After several mixing/heating cycles, the material was cooled and then mechanically sub-divided into smaller pieces. For the final SRM material, individual pieces of the resultant basalt glass material will be mounted in an epoxy casing to provide a level structure, and surface polished to provide a flat surface and then packaged into units of SRM 606 at NIST.

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 https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF (accessed May 2018).

[2] Koepke, A.; Lafarge, T.; Possolo, A.; Toman, B.; *Consensus Building for Interlaboratory Studies, Key Comparisons, and Meta-analysis*; Metrologia, Vol. 54, p. S34 (2017) available at https://consensus.nist.gov/ (accessed May 2018).

[3] Possolo, A.; *Simple Guide for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1900, (2015) available at http://nvlpubs.nist.gov/nistpubs/TechnicalNotes/NIST.TN.1900.pdf (accessed May 2018).

[4] 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 (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed May 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/tn1297/index.cfm (accessed May 2018).

[5] 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*; JCGM (2008); available at http://www.bipm.org/en/publications/guides/gum.html (accessed May 2018).

[6] NIST Uncertainty Machine, available at https://uncertainty.nist.gov (accessed May 2018). The user enters the measurement equation and standard uncertainty estimates or probability distributions describing uncertainty for the terms of the equation. For the estimate of uncertainty of the calibration value, the user would choose the "Sample values" option and provide a file containing the actual distribution of the NIST analytical results of certification analyses. Plain ASCII files for the constituents may be found at https://www-s.nist.gov/srmors/view_detail.cfm?srm=606 (accessed May 2018).

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.