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# Standard Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Absorption Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D 6357; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods pertain to the determination of antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, vanadium, and zinc in coal and coke. These test methods can also be used for the analysis of residues from coal combustion processes.

NOTE 1—These test methods may be applicable to the determination of other trace elements.

1.2 The values stated in SI units shall be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

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<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee ~~D-5~~ D05 on Coal and Coke and are the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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- D 121 Terminology of Coal and Coke<sup>2</sup>
  - D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>2</sup>
  - D 1193 Specification for Reagent Water<sup>3</sup>
  - D 2013 Method of Preparing Coal Samples for Analysis<sup>2</sup>
  - D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke<sup>2</sup>
  - D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases<sup>2</sup>
  - D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory<sup>2</sup>
  - D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures<sup>2</sup>
- 2.2 *Other Documents:*
- EPA/600/4-91/010 Methods for the Determination of Metals in Environmental Samples<sup>4</sup>

### 3. Terminology

3.1 *Definitions*—Definitions applicable to these test methods are listed in Terminology D 121.

### 4. Summary of Test Method

4.1 The coal or coke to be analyzed is ashed under controlled conditions, digested by a mixture of aqua-regia and hydrofluoric acid, and finally dissolved in 1 % nitric acid. Combustion residues are digested on an as-received basis. The concentration of individual trace elements is determined by either inductively coupled atomic emission spectrometry (ICPAES) or inductively coupled plasma mass spectrometry (ICPMS). Selected elements that occur at concentrations below the detection limits of ICPAES can be quantitatively analyzed by graphite furnace atomic absorption spectrometry (GFAA).

### 5. Significance and Use

5.1 Coal contains several elements whose individual concentrations are generally less than 0.01 %. These elements are commonly and collectively referred to as trace elements. These elements primarily occur as part of the mineral matter in coal. The potential release of certain trace elements from coal combustion sources has become an environmental concern.

5.2 The ash prepared in accordance with these provisional test methods quantitatively retains the elements listed in 1.1 and is representative of their concentrations in the coal or coke.

### 6. Apparatus

6.1 *Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES)*—The spectrometer system may be either simultaneous or sequential, vacuum or purged, but must include computer-controlled background correction.

6.1.1 *Argon Gas Supply*—High purity (99.99 %).

6.1.2 *Mass Flow Controllers*—A mass-flow controller to regulate the nebulizer gas is required. Mass flow controllers on the intermediate and outer torch gas flows are recommended.

6.2 *Inductively Coupled Plasma Mass Spectrometer (ICPMS)*—The spectrometer system must be capable of scanning the mass range of the elements to be analyzed.

6.2.1 *Argon Gas Supply*, high purity (99.99 %).

6.2.2 The use of a variable speed peristaltic pump for delivering sample solution to the nebulizer, a mass-flow controller on the gas supply to the nebulizer, and a water-cooled spray chamber are highly recommended.

6.3 *Atomic Absorption Spectrometer with Graphite Furnace (GFAA)*, having background correction capable of removing nonspecific absorbance.

6.3.1 *Single-Element Hollow Cathode or Single-Element Electrodeless Discharge Lamps*.

6.3.2 *Single-Output Device*, capable of recording and evaluating peak area and peak shape.

6.3.3 *Pyrolytic Coated Graphite Tubes and Platforms*.

6.3.4 *Argon Gas Supply*, high purity (99.99 %).

6.3.5 *Autosampler*—Although not specifically required, the use of an autosampler is highly recommended.

6.4 *Muffle Furnace*, with temperature control and with air circulation as specified in 9.1.

6.5 *Analytical Balance*, capable of weighing to 0.1 mg.

6.6 *Teflon Beakers*, 100- or 200-mL capacity.

6.7 *Hot Plate*, capable of regulating temperature between 90 to 150°C.

6.8 *Volumetric Flasks*, 100- and 10-mL capacity.

6.9 *HDPE Bottles*, 100-mL capacity.

6.10 *Crucibles*, 50-mL quartz or high silica.

### 7. Reagents

7.1 *Purity of Reagents*—All acids used in these test methods must be trace metal purity grade or equivalent. Redistilled acids are acceptable.

<sup>2</sup> Annual Book of ASTM Standards, Vol 05.06.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>4</sup> Available from Superintendent of Documents, U.S. Printing Office, Washington, DC 20402.

7.2 *Purity of Water*—The purity of the water used in these test methods shall be equivalent to ASTM Type II reagent water of Specification D 1193.

7.3 *Aqua Regia Solution*—Mix one part concentrated nitric acid ( $\text{HNO}_3$ , sp. gr. 1.42) and three parts concentrated hydrochloric acid ( $\text{HCl}$ , sp. gr. 1.9).

7.4 *Hydrofluoric Acid*—Concentrated ( $\text{HF}$ , sp. gr. 1.15).

