National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1632d

Trace Elements in Coal

(Bituminous)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques used in the analysis of coals and materials of a similar matrix. A unit of SRM 1632d consists of 50 g of bituminous coal that was ground to pass a 250 µm (60 mesh) sieve, homogenized, bottled under an argon atmosphere, and sealed in an aluminized bag.

Certified Mass Fraction Values: Certified mass fraction [1] values for elements, expressed on a dry-mass basis, are provided in Table 1. A 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 [2]. The certified values for lead, mercury, and sulfur are based on analyses by single NIST primary methods. The certified values for all elements, except lead, mercury, and sulfur, are based on analyses by two or more critically evaluated independent methods.

Reference Mass Fraction Values: Reference mass fraction values for elements, expressed on a dry-mass basis, are provided in Table 2. Reference values are provided with uncertainties that may reflect only measurement precision and may not include all sources of uncertainty [2]. The reference value for zinc is based on two independent methods. The reference values for other constituents are from a single NIST analytical method. Reference values are noncertified values that are the best estimate of the true value but do not meet NIST criteria for certification.

Information Mass Fraction Values: Information mass fraction values for elements are provided in Table 3 for information purposes only. An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2].

Expiration of Certification: The certification of **SRM 1632d** is valid, within the measurement uncertainty specified, until **01 January 2020**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This 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 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.

Technical measurements leading to certification of SRM 1632d were coordinated by E.A. Mackey of the NIST Material Measurements Laboratory. Analytical measurements leading to certification were made by D.A. Becker, R. Bindel, N.B. Buehler, R.G. Brennan, D. Cleveland, M.S. Epstein, W.R. Kelly, S.M. Lev, and M.S. Rearick formerly of NIST, R.M. Lindstrom, S.E. Long, A.F. Marlow, J. Molloy, K.E. Murphy, R. Oflaz, R.L. Paul, S.A. Rabb, J.R. Sieber, G.C. Turk, R.D. Vocke, Jr., L.J. Wood, L.L. Yu, and R.L. Zeisler of the NIST Chemical Sciences Division, J.L. Mann of the NIST Radiation Physics Division and E.A. Mackey. Analytical measurements leading to certification were also made by LECO Technical Services Laboratory.

Statistical analyses were performed by S.D. Leigh of the NIST Statistical Engineering Division.

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

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Certificate Issue Date: 14 October 2014
Certificate Revision History on Last Page.

Robert L. Watters, Jr., Director
Office of Reference Materials

INSTRUCTIONS FOR USE

Sampling: The SRM should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 250 mg should be used for analytical determinations to be related to elemental mass fraction values provided. The SRM should be stored in its original, tightly sealed bottle away from sunlight and intense sources of radiation.

Drying: To relate measurements to the certified and reference values, which are expressed on a dry-mass basis, users should determine a drying correction at the time of each analysis. The correction may be determined by oven drying a separate 1 g sample in a nitrogen or air atmosphere at 107 °C ± 3 °C to a constant mass as described in reference 3. During drying at NIST by using this thermogravimetric method, the mass loss of SRM 1632d samples stabilized between 60 min and 80 min in nitrogen and 55 min and 85 min in air. The average mass loss measured was 2.07 % (1 s = 0.05 %, n = 16) in nitrogen and 2.06 % (1 s = 0.02 %, n = 16) in air.

SOURCE, PREPARATION, AND HOMOGENEITY ASSESSMENT[(1)]

Source and Preparation of Material: The coal for this SRM was obtained from the Bailey Mine of the Consol Coal Company in southwestern Green County, PA. This mine produces bituminous coal obtained from the Pittsburgh seam. The collection of the approximately 340 kg of washed coal was performed under the direction of L.W. Rosendale, Consol Coal Research and Development. The coal was air-dried and subsequently pulverized to pass a 250 µm (60 mesh) sieve by a company under contract to NIST. At NIST, the entire lot was divided into two portions using the spinning riffler technique. One portion of the lot was further divided by the spinning riffler technique and bottled under an argon atmosphere to prepare SRM 1632c, the previous issue of this SRM, and the second portion was sealed in foil bags filled under an argon atmosphere for long-term storage. When stock of SRM 1632c was depleted, the second portion was shipped to USGS, Denver, CO, where the lot was further divided by the spinning riffler technique into bottles to prepare SRM 1632d. Bottles of SRM 1632d were shipped to NIST where they were filled with argon.

