



# Certificate of Analysis

## Standard Reference Material<sup>®</sup> 1633b

### Constituent 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 with a similar matrix. SRM 1633b is a bituminous coal fly ash that was sieved through a nominal sieve opening of 90  $\mu\text{m}$  (170 mesh) and then blended to assure homogeneity. A unit of SRM 1633b consists of 75 g of powdered material.

The certified values for the constituent elements are given in Table 1. The values are based on measurements using one definitive method or two or more independent and reliable analytical techniques. Noncertified values for a number of elements are given in Table 2 as additional information on the composition of the material. The noncertified values **should not** be used for calibration or quality control. Analytical methods used for the certification of this SRM are given in Table 3 along with analysts and cooperating laboratories. All values are based on measurements using a dry sample weight of at least 250 mg.

**Certified Values and Uncertainties:** The certified values are weighted means of results of two or more independent analytical methods, or the means of results from a single definitive method. The weights for the weighted means were computed according to the iterative procedure of Paule and Mandel [1]. The stated uncertainty includes allowances for measurement imprecision, material variability, and differences among analytical methods. Each uncertainty is the sum of the half-width of a 95 % prediction interval, and includes an allowance for the systematic error among the methods used. In the absence of systematic error, a 95 % prediction interval predicts where the true concentrations of 95 % of the samples of this SRM lie.

Mercury certification is based on cold vapor isotope dilution inductively coupled plasma mass spectrometry (CV- ID-ICP-MS) at NIST [2]. The uncertainty in the certified value for mercury is expressed as an expanded uncertainty,  $U = ku_c$ , calculated according to the methods in the ISO/NIST Guide [3]. The quantity  $u_c$  represents, at the level of one standard deviation, the potential combined effects of the uncertainty due to material and measurement variability. The quantity  $k$  is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. The value of the coverage factor,  $k = 2.034$ , is determined from the Student's  $t$ -distribution with 33 degrees of freedom and a confidence level of 95 %.

**Expiration of Certification:** The certification of this SRM is valid until **01 May 2014**, within the 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 will be nullified if the SRM is damaged or contaminated. Registration (see attached sheet) will facilitate notification.

**Stability:** This material is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certification to the purchaser.

The overall direction and coordination of the analyses were under the chairmanship of R.R. Greenberg of the NIST Analytical Chemistry Division.

Statistical consultation was provided by S.B. Schiller and D.D. Leber of the NIST Statistical Engineering Division.

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*See Certificate Revision History on Last Page*

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

## INSTRUCTIONS FOR USE

A minimum dry sample weight 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 affect complete dissolution. If volatile elements (e.g., Hg, As, Se) are to be determined, precautions should be taken in the dissolution of SRM 1633b to avoid volatilization losses.

**Instructions for Drying:** When non-volatile elements are being determined, this material should be dried to constant weight 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 0.2 mm Hg (30 Pa); 2) drying for 2 h in an oven of 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 weight. Correction should be based on a separate determination of moisture using one of the above drying procedures.

**Source and Preparation of the Material:** The fly ash was supplied by a coal fired power plant and is the product of Pennsylvania and West Virginia coals. It was selected as a typical bituminous coal fly ash and is not intended as a fly ash from a specific coal or combustion process. The material was air dried, sieved, and blended for 24 h before being placed in a series of bulk containers. X-ray fluorescence and inductively coupled plasma atomic emission (ICP-AES) analyses were performed on ten grab samples taken from the bulk for a preliminary homogeneity assessment before proceeding with bottling the material in 75 g units.

**Analysis:** The homogeneity of the bottled material was assessed by X-ray fluorescence spectrometry (XRF) and instrumental neutron activation analysis, using selected elements as indicators. In some cases, statistically significant differences between samples were seen, and the variance due to material inhomogeneity is included in the overall uncertainties of the certified values. The estimated relative standard deviation for material inhomogeneity is less than 1 % for those elements for which homogeneity was assessed, except thorium, for which material inhomogeneity was estimated to be 2 %.