7.5 *ICP Calibration Standards*—Aqueous multielement solutions made up in 1 %  $\text{HNO}_3$  are used for calibration of ICPAES and ICPMS systems. The standards may be purchased or prepared from high-purity grade chemicals or metals.

7.5.1 *GFAA Stock Standard Solution (1000 ppm)*—Single-element standards either purchased or prepared from high-purity grade chemicals or metals.

7.5.2 *GFAA Intermediate Stock Standard Solution (1 ppm)*—Add 0.1 mL of stock standard solution (7.5.1) and 1 mL of concentrated nitric acid to a 100-mL volumetric flask. Dilute to volume with water.

7.6 *Magnesium Nitrate Solution*—Matrix modifier (see Note 2), ( $106\text{-g/L Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) for the determination of arsenic and antimony, equivalent to 10 000-ppm magnesium.

NOTE 2—A matrix modifier is used to minimize GFAA interference effects by selective volatilization of either the analyte or the matrix components. Other matrix modifiers such as nickel nitrate or palladium nitrate can be used. The analyst should compare modifiers to establish optimum performance as outlined in 10.1.

7.7 *Blank Solutions*—All of the test methods in this standard require two types of blank solutions. A calibration blank that is used to establish the analytical calibration curve and a method blank which is used to evaluate possible contamination and assess spectral background.

7.7.1 *Calibration Blank*—A 1 % nitric acid solution. When using matrix modifiers of GFAA, the calibration blank shall also contain the same equivalent concentration.

7.7.2 *Method Blank*—Consists of all the reagents in the same volumes as used in preparing the samples. The method blank shall be processed through the entire sample digestion scheme.

## 8. Analysis Sample

8.1 Samples of coal and coke shall be prepared in accordance with Method D 2013 or Practice D 346.

8.2 Standard practices for the sampling and preparation of residues from coal utilization processes have not been established. Some of these materials are highly abrasive. The use of high speed pulverizers for size reduction shall be avoided. The use of jaw crushers followed by final preparation in an agate mortar and pestle is recommended to prevent contamination of the sample.

8.3 Analyze separate test portions for moisture content in accordance with Test Methods D 3173 and D 5142 so that calculations to other bases can be made.

## 9. Procedure

9.1 *Ashing*—Weigh to the nearest 0.1 mg enough of the coal or coke sample that will yield approximately 0.5 g of ash into an open 50-mL quartz or high-silica crucible. Place the crucible in a cold muffle furnace. Adjust the temperature control so that the furnace reaches a temperature of 300°C in 1 h and then 500°C in the second hour. Maintain the furnace temperature at 500°C for a minimum of 2 h, stirring the sample occasionally. Ashing is complete when no visible evidence of carbonaceous material remains. Cool the samples to room temperature under conditions that minimize the absorption of water. Grind the ash to pass a 150- $\mu\text{m}$  (No. 100) U.S.A. standard sieve in an agate mortar then reignite at 500°C for 1 h. Cool the ash and store in a desiccator. Determine the percentage of ash by analyzing under the same conditions a separate portion of the analysis sample.

NOTE 3—If all the ash from 9.1 is quantitatively transferred for digestion in 9.2, it is not necessary to sieve and grind the ash. Results from 11.2.3, 12.3, or 13.1.3.8 are then ppm of the element in the as-determined sample.

9.2 *Dissolution*—Weigh 0.2000 to 0.5000 g of the thoroughly blended ash prepared according to 9.1 into a 100- or 200-mL Teflon beaker. Add 20 mL of aqua regia and 20 mL of concentrated hydrofluoric acid to the beaker. Place the beaker on a hot plate that has been adjusted to 130 to 150°C. Heat the mixture to dryness, but do not bake. After the solution has evaporated, rinse the beaker walls with deionized water and heat this solution to dryness, again being careful not to bake the sample. Remove the beaker from the hot plate and cool to room temperature. Add 1 mL of concentrated nitric acid and 20 mL of deionized water to the beaker. Heat the contents on a hot plate at 90 to 100°C until the sample is in solution. If a residue remains after 1 h of heating, it may be ignored. The trace elements are considered to be quantitatively extracted at this point. Remove the beaker from the hot plate and allow the solution to cool to room temperature. Transfer the cool solution to a 100-mL volumetric flask and dilute to volume with deionized water. If the solution is not to be analyzed immediately, transfer to a HDPE bottle to avoid adsorption of lead during storage. Prepare a method blank (7.7.2) with each batch of samples to be analyzed.

NOTE 4—To minimize contamination, clean laboratory ware in a 1:1 solution of  $\text{HNO}_3$  followed by a 1:1 solution of  $\text{HCl}$  then rinse thoroughly with deionized water.

