National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1633c

Trace Elements in Coal Fly Ash

This Standard Reference Material (SRM) is intended for use in the evaluation of analytical methods for the determination of constituent elements in coal fly ash or materials of a similar matrix. SRM 1633c is a bituminous coal fly ash that was sieved through a nominal sieve opening of 74 μm (200 mesh) and then blended to assure homogeneity. A unit of SRM 1633c consists of 75 g of powdered material.

Certified Mass Fraction Values: Certified values for 20 constituents of SRM 1633c are reported in Table 1 as mass fractions on a dry-mass basis [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 [2]. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST and collaborating laboratories using instrumental and classical test methods.

Reference Mass Fraction Values: Reference values for 16 constituents are reported in Table 2 as mass fractions on a dry-mass basis. Reference values are non-certified values that are the present best estimates of the true values. 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 [2].

Information Values: Eight information values are reported in Table 3 as mass fractions on a dry-mass basis. An information value is considered to be a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value.

Expiration of Certification: The certification of **SRM 1633c** is valid, within the uncertainty specified, until **01 March 2021**, provided the SRM is handled and stored in accordance with the 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 changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The coordination of technical measurements for certification was performed by E.A. Mackey and J.L. Molloy of the NIST Analytical Chemistry Division.

Analyses leading to the certification of this SRM were performed by R.G. Brennan, S.E. Long, E.A. Mackey, A.F. Marlow, K.E. Murphy, R.L. Paul, S.A. Rabb, J.R. Sieber, R.O. Spatz, B.E. Tomlin, and L.L. Yu of the NIST Analytical Chemistry Division. Analytical results were also provided by Quality Associates International, Ltd., (Sechelt, BC Canada) administering the Coal and Ash Sample Proficiency Exchange (CANSPEX) proficiency testing program.

Statistical consultation for this SRM was provided by S.D. Leigh and A.L. Pintar of the NIST Statistical Engineering Division.

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

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 23 June 2011

Robert. L Watters, Jr., Chief
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INSTRUCTIONS FOR USE

The SRM should be thoroughly mixed by rotating the bottle before sampling. A minimum dry sample mass of 250 mg should be used for analytical determinations to be related to the certified values on this Certificate of Analysis.

To obtain the certified values, sample preparation procedures should be designed to achieve complete dissolution. If volatile elements (e.g., Hg, As, Se) are to be determined, precautions should be taken in the dissolution of SRM 1633c to avoid volatilization losses.

Instructions for Drying: When non-volatile elements are being determined, this material should be dried to constant mass before using. Recommended procedures for drying are: (1) vacuum drying for 24 h at ambient temperature using a cold trap at or below –50 °C and a pressure not greater than 30 Pa (0.2 mm Hg) and (2) drying for 2 h in an oven at 105 °C. Samples of the dried material weighing at least 250 mg should be used for analysis. When not in use, the material should be kept in a tightly sealed bottle. Volatile elements should be determined on an as-received basis, and corrected to dry mass. Correction should be based on a separate determination of moisture using one of the above drying procedures.

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

Source and Preparation of the Material: The fly ash was supplied by a coal-fired power plant and is the product of western Pennsylvania bituminous coal. The material was air dried, sieved, and blended for 24 h before being placed in a series of bulk containers. X-ray fluorescence spectrometry (XRF) and prompt gamma activation analysis (PGAA) were performed on 19 and 10 grab samples, respectively. Grab samples were taken from the bulk using a stratified random sampling methodology for a preliminary homogeneity assessment before proceeding with bottling the material in 75 g units.

Homogeneity Assessment: The homogeneity of the bottled material was assessed using XRF and PGAA. In some cases, statistically significant differences among samples were observed. This component of uncertainty was captured adequately by the analytical technique(s) used for values assignments. The exception is Pb for which an additional component of variance, obtained from the XRF homogeneity assessment, was included in the uncertainty calculations.

VALUE ASSIGNMENT

The analytical techniques used for measurement of each element are listed in Table 4.

Certified Mass Fraction Values: The certified values for Al, As, Ba, Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Rb, Sb, Sr, Ti, and V are weighted means of the results from two to four methods [3,4]. The uncertainty listed with each certified value is an expanded uncertainty about the mean with coverage factor 2 (approximately 95 % confidence) calculated by combining a between-method variance incorporating inter-method bias with a pooled, within-method variance following the ISO Guide [5,6]. The certified mass fraction values for Hg, Pb, and Cd are unweighted mean values based on results from a single NIST method for which a complete evaluation of all sources of uncertainty has been performed. The uncertainties for these certified values are two-sided 95 % confidence intervals for the mean (coverage factor, $k = 2$).

[(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.

