National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2791

Inorganic Constituents in Softwood Biomass Material

This Standard Reference Material (SRM) is intended for use in validating methods for the determination of elements in softwood biomass materials and similar matrices, and for qualifying in-house control materials. A unit of SRM 2791 consists of two bottles each containing approximately 30 g of material.

Certified Mass Fraction Values: Certified mass fraction values of elements in SRM 2791, reported on a dry-mass basis, are provided in Table 1. A 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 taken into account [1]. Analyses for value assignment were performed by NIST. Certified mass fraction values for elements were calculated as the means of the mean values from NIST methods. The associated uncertainties are expressed at an approximately 95 % level of confidence [2–4].

Reference Mass Fraction Values: Reference mass fraction values for additional elements, reported on a dry-mass basis, and ash in SRM 2791, are provided in Tables 2 and 3. A NIST reference mass fraction value is a noncertified value that is the best estimate of the true value based on available data; however, the values do not meet the NIST criteria for certification [1] and are provided with an uncertainty that may reflect only measurement reproducibility, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods. The reference mass fraction values were derived from results reported by NIST.

Expiration of Certification: The certification of **SRM 2791** is valid, within the measurement uncertainty specified, until **30 June 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.J. Wood and R. Oflaz of the NIST Chemical Sciences Division.

Analytical measurements at NIST were performed by J.F. Browning, C.E. Bryan, B.L. Catron, K.D. Chieh, S.E. Long, A.F. Marlow, A.J. Moors, J.M. Ness, R. Oflaz, R. Paul, R.S. Pugh, and L.J. Wood of the NIST Chemical Sciences Division.

Statistical analysis was provided by J.H. Yen 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: 22 March 2018

Steven J. Choquette, Director
Office of Reference Materials

NOTICE AND WARNING TO USERS

SRM 2791 IS INTENDED FOR RESEARCH USE; NOT FOR ANIMAL USE.

INSTRUCTIONS FOR STORAGE AND USE[1]

Storage: The SRM should be stored in the original, unopened bottle at room temperature (20 °C to 25 °C) until required for use. The bottle can be closed and test portions removed and analyzed until the material reaches its expiration date.

Use: Prior to removal of a test portion for analysis, the contents of the bottle should be mixed thoroughly. Allow the contents to settle for one minute prior to opening to minimize the loss of fine particles. To relate analytical determinations to the certified values in this Certificate of Analysis, a test portion mass size of at least 0.2 g should be used when determining Ag, Al, As, Ca, Cd, Ce, Cl, Co, Cr, Cs, Fe, K, La, Mg, Mn, Na, Rb, Sb, Sc, Se, Sm, Th, Ti, V, W and Zn; a test portion mass size of at least 0.25 g should be used when determining Hg; a test portion mass size of at least 0.5 g should be used when determining Cu; and a test portion mass size of at least 1 g should be used when determining B, C, and I. Test portions should be analyzed as received and results converted to a dry-mass basis (See "Determination of Moisture"). Analytical results obtained in analyses should include their own estimates of uncertainty and can be compared to the listed values using procedures described in references 5 and 6.

Determination of Moisture: Moisture content of SRM 2791 was determined at NIST by (1) freeze-drying to constant mass over 7 d; (2) drying over magnesium perchlorate in a desiccator at room temperature for 7 d; and (3) drying using a thermogravimetric analyzer (TGA) (LECO Model 701) for 2 h held at 105 °C. Unweighted results obtained using all three techniques were averaged to determine a conversion factor of (0.9489 ± 0.0065) gram dry-mass per gram as-received mass, which was used to convert data from an as-received to a dry-mass basis; the uncertainty shown on this value is an expanded uncertainty ($k = 2$) to represent a 95 % level of confidence. An uncertainty component for the conversion factor (0.34 %) obtained from the moisture measurements is incorporated in the uncertainties of the certified and reference values, reported on a dry-mass basis, that are provided in this certificate.

SOURCE, PREPARATION, AND ANALYSIS

Preparation: SRM 2791 was prepared from softwood bedding pellets to support biomass energy, biomass technology developments, and environmental impact assessments. The material was purchased commercially as five 1 ft^3 bags that were sent to the NIST Reference Material Production facility (ISO certified Class 7 clean room) in Charleston, SC. The material was first cryomilled and then cryohomogenized. The material was shipped to NIST Gaithersburg for jet milling, irradiation (Neutron Products, Inc., Dickerson, MD) to an absorbed dose of 7.9 kGy to 9.5 kGy, and bottling.

Particle Size Measurements: Particle size measurements for SRM 2791 were made after packaging using a Malvern Mastersizer 3000 laser-based light scattering system. Approximately 0.5 g of SRM 2791 m^3aterial was measured using ethanol as the dispersant (refractive index 1.36). The sample was introduced into the measurement cell before ten individual measurements were made at an obscuration of 12 % to 13 % of the laser beam. The calculated 10th (D_v10), 50th (D_v50) and 90th (D_v90) percentile particle sizes are $D_v10 = 6.93$ µm, $D_v50 = 32.4$ µm, and $D_v90 = 112$ µm. The volume fraction of material smaller than 75.1 µm in diameter is approximately 79 %.