## 10. Analysis

10.1 Because of the differences between various makes and models of instruments, all instrumental operating instructions cannot be provided. Instead, the analyst shall refer to the instructions provided by the manufacturer of the particular instrument.

Sensitivity, instrumental detection limit, linear dynamic range, interference effects, and appropriate background correction shall be investigated and established for each individual analyte on that particular instrument.

## 11. Test Method A—Inductively Coupled Plasma Atomic Emission Spectroscopy

11.1 Table 1 shows the elements listed in 1.1 along with some suggested wavelengths for inductively coupled plasma atomic emission spectrometry (ICPAES). Other wavelengths may be substituted if they can provide the needed sensitivity and are treated according to the provisions of 10.1. Also shown are estimated detection limits.

11.2 *Calibration Procedure*—Calibrate the instrument according to the procedure recommended by the manufacturer using a calibration blank and aqueous multielement standards made up in 1 % trace metal grade HNO<sub>3</sub>. All calibration solutions must also contain an internal standard (see Note 5). Records for all calibrations must be in accordance with Guide D 4621.

NOTE 5—An internal standard is needed to compensate for:

1. Differences in physical properties (such as viscosity) between the calibration standard and the test samples and
2. Drift caused by thermal changes in the laboratory which will affect the instrument optics.

An appropriate internal standard element should:

- (i) not be naturally present in the test samples in appreciable concentrations,
- (ii) not present spectral interferences with any analyte,
- (iii) be a strong emitter so that its relative concentration can be kept low, and
- (iv) be as chemically similar to the analyte as possible.

11.2.1 *Initial Calibration Verification*—Before analyzing test samples, analyze the method blank and verify the proper calibration of the instrument by analyzing a reference material that has traceability to an internationally recognized certifying agency such as NIST. Results for the reference material must be within the stated uncertainty limits or the calibration procedure must be repeated.

11.2.2 *Periodic Calibration Verification and Recalibration*—In accordance with Guide D 4621, analyze a control sample such as NIST on a periodic basis. Results obtained for the control sample must be within 10 % of the stated value or all results obtained since the last successful control check of that element must be rejected and the calibration procedure repeated.

11.2.3 *Calculation*—Calculate the concentration of the element in the ash as follows:

$$C = (A \times df)/(W \times 100) \quad (1)$$

where:

$C$  = weight percent of the element in the ash,

$df$  = dilution factor,

$A$  = ppm of the element in solution, and

$W$  = weight of the sample in grams.

## 12. Test Method B—Inductively Coupled Plasma Mass Spectrometry

12.1 Table 2 shows the elements listed in 1.1, the isotope, and its abundance used for ICPMS determinations. Also shown are some potential molecular interferences.

**TABLE 1 Suggested Wavelengths for ICPAES**

Element	Wavelength, nm	Estimated Detection Limit, µg/L <sup>A</sup>
As <sup>B</sup>	189.042, 228.812, 193.759	53
Be	313.042	0.3
Cd <sup>B</sup>	226.502	4
Co	228.616	7
Cr	267.716, 205.552	7
Cu	324.754	6
Mn	257.610	30
Mo	202.030, 203.844	8
Ni	231.604	15
Pb	220.353	42
Sb <sup>B</sup>	217.581, 206.833	32
V	292.402, 292.464	8
Zn	213.856	2

<sup>A</sup>Detection limits are given for informational purposes only and represent the lowest concentration that produces a instrumental response statistically different from an aqueous blank solution. Detection limits should not be confused with quantitation limits. Detection limits are sample and matrix dependent. They will vary from instrument to instrument and should be established by each user of these test methods. These values (3 sigma) are based on data contained in EPA/600/4-91/010, Method 200.7 Revision 5.4 (1994).

<sup>B</sup>As, Cd, and Sb are typically present in coal at concentrations that are below the detection limits of ICPAES.

**TABLE 2 Isotopes Used for ICPMS Trace Element Determinations**

Element	Isotope	Abundance	Interferant	Estimated Detection Limit, $\mu\text{g/L}^A$
As	75	100	$^{40}\text{Ar } ^{35}\text{Cl}+$	0.9
Be	9	100		0.1
Cd	114	28.8	$^{96}\text{Mo } ^{16}\text{O}+$	0.1
Co	59	100		0.03
Cr	52	83.8		0.07
Cu	63	69.1	$^{47}\text{Ti } ^{16}\text{O}+$	0.03
Mn	55	100		0.1
Mo	98	23.8		0.1
Ni	60	26.1		0.2
Pb	206	52.4		0.08
Sb	121	57.3		0.08
V	51	99.8	$^{35}\text{Cl } ^{16}\text{O}+$	0.02
Zn	68	18.6	$^{36}\text{S } ^{16}\text{O } ^{16}\text{O}+$	0.2

<sup>A</sup>Detection limits are given for informational purposes only and represent the lowest concentration that produces an instrument response statistically different from an aqueous blank solution. Detection limits should not be confused with quantitation limits. Detection limits are sample and matrix dependent. They will vary from instrument to instrument and should be established by each user of these test methods. The values (3 sigma) are based on data contained in EPA/600/4-91/010, Method 200.8, Revision 5.4 (1994).