Table 1. Certified Mass Fraction Values (Dry-Mass Basis) for SRM 1633c

Constituent	Mass Fraction (%)			Constituent	Mass Fraction (mg/kg)		
Al	13.28	±	0.61	As	186.2	±	3.0
Ba	0.1126	±	0.0033	Cd	0.758	±	0.005
Ca	1.365	±	0.040	Co	42.9	±	3.5
Fe	10.49	±	0.39	Cu	173.7	±	6.4
K	1.773	±	0.066	Hg	1.005	±	0.022
Mg	0.498	±	0.052	Mn	240.2	±	3.4
Na	0.1707	±	0.0059	Ni	132	±	10
Ti	0.724	±	0.030	Pb	95.2	±	2.5
				Rb	117.42	±	0.53
				Sb	8.56	±	0.29
				Sr	901	±	56
				V	286.2	±	7.9

Reference Mass Fraction Values: The reference values for Cr, Cs, Dy, Eu, La, Lu, Sc, Se, Si, Ta, Tb, Th, and U are the mean of results obtained using one analytical technique performed at NIST. The expanded uncertainties associated with these reference values are two-sided intervals with coverage factor 2 (approximately 95 % confidence) calculated from the combined uncertainty expressed at the level of one standard deviation following NIST Technical Note 1297 [6]. The Zn and P reference values are weighted means of the results from two or more methods. The S value and uncertainty were calculated from a round robin exercise involving multiple labs with the weighted means from each lab combined. The uncertainty listed for each P, S, and Zn value is an expanded uncertainty about the mean with coverage factor 2 (approximately 95 % confidence) calculated by combining a between-method variance incorporating inter-method bias with a pooled, within-method variance following the ISO Guide [3–6].

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 1633c

Constituent	Mass Fraction (%)			Constituent	Mass Fraction (mg/kg)		
S	0.110	±	0.019	Cr	258	±	6
Si	21.30	±	0.57	Cs	9.39	±	0.22
P	0.192	±	0.010	Dy	18.70	±	0.30
				Eu	4.67	±	0.07
				La	87.0	±	2.6
				Lu	1.32	±	0.03
				Sc	37.6	±	0.6
				Se	13.9	±	0.5
				Ta	1.58	±	0.03
				Tb	3.12	±	0.06
				Th	23.0	±	0.4
				U	9.25	±	0.45
				Zn	235	±	14

Table 3. Information Mass Fraction Values (Dry-Mass Basis) for SRM 1633c

Constituent	Mass Fraction (mg/kg)
Be	16
Ce	180
Ga	55
Hf	6.0
In	0.14
Nd	87
Sm	19
Yb	7.7

Table 4. Analytical Methods Used For Value Assignment

Element	Methods	Element	Methods
Al	WDXRF, INAA, CANSPEX	Mn	WDXRF, INAA, CANSPEX
As	WDXRF, INAA, CANSPEX	Na	WDXRF, INAA, CANSPEX
Ba	WDXRF, INAA, CANSPEX	Nd	INAA
Be	CANSPEX	Ni	ICP-OES, ICP-MS, CANSPEX
Ca	WDXRF, INAA, CANSPEX	P	ICP-OES, WDXRF, CANSPEX
Cd	ID-ICP-MS	Pb	ID-ICP-MS
Ce	INAA	Rb	WDXRF, INAA
Co	INAA, CANSPEX	S	CANSPEX
Cr	WDXRF	Sb	INAA, CANSPEX
Cs	INAA	Sc	INAA
Cu	ICP-OES, ICP-MS, CANSPEX	Se	INAA
Dy	INAA	Si	WDXRF
Eu	INAA	Sm	INAA
Fe	WDXRF, INAA	Sr	WDXRF, INAA, CANSPEX
Ga	INAA	Ta	INAA
Hf	INAA	Tb	INAA
Hg	ID-CV-ICP-MS	Th	INAA
In	INAA	Ti	WDXRF, INAA, CANSPEX
K	WDXRF, INAA, CANSPEX	U	INAA
La	INAA	V	ICP-OES, WDXRF, INAA, CANSPEX
Lu	INAA	Yb	INAA
Mg	WDXRF, INAA, CANSPEX	Zn	INAA, CANSPEX

Key to Methods:

WDXRF	Wavelength dispersive X-ray fluorescence spectrometry after borate fusion at NIST
ICP-OES	Inductively coupled plasma optical emission spectrometry at NIST
ICP-MS	Inductively coupled plasma mass spectrometry at NIST
ID-ICP-MS	Isotope dilution inductively coupled plasma mass spectrometry at NIST
ID-CV-ICP-MS	Isotope dilution cold vapor inductively coupled plasma mass spectrometry at NIST
INAA	Instrumental neutron activation analysis at NIST
CANSPEX	Coal and Ash Sample Proficiency Exchange program combining data from at least 17 labs using a variety of methods.

