National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 1630a

Trace Mercury in Coal

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of mercury, chlorine, sulfur, and ash content in coal and materials of a similar matrix. SRM 1630a consists of 50 g of bituminous coal ground to pass a 250 μm (60 mesh) sieve, homogenized, and bottled under an argon atmosphere.

Certified Values: The certified values for mercury, chlorine, and sulfur, expressed as mass fractions [1] on a dry basis, are provided in Table 1. The certified values for mercury and chlorine are based on two independent NIST methods. The certified value for sulfur is based on a single NIST primary method. 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 accounted for by NIST.

Reference Value: The reference value for ash content [2,3], expressed as a mass fraction on a dry basis, is provided in Table 2. The reference value for ash content is based on results from 64 laboratories participating in the Canada Centre for Mineral and Energy Technology (CANMET) Service Program for the Evaluation of Codes and Standards (CANSPECS) 54 Coal interlaboratory study. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty.

Information Value: The gross calorific value is provided in Table 3 for information purposes only. This is a noncertified value with no uncertainty assessed. In addition, data from the CANSPECS 54 Coal interlaboratory study are provided in Table 4 in order to demonstrate user experience with this material using conventional methods. The CANSPECS 54 Coal interlaboratory results should not be used as a substitute for the NIST certified or reference values.

Expiration of Certification: The certification of SRM 1630a is valid, within the measurement uncertainties specified, until **30 January 2005** 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 modified.

Maintenance of SRM Certification: NIST will monitor representative samples of 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 the technical measurements leading to certification was performed by R.R. Greenberg of the NIST Analytical Chemistry Division.

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

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 09 August 2000
See Certificate Revision History on Last Page

Nancy M. Trahey, Chief
Standard Reference Materials Program

Statistical analyses leading to certified and reference values were performed by J.H. Yen of the NIST Statistical Engineering Division.

The coal for this SRM was donated by Consol Coal Sales, Inc., Pittsburgh, PA.

INSTRUCTIONS FOR USE

Sampling: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 250 mg (dry mass) should be used for analytical determinations to be related to the mercury, chlorine, and sulfur values provided. The calorific value and ash content were determined using a minimum sample mass of 1 g. The SRM should be stored in its original tightly sealed bottle away from sunlight and intense sources of radiation.

Drying: In order to relate measurements to the certified and reference values that are expressed on a dry mass basis, users should determine a drying correction at the time of each analysis. The correction is determined by oven drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [3]. During drying at NIST, the mass loss of individual SRM 1630a samples was observed to stabilize between 77 min and 91 min. The average mass loss measured at NIST for SRM 1630a was 2.02 % (1 s = 0.13 %, n = 12).

A NIST study was also conducted to quantify the difference between drying in air and nitrogen atmospheres for SRM 1630a. For the same time and temperature conditions, the average mass loss for oven drying SRM 1630a in an air atmosphere was 1.97 % (1 s = 0.11 %, n = 12). Desiccator drying for 5 days over fresh magnesium perchlorate is also an acceptable drying method. No significant difference between this method, and the oven drying methods described above was observed. Moisture content determined by vacuum drying for 2 h at ambient temperatures was found to be lower than oven or desiccator drying by about 0.5 % to 1 % absolute.

PREPARATION, HOMOGENEITY, AND ANALYSIS

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 which is considered to be one of the most extensively mined and economically important coal seams in the United States. 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 using the spinning riffle technique into two portions. One portion was further divided by the spinning riffle technique and bottled under an argon atmosphere. The remaining portion of the lot was sealed for long term storage in foil bags filled under an argon atmosphere.

Certified Values and Uncertainties: Certification analyses for mercury, chlorine, and sulfur were performed by the NIST Analytical Chemistry Division. The certified values for mercury and chlorine are the result of two independent analytical methods as described by Schiller and Eberhardt [4]. Mercury is based on isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) performed by S.E. Long and W.R. Kelly, and radiochemical neutron activation (RNAA) performed by R.M. Lindstrom. Chlorine is based on neutron capture prompt gamma ray activation analysis (PGAA) performed by E.A. Mackey and R.M. Lindstrom, and instrumental neutron activation analysis (INAA) performed by D.A. Becker. The certified value for sulfur is based on a single NIST primary method, isotope dilution-thermal ionization mass spectrometry (ID-TIMS) [5] performed by W.R. Kelly, J.L. Mann, and R.D. Vocke.