12.2 *Calibration*—In conjunction with 11.2, calibrate the instrument by analyzing a blank consisting of deionized water and appropriate internal standards (see Note 6), and a 1 % solution of  $\text{HNO}_3$  containing 0 ppb of the elements to be analyzed and internal standards. Continue the calibration by analyzing three solutions that cover the expected concentration range of the elements to be analyzed. One of the solutions must be lower, one in the range, and one higher in concentration than that of the analyte. Suggested concentration ranges are 10, 50, and 250 ppb.

NOTE 6—Internal standards are needed to compensate for instrument drift. Drift associated with ICPMS instruments is typically mass dependent. Therefore, it is recommended that the analyst use a series of internal standards that covers the mass range of the elements to be analyzed. Elements used as internal standards should not be present in the samples to be analyzed in appreciable quantities. Li, Ge, In, and Bi are recommended as internal standards for the list of elements in 1.1. However,  $^6\text{Li}$  must be used because of the significant concentration of  $^7\text{Li}$  in most coals. Because they are not present in coal in appreciable concentrations, any isotopes of Ge, In, and Bi may be used.

12.2.1 *Initial Calibration Verification*—Before analyzing test samples, analyze the method blank and verify the proper calibration of the instrument by analyzing a reference material that has traceability to an internationally recognized certifying agency such as NIST. Results for the reference material must be within the stated uncertainty limits or the calibration procedure must be repeated.

12.2.2 *Periodic Calibration Verification and Recalibration*—In accordance with Guide D 4621, analyze a control sample on a periodic basis. Results obtained for the control sample must be within 10 % of the stated value or all results obtained since the last successful control check for that element must be rejected and the calibration procedure repeated.

12.3 *Calculation*—Calculate the concentration of the element in the ash as follows:

$$C = (A \times df)/(W \times 100) \quad (2)$$

where:

$C$  = weight percent of the element in the ash,

$df$  = dilution factor,

$A$  = ppm of the element in solution, and

$W$  = weight of the sample in grams.

### 13. Test Method C—Graphite Furnace Atomic Absorption

#### 13.1 Calibration and Sample Solution Preparation:

13.1.1 Use the intermediate stock standard solution (7.5.2) to prepare at least five working standards to cover the optimum concentration ranges specified by the instrument manufacturer for the element to be analyzed. Add an aliquot of concentrated nitric acid to obtain a final concentration of 1 %  $\text{HNO}_3$ . When preparing arsenic or antimony working standards, add 2 mL of magnesium nitrate solution (7.6).

13.1.2 *Sample Aliquot*—Add an aliquot of the sample solution (9.2) in the optimum concentration range for the element to be determined (Note 7) to a 10-mL volumetric flask. Add nitric acid to obtain a 1 % solution. The determination of arsenic and antimony require the addition of 2 mL of magnesium nitrate solution (7.6). Dilute to volume with water.

NOTE 7—To estimate the aliquot of sample solution, it may be necessary to analyze the original sample solution (9.2). In some cases, only by trial and error can the correct aliquot of sample be determined. Alternatively, ICPAES can be used to screen samples to determine which elements may require analysis by GFAA.



13.1.3 *Instrument Parameters*—As stated in 10.1, because of differences in equipment, it is impossible to specify instrument operating parameters (for example, wavelength, slit, lamp power, drying, ashing and atomization temperatures, and so forth). Instead, the analyst shall initially program the system according to the instrument manufacturer's instructions for a particular analyte. Optimize instrument performance for each analyte according to the following sections.

13.1.3.1 *Drying Temperature*—Make an injection of both a sample and a working standard solution according to 13.1.3. Use a mirror to observe the samples through the introduction port. The drying temperature should be high enough to evaporate the sample smoothly but not so hot that the sample begins to boil or spatter.

13.1.3.2 *Ashing Temperature*—As the ashing step begins, no sizzle or popping sounds should be heard. The ashing temperature should be high enough to eliminate most of the background but not so hot as to volatilize the analyte. A high flow rate of inert gas is required during the ashing stage to sweep the furnace of unwanted background material.

13.1.3.3 *Atomization Temperature*—Adjust the atomization temperature as necessary to eliminate low, broad, misshapen, or doublet peaks. Adjustments should be made in 100°C increments. Peak shape may also dictate the mode of measurement (peak height or peak area) and the choice of graphite tube and platforms (Note 8).