Table 1. Certified Values

Element	Mass Fraction (%)		Element	Mass Fraction (mg/kg)	
Al	15.05	± 0.27	As	136.2	± 2.6
Ca	1.51	± 0.06	Ba	709	± 27
Fe	7.78	± 0.23	Cd	0.784	± 0.006
Mg	0.482	± 0.008	Cr	198.2	± 4.7
K	1.95	± 0.03	Cu	112.8	± 2.6
Si	23.02	± 0.08	Pb	68.2	± 1.1
Na	0.201	± 0.003	Mn	131.8	± 1.7
S	0.2075	± 0.0011	Hg	0.1431	± 0.0018
Ti	0.791	± 0.014	Ni	120.6	± 1.8
			Se	10.26	± 0.17
			Sr	1041	± 14
			Th	25.7	± 1.3
			U	8.79	± 0.36
			V	295.7	± 3.6

Table 2. Noncertified Values

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Sb	6	P	2300
Br	2.9	Rb	140
Ce	190	Sc	41
Co	50	Sm	20
Cs	11	Ta	1.8
Dy	17	Tb	2.6
Eu	4.1	Tl	5.9
Gd	13	Tm	2.1
Hf	6.8	W	5.6
Ho	3.5	Yb	7.6
La	94	Zn	210
Lu	1.2		
Nd	85		

Table 3. Analytical Methods Used for Certification Analyses

Element	Certification Methods
Al	INAA, XRF
As	FIA-HAAS, INAA
Ba	ICP-MS, INAA
Ca	ICP, INAA, XRF
Cd	ETAAS, IDTIMS
Cr	FAAS, INAA
Cu	FAAS, ICP-MS
Fe	INAA, XRF
Hg	CV-ID-ICP-MS
K	FAES, INAA, XRF
Mg	ICP, IDTIMS
Mn	FAAS, INAA
Na	FAES, INAA
Ni	ETAAS, ICP
Pb	ETAAS, ICP-MS
Rb	FAES, INAA
S	IDTIMS
Sb	ETAAS, INAA
Se	FIA-HAAS, INAA
Si	GRAV, XRF
Sr	FAES, INAA, IDTIMS
Th	ICP-MS, INAA
Ti	INAA, XRF
U	ICP-MS, INAA
V	ICP, INAA

ID-TIMS	Isotope Dilution Thermal Ionization Mass Spectrometry; mixed acid digestion
ICP-MS	Inductively Coupled Plasma Mass Spectrometry; mixed acid digestion
INAA	Instrumental Neutron Activation Analysis
XRF	Wavelength Dispersive X-ray Fluorescence on fused borate discs
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry; mixed acid digestion
ETAAS	Electrothermal Atomic Absorption Spectrometry; mixed acid digestion
CV-ID-ICP-MS	Cold Vapor Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
FIA-HAAS	Flow Injection Analyses - Hydride Generation Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry; mixed acid digestion except for Au, leached with HBr-Br <sub>2</sub>
GRAV	Gravimetry; sodium carbonate fusion

Most information values were determined by INAA only; P was determined by ICP-AES and XRF; Ti was determined by ICP-MS; Zn was determined by FAAS and ICP-AES.

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## REFERENCES

- [1] Paule, R.C.; Mandel, J.; *Consensus Values and Weighting Factors*; J. Res. Natl. Bur. Stand., Vol. 87, pp. 377–385 (1982).
- [2] Christopher, S.J.; Long, S.E.; Rearick, M.S.; *Development of High Accuracy Vapor Generation ICP-MS and its Application to the Certification of Mercury in Standard Reference Materials*; Anal. Chem., Submitted for Publication (November 2000).
- [3] ISO; *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); 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/>.

<p><b>Certificate Revision History:</b> 10 December 2004 (This revision reflects an update of the certified value for Hg based on new methodology, update expiration date, and editorial changes); 22 June 1993 (Original certificate date).</p>
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*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) 975-6776; fax (301) 926-4751, email [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*