National Institute of Standards & Technology

Report of Investigation

Reference Material 8704

Buffalo River Sediment

This Reference Material (RM) is intended primarily for use in the analysis of sediments, soils, or materials of a similar matrix. A unit of RM 8704 consists of 50 g of freeze-dried, radiation-sterilized, homogenized, river sediment that is very similar in composition to SRM 2704, Buffalo River Sediment, having been collected at the same time and location (see Source and Preparation of Material).

Reference Concentration Values: Reference values for concentrations of 25 elements are given in Table 1. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty.

Information Concentration Value: An information value for arsenic is provided in Table 2. An information value is a noncertified value for which there is insufficient information to assign an uncertainty.

Expiration of Reference Values: The reference values of RM 8704 are valid, within the measurement uncertainties specified, until **01 January 2008**, provided the RM is handled in accordance with instructions given in this report (see Instructions for Use). The reference values are nullified if the RM is contaminated or otherwise modified.

Maintenance of Reference Values: NIST will monitor this RM over the period of its validity. If substantive changes occur that affect the reference values before expiration, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

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

The overall direction and coordination of the analyses were provided by G.C. Turk of the NIST Analytical Chemistry Division.

Spectrometric measurements were performed by A.P. Lindstrom, G.C. Turk, L.J. Wood, and L.L. Yu of the NIST Analytical Chemistry Division. Instrumental Neutron Activation Analysis was performed by R.R. Greenberg of the NIST Analytical Chemistry Division.

The support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald.

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SOURCE, PREPARATION, AND ANALYSIS

Source and Preparation of Material: The river sediment for SRM 2704 Buffalo River Sediment and RM 8704 Buffalo River Sediment was collected from the Buffalo River in the area of the Ohio Street Bridge, Buffalo, NY. The U.S. Army Corps of Engineers, under contract to NIST, collected and screened approximately 908 kg of river sediment and placed it in six 55-gallon, Teflon®[1]-lined drums. The drums were loaded onto a refrigerated truck and transported to the Technimed Corporation, Fort Lauderdale, FL for freeze-drying of the contents. The freeze-dried sediment was shipped to a laboratory contracted by NIST where it was screened and passed through a 150 μm (100 mesh) sieve and retained on a 38 μm (400 mesh) sieve. The SRM 2704 portion of the freeze-dried sediment was sieved and blended at NIST and subsequently radiation-sterilized, and bottled into 50 g units. The RM 8704 portion of the freeze-dried and sieved sediment was retained for approximately 6 years before being blended, radiation-sterilized, divided by a spinning riffler, and bottled into 50 g units.

Methods of Analysis

Spectrometric Comparison to SRM 2704: Samples weighing approximately 0.25 g were taken from each of 8 bottles of RM 8704 and 8 bottles of SRM 2704. The samples were put into solution using a lithium metaborate fusion procedure. The solutions of the two materials were spectrometrically compared using both inductively coupled plasma mass spectrometry (ICPMS) and inductively coupled plasma optical emission spectrometry (ICPOES). Mass fraction values for 18 elements in RM 8704 were calculated from the relative signal intensities (optical and/or mass spectrometric) of RM 8704 versus SRM 2704 and the certified mass fractions of SRM 2704. ICPMS measurements were made for arsenic, barium, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, nickel, lead, titanium, thallium, uranium, vanadium, and zinc. For some elements ICPMS signals were measured at more that one mass, and the equally-weighted mean value was used as the ICPMS value. ICPOES measurements were made for aluminum, barium, calcium, cobalt, chromium, iron, potassium, magnesium, manganese, sodium, lead, titanium, uranium, vanadium, and zinc. For the elements for which both ICPMS and ICPOES measurements were made, the equally-weighted mean value was used.

Combustion Analysis: Carbon was determined in 8 bottles of RM 8704 and 8 bottles of SRM 2704 at LECO Corporation, Inc. using combustion analysis with infrared detection. In a manner analogous to the spectrometric comparison, the mass fraction of carbon was calculated from the relative carbon signals of RM 8704 versus SRM 2704 and the certified mass fraction of carbon in SRM 2704. The sample size was 0.25 g.

Instrumental Neutron Activation Analysis (INAA): Samples weighing approximately 0.25 g were taken from each of 8 bottles of RM 8704 and 2 bottles of SRM 2704. Using standards prepared from dried filter papers onto which known amounts of the analytes of interest had been deposited, cerium, cobalt, chromium, cesium, europium, iron, hafnium, antimony, scandium, and thorium, were determined by INAA. SRM 2704 was analyzed as a quality control sample.

NOTICE AND WARNINGS TO USERS

Use: A minimum sample weight of 0.25 g (dry weight - see Instructions for Drying) should be used for analytical determinations relating to the reference values on this report of investigation.

Sample preparation procedures should be designed to effect complete dissolution. If volatile elements (i.e., mercury, arsenic, selenium) are to be determined, precautions should be taken in the dissolution of RM 8704 to avoid volatilization losses.

Instructions for Drying: When nonvolatile elements are to be determined, samples should be dried for 2 hours at 110 °C. Volatile elements (i.e., mercury, arsenic, selenium) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture is to be made to the data for volatile elements before comparing to the reference values. This procedure, which was used for the determination of the volatile elements, ensures that these elements are not lost during drying. The approximate mass loss on drying has been found to be 0.8 %.