NOTE 8—Graphite platforms significantly improve instrument performance for the determination of Cd, Pb, As, and Sb. It is strongly recommended that they be tried as part of optimizing instrument performance for each element to be determined.

13.1.3.4 Refer to the instrument manufacturer's instructions for further information on optimizing performance.

13.1.3.5 Repeat the steps in 13.1 through 13.3.4 for each element to be determined.

13.1.3.6 *Initial Calibration Verification*—Before analyzing test samples, analyze the method blank and verify the proper calibration of the instrument by analyzing a reference material that has traceability to an internationally recognized certifying agency such as NIST. Results for the reference material must be within the stated uncertainty limits or the calibration procedure must be repeated.

NOTE 9—**Caution:** Matrix problems are prevalent when analyzing the types of samples described in 1.1 by GFAA. If the sample matrix varies significantly from that of the reference material, validation of the test methods with the reference material may lead to an incorrect assumption that the test methods are applicable to other matrices.

13.1.3.7 *Periodic Calibration, Verification, and Recalibration*—In accordance with Guide D 4621, analyze a control sample such as NIST on a periodic basis. Results obtained for the control sample must be within 10 % of the stated value or all results obtained since the last successful control check for that element must be rejected and the calibration procedure repeated.

13.1.3.8 *Calculation*—Calculate the concentration of the element in the ash as follows:

$$C = (A \times df)/(W \times 100) \quad (3)$$

where:

$C$  = weight percent of the element in the ash,

$df$  = dilution factor,

$A$  = ppm of the element in solution, and

$W$  = weight of the sample in grams.

## 14. Report

14.1 Convert concentration of the element in the ash to the whole coal basis for reporting as follows:

$$C = (AB/100) \quad (4)$$

where:

$C$  = ppm in the coal,

$A$  = ppm determined in the ash, and

$B$  = % ash in the coal.

14.2 For reporting analyses to other than the as-determined basis, refer to Practice D 3180.

## 15. Precision and Bias

15.1 *Precision*—The precision of this test method for the determination of priority trace elements in coal, coke, and solid combustion residues are shown in Table 3. The precision characterized by the repeatability ( $S_r$ ,  $r$ ) and reproducibility ( $S_R$ ,  $R$ ) is described in ~~Table A1.1 in the Annex. A1.1.~~

15.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

15.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as nearly homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

15.2 *Bias*—~~The NIST standard reference materials NBS 1632b, NIST 1635, and NIST 1633b were included in the priority trace element interlaboratory study to ascertain possible bias between reference material values and those determined by the new~~

**TABLE 3 Concentration Range and Limits for Repeatability and Reproducibility for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues**

Priority Element	Concentration Range, µg/g	Repeatability Limit, $r$	Reproducibility Limit, $R$
Sb	0.17–5.71	$-0.06 + 0.29 \bar{x}^A$	$0.08 + 0.44 \bar{x}^A$
As	0.56–138.79	$0.42 + 0.13 \bar{x}^A$	$1.73 + 0.23 \bar{x}^A$
Be	0.42–13.11	$0.08 + 0.08 \bar{x}^A$	$0.14 + 0.30 \bar{x}^A$
Cd	0.02–0.84	$0.03 + 0.16 \bar{x}^A$	$0.04 + 0.43 \bar{x}^A$
Co	0.76–47.18	$0.28 + 0.11 \bar{x}^A$	$1.26 + 0.18 \bar{x}^A$
Cr	2.37–221	$1.03 + 0.09 \bar{x}^A$	$1.50 + 0.18 \bar{x}^A$
Cu	3.43–107.06	$0.62 + 0.10 \bar{x}^A$	$-0.31 + 0.28 \bar{x}^A$
Mn	11.69–419.61	$0.98 + 0.10 \bar{x}^A$	$8.12 + 0.15 \bar{x}^A$
Mo	0.40–20.52	$0.23 + 0.11 \bar{x}^A$	$0.80 + 0.18 \bar{x}^A$
Ni	2.00–113.32	$0.35 + 0.13 \bar{x}^A$	$1.26 + 0.19 \bar{x}^A$
Pb	1.57–66.99	$0.26 + 0.16 \bar{x}^A$	$0.13 + 0.30 \bar{x}^A$
Zn	3.76–202.31	$0.70 + 0.10 \bar{x}^A$	$2.98 + 0.18 \bar{x}^A$
V	4.50–293.17	$0.75 + 0.13 \bar{x}^A$	$2.02 + 0.21 \bar{x}^A$

<sup>A</sup>Where  $\bar{x}$  is the average of two single test results.

method. A comparison of the NIST values and those obtained in the interlaboratory study are given in Tables 4-6. Trace element values are not certified for the elements beryllium, molybdenum, and antimony, therefore, bias cannot be determined for these elements at this time.