Homogeneity Assessment: The homogeneity was assessed for selected elements in the bottled material using X-ray fluorescence spectrometry (XRF) and instrumental neutron activation analysis (INAA). The estimated relative standard deviation for material inhomogeneity is ≤1 % for most elements evaluated.

VALUE ASSIGNMENT

A statistical evaluation was performed to determine whether there were any significant differences between the element mass fraction values in SRMs 1632c and 1632d. No significant differences were found for any elements determined. Therefore, results from analyses performed at NIST of both SRM 1632c and SRM 1632d were combined to provide the certified, reference, and information values shown in Tables 1, 2, and 3, respectively. The analytical techniques used for each element are listed in Table 4. Because only elements for which NIST data were available were included on this Certificate of Analysis, fewer elements are reported here than were reported for SRM 1632c.

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Assurance International, Ltd. for the Coal and Ash Sample Proficiency Exchange (CANSPEX) 2009-1 Round Robin using SRM 1632d as an unknown coal sample are provided in the Appendix to this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The CANSPEX Round Robin results should **NOT** be used as substitutes for NIST values.

[(1)]Certain commercial equipment, instruments, or materials are identified in this certificate in order 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.

Certified Mass Fraction Values: The measurands are the total mass fraction values of the elements listed in Table 1. The reference values are metrologically traceable to the SI units indicated in Table 1.

The certified mass fraction value for sulfur is an unweighted mean based on results from one primary method, isotope dilution thermal ionization mass spectrometry (ID-TIMS). The observed sulfur variation was greater than expected for the analytical technique used. Therefore, the uncertainty in the certified value for sulfur is expressed as a 95 % – 95 % tolerance designed to capture 95 % of the underlying population of sulfur values with a confidence of 95 % [4]. This expanded uncertainty in the form of tolerance is calculated as $U = ks$, where s is the standard deviation of the data and $k = 3.53$.

The certified mass fraction value for mercury is an unweighted mean based on results from a single NIST method (see Table 4) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty in the certified value for mercury is a two-sided 95 % confidence interval for the mean ($k = t_{(0.975, 7)}$).

The certified value for lead is based on results from a single NIST method (see Table 4) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty represents an expanded uncertainty with a coverage factor of 2.15, with uncertainty components combined following the ISO Guide [5].

Certified values for all other elements are the weighted means of results from multiple analytical methods [6,7]. The uncertainty listed with each certified value is an expanded uncertainty about the mean [8] with a coverage factor 2 (approximately 95 % confidence) calculated by combining a between-method variance incorporating between-method bias with a pooled, within-method variance.

Table 1. Certified Mass Fraction Values for Elements (Dry-Mass Basis) in SRM 1632d

Major Constituents

	Mass Fraction (%)
Hydrogen (H)	5.10 ± 0.05
Sulfur (S)	1.462 ± 0.074

Minor Constituents

	Mass Fraction (%)
Potassium (K)	0.1094 ± 0.0026
Chlorine (Cl)	0.1142 ± 0.0011
Iron (Fe)	0.749 ± 0.016

Trace Elements

	Mass Fraction (mg/kg)
Antimony (Sb)	0.445 ± 0.015
Barium (Ba)	40.42 ± 0.89
Cobalt (Co)	3.424 ± 0.048
Copper (Cu)	5.83 ± 0.31
Lead (Pb)	3.845 ± 0.042
Mercury (Hg)	0.0928 ± 0.0033
Rubidium (Rb)	7.36 ± 0.20

	Mass Fraction (mg/kg)
Sodium (Na)	296.9 ± 4.2
Strontium (Sr)	63.5 ± 1.2
Thorium (Th)	1.428 ± 0.035
Titanium (Ti)	477 ± 10
Uranium (U)	0.517 ± 0.012
Vanadium (V)	23.74 ± 0.10

Reference Mass Fraction Values: Reference mass fraction values are based on results from one or more analytical method performed at NIST for all elements except carbon, nitrogen, and zinc. The measurands are the mass fraction values of the analyte listed in Table 2 as determined by the methods indicated in Table 4. The reference values are metrologically traceable to the SI unit indicated in Table 2.