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Assurance International, Ltd. for the CANSPEX 2008-4 Round Robin using SRM 1633c as an unknown fly ash 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.

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/index.cfm/ (accessed June 2011).

[2] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions 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 http://www.nist.gov/srm/publications.cfm (accessed June 2011).

[3] DerSimonian, R.; Laird, N.; *Meta-analysis in Clinical Trials*; Control. Clin. Trials, Vol. 7, pp. 177–188 (1986).

[4] Rukhin, A. L.; *Weighted Means Statistics in Interlaboratory Studies*; Metrologia,Vol. 46, No. 3, pp 323–331 (2009)

[5] Horn, R.A.; Horn, S.A.; Duncan, D.B.; *Estimating Heteroscedastic Variance in Linear Models*; J. Am. Stat. Assoc., Vol. 70, pp. 380–385 (1975).

[6] 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 (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed June 2011); 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://physics.nist.gov/Pubs/ (accessed June 2011).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: 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 1633c were analyzed as unknown samples in the round robin study CANSPEX 2008-4, conducted by Quality Associates International, Ltd. These results are provided 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.

Table A1. SRM 1633c CANSPEX Round Robin Results

Parameter	Most Likely Value	95 % Coverage Interval of Most Likely Value	Pooled Within Lab Standard Deviation, (s_w)	Pooled Between Lab Standard Deviation, (s_B)	Total Number of Labs
Major &Minor Elements (as Oxide)	(%)	(%)	(%)	(%)	
SiO_2	49.02	0.37	0.38	1.28	56
Al_2O_3	26.23	0.23	0.25	0.82	56
Fe_2O_3	16.20	0.24	0.20	0.81	57
CaO	1.99	0.04	0.05	0.14	57
MgO	0.84	0.02	0.02	0.07	57
Na_2O	0.23	0.01	0.01	0.04	58
K_2O	2.20	0.04	0.03	0.14	56
P_2O_5	0.46	0.02	0.01	0.05	50
TiO_2	1.25	0.02	0.02	0.08	54
BaO	0.13	0.01	0.004	0.015	33
SrO	0.11	0.01	0.004	0.018	33
SO_3	0.26	0.04	0.015	0.132	47
Trace Elements	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
As	187	12	4	25	23
Be	16	2	0.42	3.7	17
Cd	0.79	0.16	0.02	0.34	20
Cr	217	20	5	47	26
Co	44	5	1	10	22
Cu	170	10	4	22	28
Mn	243	16	6	39	25
Ni	129	9	3	22	25
Pb	91	9	2	20	25
Sb	7.8	1.3	0.4	2.4	18
V	285	17	7	37	27
Z	245	14	5	33	27

Table A2. Derived Standard Deviation (%) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX Round Robin[a] - Major & Minor Elements as Oxides

Parameter	Total Number of Labs	Standards Australia (AS)				ASTM International				Deutsches Institut für Normung (DIN)				China National Standards (GB)				In-house[b]
		AS	s_r	s_R	No.	ASTM	s_r	s_R	No.	DIN	s_r	s_R	No.	GB	s_r	s_R	No.	No.
SiO_2 (%)	56	1038.14.3	0.15	0.51	1	D3682	0.81	2	20	51729	0.87	2.61	1	T1574	0.35	0.71	1	10
						D4326	0.45	1.56	9									
						D6349	1.52	2.45	14									
Al_2O_3 (%)	56	1038.14.3	0.09	0.36	1	D3682	0.28	0.75	20	51729	0.47	1.4	1	T1574	0.28	0.53	1	10
						D4326	0.29	1.11	9									
						D6349	0.62	0.96	14									
Fe_2O_3 (%)	57	1038.14.3	0.05	0.18	1	D3682	0.35	0.47	21	51729	0.57	1.15	1	T1574	0.28	0.53	1	10
						D4326	0.1	0.55	9									
						D6349	0.05	1.32	14									
CaO (%)	57	1038.14.3	0.01	0.03	1	D3682	0.1	0.13	21	51729	0.04	1.06	1	T1574	0.07	0.14	1	10
						D4326	0.06	0.13	9									
						D6349	0.04	0.18	14									
MgO (%)	57	1038.14.3	0.03	0.05	1	D3682	0.02	0.04	21	51729	0.01	0.04	1	T1574	0.04	0.07	1	10
						D4326	0.04	0.08	9									
						D6349	0.03	0.07	14									
Na_2O (%)	59	1038.14.3	0.02	0.04	1	D3682	0.02	0.03	23	51729	-[c]	-	1	T1574	0.04	0.07	1	10
						D4326	0.07	0.15	9									
						D6349	0.03	0.05	14									
K_2O (%)	56	1038.14.3	0.01	0.05	1	D3682	0.03	0.06	20	51729	-	-	1	T1574	0.07	0.14	1	10
						D4326	0.05	0.06	9									
						D6349	0.11	0.28	14									
P_2O_5 (%)	50	1038.14.3	0.01	0.02	1	D3682	-	-		51729	-	-	1	T1574	-	-	1	24
						D4326	0.02	0.08	9									
						D6349	0.03	0.09	14									
TiO_2 (%)	54	1038.14.3	0.01	0.04	1	D3682	0.05	0.07	18	51729	0.04	0.13	1	T1574	0.07	0.14	1	10
						D4326	0.02	0.09	9									
						D6349	0.04	0.07	14									
BaO (%)	33	1038.14.3	0.007	0.015		D3682	-	-		51729	-	-	1	T1574	-	-		13
						D4326	0.008	0.03	8									
						D6349	0.008	0.014	11									
SrO (%)	33	1038.14.3	0.0014	0.069		D3682	-	-		51729	-	-	1	T1574	-	-		13
						D4326	0.014	0.05	8									
						D6349	0.004	0.009	11									
SO_3 (%)	47	1038.14.3	0.005	0.057		D3682	-	-		51729	0.002	0.009	1	T1574	0.071	0.142	1	17
						D4239	0.01	0.037	6									
						D4326	0.079	0.212	2									
						D5016	0.027	0.089	13									
						D6349	0.024	0.029	7									