15.3 An interlaboratory study, designed consistent with Practice E 691, was conducted in 1997. Twelve laboratories participated.<sup>5</sup>

## 16. Keywords

16.1 coal; coal ash; graphite furnace atomic absorption spectrometer; inductively coupled plasma atomic emission spectrometer; inductively coupled plasma mass spectrometer; trace elements

<sup>5</sup> Supporting data will be available from ASTM Headquarters soon.

**TABLE 4 Comparison of Certified Values for Standard Reference Material NBS 1632b with Interlaboratory Study Values for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues**

Elemental Oxide	RR Value	NIST Value	Bias, %	Significant (95 % Confidence Level)
As	$3.64 \pm 0.21$	$3.72 \pm 0.09$	-2.15	no
Cd	$0.065 \pm 0.01$	$0.057 \pm 0.0027$	14.04	yes
Co	$2.18 \pm 0.15$	$2.29 \pm 0.17$	-4.80	no
Cu	$6.31 \pm 0.36$	$6.28 \pm 0.30$	0.48	no
Mn	$11.7 \pm 0.64$	$12.4 \pm 1.0$	-5.65	no
Ni	$6.20 \pm 0.37$	$6.10 \pm 0.27$	1.64	no
Pb	$3.74 \pm 0.33$	$3.67 \pm 0.26$	1.91	no
Zn	$11.30 \pm 0.52$	$11.89 \pm 0.78$	-4.96	no

**TABLE 5 Comparison of Certified Values for Standard Reference Material NBS 1635 with Interlaboratory Study Values for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues**

Elemental Oxide	RR Value	NIST Value	Bias, %	Significant (95 % Confidence Level)	
As	0.56 ± 0.11	0.42 ± 0.15	33.3	no	
Cd	0.03 ± 0.01	0.03 ± 0.01	0.0	no	
Cr	2.4 ± 0.2	2.5 ± 0.3		-4.00	no
Cu	3.4 ± 0.3	3.6 ± 0.3		-5.56	no
Mn	20.4 ± 1.2	21.4 ± 1.5	-4.67		no
Ni	2.00 ± 0.28	1.74 ± 0.10	14.94		no
Pb	1.6 ± 0.1	1.9 ± 0.2		-15.79	yes
V	4.5 ± 0.2	5.2 ± 0.5		-13.46	yes
Zn	5.00 ± 0.7	4.7 ± 0.5		6.38	no

**TABLE 6 Comparison of Certified Values for Standard Reference Material NBS 1633b with Interlaboratory Study Values for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues**

Elemental Oxide	RR Value	NIST Value	Bias, %	Significant (95 % Confidence Level)	
As	138.8 ± 6.5	136.2 ± 2.6	1.91	no	
Cd	0.845 ± 0.080	0.784 ± 0.006	7.78	no	
Cr	184.1 ± 7.7	198.2 ± 4.7	-7.11	yes	
Cu	107.1 ± 3.8	112.8 ± 2.6	-5.05	yes	
Mn	130.6 ± 4.2	131.8 ± 1.7	-0.91	no	
Ni	113.3 ± 6.0	120.6 ± 1.8	-6.05	yes	
Pb	67.0 ± 3.8	68.2 ± 1.1	1.76	no	
V	293.2 ± 11.1	295.7 ± 3.6	-0.85	no	

**ANNEX**

**(Mandatory Information)**

**A1. PRECISION STATISTICS**

A1.1 The precision of these test methods, characterized by repeatability ( $S_r$ ,  $r$ ) and reproducibility ( $S_R$ ,  $R$ ) has been determined for the following materials as listed in Table A1.1.

**TABLE A1.1 Repeatability ( $S_r$ ,  $R_r$ ) and Reproducibility ( $S_R$ ,  $R$ ) Parameters Used for Calculation of Precision Statement**

<b>Sb</b>						<b>As</b>					
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
NIST 1635	0.169 79	0.021 22	0.037 39	0.059 42	0.104 7	NIST 1635	0.563	0.109	0.165	0.304	0.462
NIST 1632b	0.280 17	0.011 78	0.072 02	0.032 98	0.201 66	Coal D	1.724	0.143	0.327	0.399	0.916
Coal D	0.571 96	0.021 7	0.095 67	0.060 76	0.267 89	Coal G	2.49	0.375	0.481	1.051	1.346
Coal A	0.622 63	0.060 4	0.120 82	0.169 13	0.338 29	Ash J	2.538	0.476	0.548	1.333	1.534
Ash J	0.649 83	0.092 04	0.132 26	0.257 7	0.370 32	NIST 1632b	3.642	0.21	0.279	0.587	0.782
Coal E	0.920 96	0.078 48	0.208 73	0.219 75	0.584 45	Coal A	3.72	0.335	0.669	0.938	1.874
NIST 2776	1.110 04	0.075 55	0.237 18	0.211 55	0.664 1	NIST 2776	8.024	0.705	1.207	1.975	3.38
Coal G	1.828 33	0.089 6	0.290 64	0.250 87	0.813 8	Coal E	11.338	0.671	1.843	1.879	5.159
NIST 1633b	5.713 75	0.594 45	0.929 88	1.664 47	2.603 67	NIST 1633b	138.792	6.469	11.376	18.113	31.854