NIST Analytical Approach for Determination of Elements: Value assignment of the mass fractions of elements in SRM 2791 was based on the combination of measurements provided by NIST using inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID/CV ICP-MS), instrumental neutron activation analysis (INAA), and thermal neutron prompt gamma-ray activation analysis (PGAA).

NIST Analyses for As, Cr, Co, Cs, Cu, Fe, K, Mg, Mn, Na, Se, V, and Zn using ICP-MS and ICP-OES: Mass fractions of arsenic, cesium, chromium, cobalt, copper, iron, magnesium, manganese, potassium, selenium, sodium, vanadium, and zinc were determined by either ICP-MS or ICP-OES in duplicate, 0.5 g, test portions taken from each of six bottles of SRM 2791. Samples were digested in a microwave sample preparation system using a HNO_3:HF solution. Quantification was based on the method of standard additions using calibration solutions prepared from the SRM 3100 series of single-element standard solutions.

NIST Analyses for Hg using ID/CV ICP-MS: The mass fraction of mercury was determined by ID/CV ICP-MS in single, nominal 0.25 g, test portions taken from each of eight bottles of SRM 2791. Samples were digested in a

[1] Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

microwave sample preparation system using a HNO_3:HCl solution. Measurements were made using cold-vapor mercury generation coupled with ICP-MS. Quantification was based on reverse isotope dilution with a ^{201}Hg stock solution and SRM 1641d *Mercury in Water.*

NIST Analyses for Ag, Al, As, Ca, Cd, Ce, Cl, Co, Cr, Cs, Fe, K, La, Mg, Mn, Na, Rb, Sb, Sc, Se, Sm, Th, Ti, V, W, and Zn using INAA: Mass fractions of aluminum, antimony, arsenic, calcium, cadmium, cerium, cesium, chlorine, chromium, cobalt, iron, lanthanum, magnesium, manganese, potassium, rubidium, samarium, scandium, selenium, silver, sodium, thorium, titanium, tungsten, vanadium, and zinc were determined by INAA using duplicate, nominal 0.2 g, test portions taken from each of 12 bottles of SRM 2791. For the analysis of antimony, arsenic, cadmium, cerium, cesium, chromium, cobalt, iron, lanthanum, rubidium, samarium, scandium, selenium, silver, thorium, tungsten, and zinc, powders were pressed into cylindrical pellets, and samples, standards, and controls were packaged individually in clean polyethylene bags and irradiated individually at 20 MW for 16 h with a 180-degree inversion after 8 h. Nuclides were counted for 24 h after a 14 d decay (Ag, Ce, Co, Cr, Cs, Fe, Rb, Sb, Sc, Se, Th, Zn) or 2 h after a 5 d decay (As, Cd, La, Sm, W). For analysis of aluminum, calcium, chlorine, magnesium, manganese, potassium, sodium, titanium, and vanadium, each sample, standard, or control material was individually irradiated together with one flux monitor foil for 120 s at a reactor power of 20 MW. Nuclides were counted for 5 min to 30 min after decays of 5 min to 15 min. Quantification is based on validated pure metal foils, pure compounds, or the SRM 3100 series of single-element standard solutions.

NIST Analyses for B, C, and H using PGAA: Mass fractions of boron, carbon, and hydrogen were determined by PGAA using single, nominal 1 g, test portions taken from each of eight bottles of SRM 2791. Samples were irradiated for 6 h to 24 h. Gamma rays were measured using a reverse electrode high purity germanium detector. The 2223 keV, 477 keV, and 4945 keV peaks were integrated for hydrogen, boron, and carbon, respectively. Quantification was based on SRM 912 *Urea* and SRM 3107 *Boron (B) Standard Solution (Lot # 110830).*

NIST Analytical Approach for Determination of Ash: Value assignment of the mass fraction of ash in SRM 2791 was based on the measurements provided by NIST using TGA. Nominal 1 g samples were held for 3 h held at 575 °C.

Homogeneity Assessment: To address issues of possible inhomogeneity of the SRM, analyses of variance with a 5 % significance level and graphical analyses were performed on NIST data. For ash, Ca, Fe, and La, the uncertainty incorporates a component for possible inhomogeneity based on the standard deviation.

Value Assignment: Each certified mass fraction value in this SRM was derived from results of analyses performed by NIST using the mean of the mean values from NIST results. The uncertainty of the combined mean was estimated using a bootstrap procedure based on a Gaussian random effects model for the between-method effects [2-4].