[a]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.

Above referenced methods are available through the following websites:

AS http://www.standards.org.au (accessed June 2011)

ASTM http://www.astm.org (accessed June 2011)

DIN http://www.din.de/cmd?level=tpl-home&languageid=en (accessed June 2011)

GB http://www.standardsportal.org.cn/prc_en/global_resource.aspx (accessed June 2011)

Table A3. Derived Standard Deviation (μg/g) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Standard Methods Used in CANSPEX Round Robin[a] - Trace Elements

Parameter	Total Number of Labs	ASTM International				European Standards (EN)				China National Standards (GB)				In-house[b]
		ASTM	s_r	s_R	No.	EN	s_r	s_R	No.	GB	s_r	s_R	No.	
As (mg/kg)	23	D3683	-[c]	-		13656:2002	-	-		T3058	7	11	1	10
		D6357	9	16	12					T16658				
										T19225				
Be (mg/kg)	17	D3683	1.0	3	3	13656:2002	-	-		T3058	-	-		4
		D6357	0.48	1.7	10					T16658				
										T19225				
Cd (mg/kg)	20	D3683	-	-		13656:2002	-	-		T3058	-	-		8
		D6357	0.06	0.13	11					T16658	0.18	-	1	
										T19225				
Cr (mg/kg)	26	D3683	15	26	2	13656:2002	-	-	1	T3058	-	-		11
		D6357	76	14	12					T16658	1	-		
										T19225				
Co (mg/kg)	22	D3683	-	-	11	13656:2002	-	-		T3058	-	-		10
		D6357	2	3						T16658				
										T19225	0.18	-	1	
Cu (mg/kg)	28	D3683	10	15	3	13656:2002	-	-	1	T3058	-	-		11
		D6357	6	17	12					T16658				
										T19225	0.71	1.1	1	
Mn (mg/kg)	25	D3683	15	31	3	13656:2002	-	-	1	T3058	-	-		9
		D6357	9	16	12					T16658				
										T19225				
Ni (mg/kg)	25	D3683	15	46	2	13656:2002	-	-	1	T3058	-	-		9
		D6357	6	9	12					T16658				
										T19225	0.35	1.1	1	
Pb (mg/kg)	25	D3683	10	46	2	13656:2002	-	-	1	T3058	-	-		9
		D6357	5	10	12					T16658	2	-	1	
										T19225				
Sb (mg/kg)	18	D3683	-	-		13656:2002	-	-	1	T3058	-	-		8
		D6357	0.78	1.3	9					T16658				
										T19225				
V (mg/kg)	27	D3683	26	46	2	13656:2002	-	-		T3058	-	-		13
		D6357	13	22	12					T16658				
										T19225				
Zn (mg/kg)	27	D3683	15	20	3	13656:2002	-	-	1	T3058	-	-		10
		D6357	9	17	12					T16658				
										T19225	2.8	6.0	1	

[a]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.

Above referenced methods are available through the following websites:

ASTM http://www.astm.org (accessed June 2011)

EN http://www.cen.eu/cen/Products/EN/Pages/default.aspx (accessed June 2011)

GB http://www.standardsportal.org.cn/prc_en/global_resource.aspx (accessed June 2011)