  

<b>Be</b>						<b>Cd</b>					
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
Coal D	0.4253	0.034	0.056	0.0952	0.1567	NIST 2776	0.021 92	0.004 28	0.008 88	0.011 98	0.024 86
NIST 1635	0.4544	0.0239	0.0528	0.0668	0.1479	NIST 1635	0.034 92	0.010 87	0.012 49	0.030 43	0.034 98
NIST 1632B	<del>0.6587</del>	<del>0.0268</del>	<del>0.0559</del>	<del>0.0754</del>	<del>0.1566</del>	NIST 1632B	<del>0.064 74</del>	<del>0.010 06</del>	<del>0.012 23</del>	<del>0.028 16</del>	<del>0.034 26</del>
NIST 1632b	0.6587	0.0268	0.0559	0.0751	0.1566	NIST 1632b	0.064 71	0.010 06	0.012 23	0.028 16	0.034 26
Coal E	0.7353	0.0274	0.132	0.0768	0.3697	Coal D	0.084 71	0.010 64	0.018 31	0.029 78	0.051 25
Coal G	1.2868	0.0639	0.1381	0.1789	0.3866	Coal G	0.089 42	0.006 17	0.027 8	0.017 28	0.077 85
Coal A	1.371	0.0601	0.2164	0.1683	0.606	Coal E	0.146 5	0.042 76	0.067 45	0.119 74	0.188 85
NIST 2776	2.1238	0.1796	0.535	0.5029	1.4981	Ash J	0.176	0.030 4	0.068 13	0.085 12	0.190 77
Ash J	8.089	0.3147	0.8682	0.8812	2.431	Coal A	0.750 12	0.026 02	0.127 74	0.072 86	0.357 66
NIST 1633B	13.106	0.3904	1.4911	1.0922	4.1754	NIST 1633B	<del>0.844 62</del>	<del>0.080 35</del>	<del>0.141 5</del>	<del>0.244 98</del>	<del>0.396 2</del>