Reference values for carbon and nitrogen are based on results provided by one collaborating laboratory. Uncertainties in the reference values for carbon and nitrogen represent $ts/\sqrt{n}$, where $t = 2.093$, $n = 20$. The reference value for zinc is the weighted mean of results from two analytical methods [6,7]. The uncertainty listed with the reference value for zinc is an expanded uncertainty about the mean [8] with a coverage factor 2 (approximately 95 % confidence) calculated by combining a between-method variance incorporating between-method bias with a pooled, within-method variance.

The reference mass fraction value for silicon is based on results from analysis of SRM 1632c obtained by using one method at NIST. The uncertainty associated with the reference value for silicon represents an expanded uncertainty with a coverage factor of 2.1, with combined uncertainty components [5].

Reference mass fraction values for the remaining elements are weighted means of the results from two different experiments using one analytical method at NIST: one experiment for analysis of SRM 1632c and the other for SRM 1632d [6,7]. The uncertainties for these reference values are the expanded uncertainties about the mean [8] with a coverage factor of 2, calculated by combining a between-method variance incorporating between-method bias with a pooled, within-method variance [5].

Table 2. Reference Mass Fraction Values for Selected Elements (Dry-Mass Basis) in SRM 1632d

Major Constituents

	Mass Fraction (%)
Carbon (C)	76.88 ± 0.15
Nitrogen (N)	1.59 ± 0.01
Silicon (Si)	1.65 ± 0.03

Minor Constituents

	Mass Fraction (%)
Aluminum (Al)	0.912 ± 0.005
Calcium (Ca)	0.144 ± 0.003

Trace Elements

	Mass Fraction (mg/kg)
Arsenic (As)	6.1 ± 0.2
Boron (B)	62 ± 1
Cadmium (Cd)	0.08 ± 0.01
Cerium (Ce)	11.7 ± 0.4
Chromium (Cr)	13.7 ± 0.1
Cesium (Cs)	0.598 ± 0.006
Europium (Eu)	0.217 ± 0.006
Magnesium (Mg)	390 ± 6
Manganese (Mn)	13.1 ± 0.4
Scandium (Sc)	2.89 ± 0.03
Selenium (Se)	1.29 ± 0.03
Zinc (Zn)	12.9 ± 1.2

Information Mass Fraction Values: The information mass fraction values given in Table 3 are provided without uncertainty estimates and are given as additional information on the matrix. Information values cannot be used to establish metrological traceability.

Table 3. Information Mass Fraction Values (Dry-Mass Basis) for Elements in SRM 1632d

Element	Mass Fraction (mg/kg)
Dysprosium (Dy)	0.9
Hafnium (Hf)	0.5
Lanthanum (La)	6
Nickel (Ni)	10
Samarium (Sm)	1

Table 4. Methods of Analysis

Methods	Element
Flame emission spectrometry (FES) at NIST	Na
Inductively coupled plasma mass spectrometry (ICP-MS) at NIST	Sb, Cd, Co, Cu, Th, U, V, Zn
Inductively coupled plasma optical emission spectrometry (ICP-OES) at NIST	Ba, Cu, Ni
Isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) at NIST	Hg
Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) at NIST	Ba, Pb, K, Rb, Sr, Th U
Isotope dilution thermal ionization mass spectrometry (ID-TIMS) at NIST	Cl, S
Instrumental neutron activation analysis (INAA) at NIST	Al, Sb, As, Ba, Ca, Ce, Cs, Cl, Cr, Co, Dy, Eu, Hf, Fe, La, Mg, Mn, K, Rb, Sm, Sc, Se, Na, Sr, Th, Ti, U, V, Zn,
LECO instrumental analyzer for H, C, and N at LECO Technical Services Laboratory	C, H, N,
Prompt gamma activation analysis (PGAA) at NIST	B, Cl, H. Fe, K, Ti,
Wavelength dispersive X-ray fluorescence (WDXRF) at NIST	K, Si,