Certified Mass Fraction Values: Each certified mass fraction value is the combined mean from each set of analyses by NIST. Values are expressed as $x \pm U_{95\%}(x)$, where x is the certified value and $U_{95\%}(x)$ is the expanded uncertainty of the certified value. The true value of the analyte is believed to lie within the interval $x \pm U_{95\%}(x)$ with 95 % confidence. To propagate this uncertainty, treat the certified value as a normally distributed random variable with mean x and standard deviation $U_{95\%}(x)/2$ [2–4]. The measurand is the total mass fraction for each analyte listed in Table 1, on a dry-mass basis. Metrological traceability is to the SI derived unit for mass fraction (expressed as milligrams per kilogram).

Table 1. Certified Mass Fraction Values for Elements in SRM 2791

	Mass Fraction (mg/kg)		
Arsenic (As)[a,b]	0.0067	±	0.0016
Cesium (Cs)[a,b]	0.00505	±	0.00062
Cobalt (Co)[a,b]	0.0551	±	0.0044
Iron (Fe)[b,c]	9.6	±	2.8
Magnesium (Mg)[b,c]	155	±	26
Manganese (Mn)[b,c]	39.92	±	0.74
Mercury (Hg)[d]	0.00923	±	0.00014
Potassium (K)[b,c]	428	±	12
Selenium (Se)[a,b]	0.0165	±	0.0035
Sodium (Na)[b,c]	14.2	±	1.6
Vanadium (V)[a,b]	0.0448	±	0.0030
Zinc (Zn)[b,c]	19.3	±	3.7

[a] ICP-MS
[b] INAA
[c] ICP-OES
[d] ID/CV ICP-MS

Reference Mass Fraction Values for Elements: Each reference mass fraction value is the mean from each set of analyses by NIST. Values are expressed as $x \pm U_{95\%}(x)$, where x is the reference value and $U_{95\%}(x)$ is the expanded uncertainty of the value at a confidence level of approximately 95 %. The measurand is the mass fraction for each element listed in Table 2, on a dry-mass basis, as determined by the method indicated. Metrological traceability is to the SI derived unit for mass fraction (expressed as % or milligrams per kilogram) as realized by the method used.

Table 2. Reference Mass Fraction Values for Elements in SRM 2791

	Mass Fraction (%)
Carbon (C)[a]	53.4 ± 1.1
Hydrogen (H)[a]	6.39 ± 0.15

	Mass Fraction (mg/kg)
Aluminum (Al)[b]	73.6 ± 1.0
Antimony (Sb)[b]	0.0399 ± 0.0015
Boron (B)[a]	2.704 ± 0.089
Cadmium (Cd)[b]	0.0821 ± 0.0058
Calcium (Ca)[b]	527 ± 53
Cerium (Ce)[b]	0.1692 ± 0.0054
Chlorine (Cl)[b]	37.1 ± 1.1
Chromium (Cr)[b]	0.187 ± 0.033
Copper (Cu)[c]	0.687 ± 0.043
Lanthanum (La)[b]	0.140 ± 0.029
Rubidium (Rb)[b]	0.807 ± 0.024
Samarium (Sm)[b]	0.01338 ± 0.00051
Scandium (Sc)[b]	0.00615 ± 0.00038
Silver (Ag)[b]	0.01491 ± 0.00063
Thorium (Th)[b]	0.00507 ± 0.00015
Titanium (Ti)[b]	55.6 ± 1.3
Tungsten (W)[b]	0.0201 ± 0.0029

[a] PGAA
[b] INAA
[c] ICP-OES

Reference Mass Fraction Value for Ash: The reference mass fraction value for ash is the mean from the set of analyses by NIST using TGA. Values are expressed as $x \pm U_{95\%}(x)$, where x is the reference value and $U_{95\%}(x)$ is the expanded uncertainty of the value at a confidence level of approximately 95 %. The measurand is the mass fraction for ash listed in Table 3, as determined by the method indicated. Metrological traceability is to mass fraction (expressed as grams per 100 grams) as realized by the method used.

Table 3. Reference Mass Fraction Values for Ash in SRM 2791

	Mass Fraction (g/100 g)
Ash	0.52 ± 0.42

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; U.S. Government Printing Office: Washington, DC (2000); available at https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF (accessed Mar 2018).

[2] 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 Mar 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/nist-technical-note-1297 (accessed Mar 2018).

[3] JCGM 101:2008; *Evaluation of Measurement Data – Supplement 1 to the Guide to Expression of Uncertainty in Measurement - Propagation of Distributions Using a Monte Carlo Method*; JCGM (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Mar 2018).

[4] Efron, B.; Tibshirani, R.J.; *An Introduction to the Bootstrap*; Chapman & Hall, London, UK (1993).

[5] Rukhin, A.L. *Compatibility verification of certified reference materials and user measurements.* Metrologia, Vol. 51, pp. 11–17 (2014).

[6] Sharples, K.E.; Duewer, D.L.; Standard Reference Materials for Analysis of Dietary Supplements; J. AOAC Int., Vol. pp. 1298–1302 (2008).

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.