TABLE A1.1 Continued

Co						Cr					
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
NIST 1633b	13.106	0.3901	1.4911	1.0922	4.1751	NIST 1633b	0.844 62	0.080 35	0.141 5	0.244 98	0.396 2
NIST 1635	-0.7598	-0.0783	-0.132	-0.2194	-0.3695	NIST 1635	-2.369	0.206	-0.414	-0.576	-1.16
NIST 1635	0.7598	0.0783	0.132	0.2192	0.3695	NIST 1635	2.369	0.206	0.414	0.576	1.16
Coal D	1.1258	0.165	0.3618	0.4619	1.0131	Coal D	4.425	0.44	0.565	1.231	1.583
NIST 1632b	2.1806	0.1514	0.2721	0.424	0.7618	Coal E	7.326	0.57	0.86	1.597	2.408
Coal E	2.2175	0.1962	0.428	0.5493	1.1984	Coal G	8.63	0.48	0.817	1.344	2.286
Coal G	-3.7797	-0.207	-0.3664	-0.5796	-1.026	NIST 1632B	-10.094	0.594	-0.858	-1.655	-2.402
Coal G	3.7797	0.207	0.3664	0.5796	1.026	NIST 1632b	10.094	0.591	0.858	1.655	2.402
Coal A	3.9509	0.216	0.467	0.6047	1.3075	NIST 2776	15.72	0.713	1.814	1.997	5.079
NIST 2776	10.0456	0.6751	2.6224	1.8902	7.3427	Coal A	29.237	1.879	3.61	5.262	10.107
Ash J	25.5969	1.0368	2.7019	2.903	7.5653	NIST 1633B	184.1	7.744	11.782	21.683	32.991
NIST 1633b	-57.1844	-1.913	-2.8735	-5.3565	-8.0459	Ash J	224	6.177	14.905	17.294	41.734
NIST 1633b	47.1844	1.913	2.8735	5.3565	8.0459	Ash J	221	6.177	14.905	17.294	41.734
Cu						Pb					
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
NIST 1635	3.427	0.269	0.435	0.753	1.218	NIST 1635	1.5689	0.1437	0.2799	0.4024	0.7837
NIST 1632b	6.306	0.36	0.654	1.007	1.831	Coal E	2.3943	0.2082	0.4421	0.5829	1.238
Coal E	7.727	0.466	0.709	1.305	1.985	NIST 1632b	3.7425	0.3299	0.3969	0.9238	1.112
Coal D	8.474	0.372	0.558	1.041	1.562	Coal D	4.5039	0.315	0.8796	0.8819	2.4629
Coal G	10.668	0.456	0.568	1.278	1.674	NIST 2776	4.7111	0.3363	0.6798	0.9418	1.9035
Coal A	10.822	0.359	1.031	1.006	2.887	Coal G	8.8061	0.8143	0.9541	2.28	2.6714
NIST 2776	19.444	0.978	2.113	2.737	5.915	Ash J	9.835	0.6297	0.8747	1.7631	2.4491
Ash J	38.731	2.779	3.304	7.781	9.25	Coal A	10.5625	0.5502	0.6714	1.5407	1.88
NIST 1633b	107.056	3.852	10.544	10.785	29.522	NIST 1633b	66.9893	3.8516	7.2194	10.7846	20.2144
Mo						Ni					
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
NIST 1635	0.4016	0.0472	0.1307	0.1321	0.3658	NIST 1635	1.996	0.28	0.522	0.783	1.462
NIST 1632b	0.89	0.2025	0.3278	0.5671	0.9178	Coal D	2.341	0.244	0.62	0.683	1.737
Coal G	1.7286	0.1535	0.2826	0.4297	0.7912	Coal E	5.63	0.385	1.37	1.078	3.836
NIST 2776	2.1686	0.2011	0.5222	0.5632	1.462	NIST 1632b	6.184	0.369	0.374	1.033	1.047
Coal E	2.9182	0.1816	0.2697	0.5085	0.7553	Coal G	6.776	0.397	0.769	1.111	2.153
Coal D	7.0164	0.3762	0.5594	1.0535	1.5664	NIST 2776	14.622	0.995	1.81	2.787	5.067
Coal A	7.6318	0.303	0.8352	0.8485	2.3384	Coal A	17.82	0.931	1.367	2.608	3.829
Ash J	10.0896	0.4888	1.8675	1.3687	5.2289	Ash J	97.03	4.127	7.575	11.555	21.211
NIST 1633b	-20.5214	-0.9182	-1.2339	-2.574	-3.4548	NIST 1633b	113.325	5.966	-7.714	16.704	21.598
NIST 1633b	20.5214	0.9182	1.2339	2.571	3.4548	NIST 1633b	113.325	5.966	7.714	16.704	21.598
Mn						Zn					
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
NIST 1632b	11.69	0.638	0.924	1.786	2.586	Coal D	3.757	0.309	1.325	0.866	3.71
NIST 1635	20.4	1.253	2.622	3.507	7.342	NIST 1635	4.998	0.686	0.762	1.922	2.133
NIST 2776	28.357	2.004	8.418	5.611	23.571	Coal E	9.283	0.25	0.426	0.699	1.192
Coal A	-45.257	-2.128	-5.955	-5.957	-14.155	NIST 1632B	-11.309	0.519	-0.924	-1.454	-2.589
Coal A	45.257	2.128	5.055	5.957	14.155	NIST 1632b	11.309	0.519	0.924	1.454	2.589
Coal G	76.88	2.891	7.35	8.094	20.581	NIST 2776	11.967	0.785	1.545	2.198	4.325
Coal E	122.409	4.392	12.382	12.297	34.67	Coal G	15.639	0.75	1.985	2.1	5.557
NIST 1633b	130.659	4.249	8.167	11.897	22.866	Coal A	88.803	4.174	11.319	11.686	31.694
Coal D	138.932	5.654	10.333	15.83	28.933	Ash J	113.303	3.569	8.839	9.992	24.749
Ash J	419.614	15.64	25.935	42.794	72.618	NIST 1633B	202.306	7.348	41.597	20.574	32.474
Ash J	419.614	15.64	25.935	42.791	72.618	NIST 1633b	202.306	7.348	11.597	20.574	32.471
V											
Material	Average	$S_r$	$S_R$	$r$	$R$	Material	Average	$S_r$	$S_R$	$r$	$R$
NIST 1635	4.498	0.242	0.308	0.678	0.864						
Coal D	8.698	0.342	0.89	0.958	2.492						
NIST 1632b	14.12	0.719	1.152	2.014	3.227						
Coal E	14.72	0.413	1.472	1.156	4.121						
Coal G	24.06	1.273	2.001	3.565	5.604						
NIST 2776	28.125	2.704	3.992	7.571	11.178						
Coal A	35.685	1.228	4.497	3.438	12.591						
Ash J	218.8	13.3	20.49	37.239	57.371						
NIST 1633b	293.175	11.128	20.75	31.157	58.1						

A1.1.1 Repeatability Standard Deviation ( $S_r$ )—The standard deviation of test results obtained under repeatability conditions.

A1.1.2 Reproducibility Standard Deviation ( $S_R$ )—The standard deviation of test results obtained under reproducibility conditions.

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