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 http://www.nist.gov/pml/pubs/ (accessed Oct 2014).

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Certificate Revision History: 14 October 2014 (Extension of the certification period); 08 February 2011 (Original certificate date).

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; or via the Internet at http://www.nist.gov/srm.

APPENDIX

Portions of SRM 1632d were analyzed as unknown samples in the round robin study CANSPEX 2009-1, conducted by Quality Associates International, Ltd. Summary results shown in Table A1 were provided by Quality Associates International, Ltd. These results are included as an Appendix to the Certificate of Analysis for SRM 1632d to demonstrate user experience with this material using conventional methods and to better characterized the matrix. Results from this study should NOT be used as substitutes for the NIST values.

Table A1. SRM 1632d CANSPEX Round Robin Results

Parameter	Mean[(a)]	Unit	95 % Coverage Interval of Mean value	Pooled Within Lab Standard Deviation (s_w)	Pooled Between Lab Standard Deviation (s_B)	Total Number of Labs
Moisture	1.914	%	0.024	0.051	0.124	122
Ash	7.078	%	0.012	0.046	0.064	119
Volatile	36.04	%	0.15	0.17	0.70	94
Btu	13 821	per lb	9	19	43	110
Carbon	77.90	%	0.32	0.31	1.10	54
Hydrogen	5.057	%	0.041	0.041	0.133	48
Nitrogen	1.546	%	0.020	0.025	0.062	47
Total Sulfur	1.475	%	0.011	0.016	0.055	113
Pyritic Sulfur	0.540	%	0.040	0.012	0.074	21
Sulfate Sulfur	0.080	%	0.016	0.009	0.029	19
Chlorine	1086	µg/g	38	31	117	47
Fluorine	63.6	µg/g	5.3	2.8	13.8	31
Mercury	93.7	ng/g	4.5	4.7	11.9	32
Selenium	1.13	µg/g	0.18	0.08	0.28	12
FSI[(b)]	7.25		0.2	0.4	0.5	50

[(a)] Values are expressed on a dry-mass basis for all parameters except moisture. The moisture value is expressed on an "as received" basis.
[(b)] Free Swelling Index