Table 1. Certified Values (Dry Basis)

Element	Mass Fraction
Chlorine	1144 mg/kg ± 32 mg/kg
Mercury	93.8 µg/kg ± 3.7 µg/kg
Sulfur	1.462 % ± 0.051%

The uncertainty in the value certified for mercury and chlorine is expressed as an expanded uncertainty, U, and is calculated as $U = ku_c + B$. The quantity, u_c, is the combined standard uncertainty calculated according to ISO Guide [6], which accounts for the combined effect of the within variance for all methods at one standard deviation.

The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate degrees of freedom and 95 % confidence for each element. B is a bias adjustment for the difference between methods, which is the maximum difference between the certified value and the method means [4].

The uncertainty in the certified value for sulfur is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide [6]. The observed sulfur variation was much greater than expected for the analytical technique used. Therefore a prediction interval was used to account for the sulfur variability in this material. 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 effect of uncertainty components associated with the measurement uncertainty and sulfur inhomogeneity, and k is a coverage factor. The coverage factor, $k = 2.3$, is determined from the Student's t-distribution with 8 degrees of freedom, and corresponds to a 95 % prediction interval [7].

Reference Value and Uncertainty: The reference value for ash content is based on data obtained from the CANSPECS 54 Coal interlaboratory study by combining the results from laboratories using method ASTM D 3174-93 [2] with those from the laboratories using method ASTM D 5142-90 [3].

Table 2. Reference Value (Dry Basis)

Element	Mass Fraction
Ash	7.16 % ± 0.05 %

The uncertainty in the ash content reference value is calculated as an expanded uncertainty, $U = ku_c + B$. The quantity u_c is intended to represent, at the level of one standard deviation, the combined effect of within-laboratory measurement uncertainty and between-laboratory uncertainty [6]. The coverage factor for this interval, $k = 2.0$, is determined from the Student's t-distribution with 41 degrees of freedom. B is a bias adjustment for the difference between methods, which is the maximum difference between the reference value and the method means [4].

Supplemental Information: The information value given in Table 3 is based on the CANSPECS No. 54 Coal interlaboratory study. This value is not certified and is given as additional information on the matrix. **NOTE:** Gross calorific value may decrease with time due to sample degradation.

Table 3. Information Value (Dry basis)

Gross Calorific Value	32.10 MJ·kg^{-1} (13 802 Btu$_{th}$ · lb^{-1})

In order to demonstrate user experience with this material by conventional methods for mercury, chlorine, sulfur, and ash, summary statistics, as reported in the CANSPECS 54 Coal interlaboratory study, are given in Table 4. The CANSPECS 54 Coal interlaboratory results should not be used as a substitute for the NIST certified or reference values. The most common methods of analysis performed by the participating laboratories were ASTM D 3684-94 for mercury [8], ASTM D 4208-88 for chlorine [9], ASTM D 4239-94 [10] for total sulfur and ASTM D 3174-93 [2] for ash content.

Table 4. Summary Statistics for Mercury, Chlorine, Sulfur, and Ash
as Reported in the CANSPECS 54 Coal Interlaboratory Study (in mg/kg, Dry basis)

Measurand	n	Median	Repeatability as Measured	ASTM Repeatability		Reproducibility as Measured	ASTM Reproducibility	
Mercury	15	0.082	0.023	0.019	(D 3684)	0.036	0.031	(D 3684)
Chlorine	31	1124	98	195	(D 4208)	276	459	(D 4208)
Sulfur	77	14 900	400	900	(D 4239C)	1300	1400	(D 4239C)
Ash	79	71 600	1200	3000	(D 3174)	2100	5000	(D 3174)

REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

[2] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

[3] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

[4] Schiller, S.B. and Eberhardt, K.R., "Combining Data from Independent Analysis Methods," Spectrochemical Acta, **46B** No. 12, pp. 1607-1613, (1991).

[5] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T. "Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry," Anal. Chem., **66**, p. 2505, (1994).

[6] G*uide 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); available at http://physics.nist.gov/Pubs/.

[7] Hahn, G.J. and Meeker, W.Q, "Statistical Intervals A Guide for Practitioners," John Wiley & Sons, Inc., NY, (1991).

[8] ASTM D 3684-94, "Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

[9] ASTM D 4208-88 (1997), "Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

[10] ASTM D 4239-94, "Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

Certification Revision History: 09 August 2000 (Certified mercury value added; reference mercury value removed); 11 February 1999 (Original certificate date).

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; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.