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

Table 1. Reference Concentration Values for Selected Elements for RM 8704

Element	Mass Fraction (%)		
Aluminum	6.10	±	0.18
Calcium	2.641	±	0.083
Carbon	3.351	±	0.017
Iron	3.97	±	0.10
Magnesium	1.200	±	0.018
Potassium	2.001	±	0.041
Sodium	0.553	±	0.015
Titanium	0.457	±	0.020

Element	Mass Fraction (mg/kg)		
Antimony	3.07	±	0.32
Barium	413	±	13
Cadmium	2.94	±	0.29
Cerium	66.5	±	2
Cesium	5.83	±	0.12
Chromium	121.9	±	3.8
Cobalt	13.57	±	0.43
Europium	1.31	±	0.038
Hafnium	8.4	±	1.5
Lead	150	±	17
Manganese	544	±	21
Nickel	42.9	±	3.7
Scandium	11.26	±	0.19
Thorium	9.07	±	0.16
Uranium	3.09	±	0.13
Vanadium	94.6	±	4.0
Zinc	408	±	15

Reference Value Uncertainties: The uncertainty in the reference values for aluminum, calcium, potassium, and sodium, derived from spectrometric comparison to SRM 2704 using ICPOES, is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the ISO Guide [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of the ICPOES measurement uncertainty and the uncertainty of the SRM 2704 certified value. The uncertainty for the SRM 2704 certified value has been recalculated from the original data according to ISO measurement uncertainty guidelines. The coverage factor, k, was obtained from the Student's t-distribution corresponding to the calculated effective degrees of freedom of u_c using a level of confidence of 95 %.

The uncertainty in the reference values for cadmium and nickel, derived from spectrometric comparison to SRM 2704 using ICPMS, is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the ISO Guide [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of the ICPMS measurement uncertainty and the uncertainty of the certified value of SRM 2704. The uncertainty for the certified value of SRM 2704 has been recalculated from the original data according to ISO measurement uncertainty guidelines. The coverage factor, k, was obtained from the Student's t-distribution corresponding to the calculated effective degrees of freedom of u_c using a level of confidence of 95 %.

The uncertainty in the reference values for magnesium, titanium, barium, manganese, lead, uranium, vanadium, and zinc, derived from spectrometric comparison to SRM 2704 using the equally weighted mean of ICPMS and ICPOES measurements, is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the ISO Guide [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of the ICPOES measurement uncertainty, the ICPMS measurement uncertainty, and the uncertainty of the SRM 2704 certified value. The uncertainty for the SRM 2704 certified value has been recalculated from the original data according to ISO measurement uncertainty guidelines. The coverage factor, k, was obtained from the Student's t-distribution corresponding to the calculated effective degrees of freedom of u_c using a level of confidence of 95 %.

The uncertainty in the reference values for iron, cobalt, and chromium, derived from the equally weighed mean of a

spectrometric comparison to SRM 2704 (using both ICPMS and ICPOES) and an independent INAA analysis, is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the ISO Guide [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of the uncertainty in the spectrometric comparison (which includes ICPMS measurement uncertainty, ICPOES measurement uncertainty, and the uncertainty of the SRM 2704 certified value), the uncertainty of the INAA measurement, and the uncertainty of corrections for method biases [2]. The uncertainty for the SRM 2704 certified value has been recalculated from the original data according to ISO measurement uncertainty guidelines. The coverage factor, k, was obtained from the Student's t-distribution corresponding to the calculated effective degrees of freedom of u_c using a level of confidence of 95 %.

The uncertainty in the reference values of cerium, cesium, europium, hafnium, antimony, scandium, and thorium, derived from INAA analysis alone, is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the ISO Guide [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the uncertainty of the INAA measurements. The coverage factor, k, was obtained from the Student's t-distribution corresponding to the calculated effective degrees of freedom of u_c using a level of confidence of 95 %.

The uncertainty in the reference value of carbon, derived from comparison to SRM 2704 using combustion analysis, is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the ISO Guide [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of the combustion analysis measurement uncertainty and the uncertainty of the SRM 2704 certified value. The uncertainty for the SRM 2704 certified value has been recalculated from the original data according to ISO measurement uncertainty guidelines. The coverage factor, k, was obtained from the Student's t-distribution corresponding to the calculated effective degrees of freedom of u_c using a level of confidence of 95 %.

Table 2. Information Concentration Value for Arsenic for RM 8704

Element	Mass Fraction (mg/kg)
Arsenic	17

Information Value for Arsenic: This information value was determined by spectrometric comparison to SRM 2704 using ICPMS after adjusting the certified value of arsenic in SRM 2704 downward by 6 %. The adjustment is based on measurements made at NIST since 1996, that indicate the certified value for SRM 2704 is no longer valid due to a loss of approximately 6 % of the arsenic from SRM 2704. The arsenic value in RM 8704 is given for information only because there is insufficient information to assign an uncertainty.

REFERENCES

[1] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and 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).
[2] Levenson, M.S., et al, "An ISO GUM Approach to Combining Results from Multiple Methods," unpublished manuscript.

Users of this RM should ensure that the report of investigation in their possession is current. This can be accomplished by contacting the SRM Program at: Phone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the Internet http://ts.nist.gov/srm.