Parameter	Total Number of Labs	Table A2. Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX Round Robin[a]																																
		Standards Australia (AS)				ASTM International				British Standards Institution (BSI)				Deutsches Institut für Normung (DIN)				China National Standards (GB)				International Organization for Standardization				Association Francaise de Normalisation (NF)				South African Bureau of Standards (SABS)				In-house[b]
		AS	s_r	s_R	No.	ASTM	s_r	s_R	No.	BSI	s_r	s_R	No.	DIN	s_r	s_R	No.	GB	s_r	s_R	No.	ISO	s_r	s_R	No.	NF	s_r	s_R	No.	SABS	s_r	s_R	No.	No.
Moisture %	122	1038.3	0.04	-[c]	1	D2013	0.04	0.10	1	1016	0.04	-	1	51718	0.07	-	2	212	0.07	-	1	589	0.11	-	2	3-037	-	-	1	925	-	-	1	10
						D3173	0.04	0.10	55													11722	0.04	-	5									
						D3302	0.04	0.10	11													5068	0.07	-	1									
						D5142	0.08	0.11	30																									
Ash % dry basis	119	1038.3	0.04	0.05	1	D3174	0.08	0.11	62	1016	0.05	0.11	1	51719	0.07	0.11	2	212	0.07	0.11	1	1171	0.07	0.11	9	3-003	-	-	1		-	-		9
						D5142	0.08	0.11	33																									
Volatile % dry basis	94	1038.3	0.07	0.35	1	D3175	0.18	0.35	47	1016	0.11	0.35	1	51720	0.38	0.51	2	212	0.18	0.35	1	562	0.38	0.51	11									7
						D5142	0.28	0.82	24																									
Btu/lb dry basis	110	1038.5	20	46	1	D1989	23	39	5	1016	18	43	1	51900	18	46	4	213	18	46	1	1928	43	106	11									5
						D2015	24	38	3																									
						D3286	18	35	4																									
						D5865	24	38	75																									
Carbon % dry basis	54	1038.6.4	0.11	0.21	1	D3178	0.11	-	2					51732	-	-	1	476	0.18	0.35	1	609	0.09	0.18	2									7
						D5373	0.16	0.35	38													12902	-	-	2									
Hydrogen % dry basis	48	1038.6.4	0.04	0.07	1	D3178	0.02	-	3					51732	-	-	1	476	0.05	0.09	1	609	0.04	0.09	2									3
						D5373	0.04	0.09	35													12902	-	-	2									
Nitrogen % dry basis	47	1038.6.4	0.01	0.03	1	D3179	0.08	0.13	3					51732	-	-	1	476	0.03	0.05	1	333	0.02	0.04	2									3
						D5373	0.02	0.05	34													12902	-	-	2									
Total Sulfur % dry basis	117	1038.6.3.3	0.01	0.02	1	D3177	0.02	0.04	3	1016	0.02	0.04	1	51724-3	0.01	0.02		214	0.04	0.09	1	351	0.02	0.04	2	3-038	-	-	1		-	-		11
						D4239	0.02	0.05	88																									
						D5016	0.05	0.18	5																									
Pyritic Sulfur % dry basis	21	1038.11	0.02	0.05	1	D2492	0.05	0.10	17									215	0.02	0.04	1													2
Sulfate Sulfur % dry basis	19	1038.11	0.007	0.011	1	D2492	0.007	0.014	17									215	0.01	0.04	1													0
Chlorine µg/g dry basis	47		-	-		D2361	106	213	3					51727	71	106	2	3558	35	71	1					3-009	-	-	1		-	-		14
						D4208	67	159	19																									
						D6721	24	29	7																									
Fluorine µg/g dry basis	31					D3761	5	5	13					51723	8	14	1	4663	6	7	1	11724	4	7	2									11
						D5987	4	7	3																									
Mercury ng/g dry basis	32					D6414	8	9	4					22022	-	-	1																	5
						D6722	3	7	22																									
Selenium µg/g dry basis	12					D4606	0.190	0.16	3																									9
FSI	50	1038.17	0.18	0.35	1	D720	0.35	0.71	43	1016	-	-	1	51741	-	-	1	5448	0.35	0.53	1	501	0.35	0.18	3									

[a] The above precision standard deviations are derived from the division of each method's published precision values by an estimate of the coverage factor used.
[b] Method is designated "In-house" if lab reports method as In-house; lab reports methods as modified; or does not report a method. CANSPEX does not provide repeatability or reproducibility information for In-house methods.
[c] "-" indicates documentation confirming the repeatability or reproducibility is not available.

The above referenced methods are available through the following websites:

AS http://www.standards.org.au (accessed Oct 2014)
ASTM hhttp://www.astm.org/. (accessed Oct 2014)
BSI http://www.bsigroup.com/ (accessed Oct 2014)
DIN http://www.din.de/cmd?level=tpl-home&languageid=en (accessed Oct 2014)
GB http://www.standardsportal.org.cn/zmen/English/Resources/ (accessed Oct 2014)
ISO http://www.iso.org/iso/iso_catalogue.htm (accessed Oct 2014)
NF http://www2.afnor.org/portail.asp?Lang=English (accessed Oct 2014)
SABS https://www.sabs.co.za/ (accessed Oct 2014)