Designation: D3683 – 04

Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption[1]

This standard is issued under the fixed designation D3683; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method[2] describes a procedure for the determination of beryllium, chromium, copper, manganese, nickel, lead, vanadium, and zinc in coal ash or coke ash.

NOTE 1—Although not included, this test method can be applicable to the determination of other trace elements, for example, cadmium.

1.2 *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.*

1.3 The values stated in SI units (IEEE/ASTM SI 10) should be regarded as the standard.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis

D1193 Specification for Reagent Water

D2013 Practice for Preparing Coal Samples for Analysis

D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke

D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases

D5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System

NOTE 2—Practice D2013 specifies coal ground to pass through a 60-mesh (250-μm) screen. For the trace element determinations in this test method –100-mesh (150-μm) coal is recommended.

3. Summary of Test Method

3.1 Coal or coke is ashed, the ash is dissolved by mineral acids, and the individual elements determined by atomic absorption spectrometry.

4. Significance and Use

4.1 Many trace elements occur in coal, primarily as a part of the mineral matter but may also be associated with the organic matrix. Concern over release of certain trace elements to the environment as a result of coal utilization has made the determination of these elements an increasingly important aspect of coal analysis.

4.2 When coal ash is prepared in accordance with this test method, the eight elements listed in 1.1 are quantitatively retained in the ash and are representative of concentrations in the coal. Concentrations of these and other elements in power plant ash, industrial process ash, fly ash, and so forth, may or may not be representative of total quantities in the coal.

5. Apparatus

5.1 *Atomic Absorption Spectrometer*—Any dual-channel instrument using a deuterium (D_2) arc background corrector or other comparable simultaneous background correction system.

5.2 *Muffle Furnace*, with temperature control.

5.3 *Bottles*, polyethylene or polytetrafluoroethylene, 125-mL capacity, with screw-cap lids, capable of withstanding temperatures up to 130°C.

5.4 *Volumetric Flasks*, 100-mL capacity.

5.5 *Steam Bath*.

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

[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke, and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements in Coal.

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[2] For information concerning experimental work on which this test method is based, see Bernas, B., "A New Method for the Decomposition and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry," *Analytical Chemistry*, ANCHA, Vol 40, 1968, pp 1682–86.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Reagent Water*—Reagent water, conforming to Type II of Specification D1193, shall be used for preparation of reagents.

6.3 *Aqua Regia Solution*—Mix one part concentrated nitric acid (HNO_3, sp gr 1.42), three parts concentrated hydrochloric acid (HCl, sp gr 1.19), and one part water.

6.4 *Boric Acid Solution, Saturated*—Dissolve 60 g of boric acid (H_3BO_3) in 1 L of deionized water.

6.5 *Stock Solutions, Standard*—Prepare standard stock solutions from high-purity (99.9 % or better) metals, oxides, or salts. Stock solutions of at least 100 ppm (µg/ml) for each metal are convenient for preparation of dilute standards in the range from 10 to 0.01 ppm (µg/mL) depending upon the sensitivity of the element and the instrumentation used.

6.6 *Hydrofluoric Acid* (*sp gr 1.15*)—Concentrated hydrofluoric acid (HF).

7. Sample

7.1 Prepare the analysis sample in accordance with Practice D2013 or Practice D346 by pulverizing the material to pass 250-µm (No. 60) sieve (Note 3).

NOTE 3—Analysis samples ground to pass a 150-µm (No. 100) sieve are recommended for this test method.

7.2 Analyze separate test portions for moisture content in accordance with Test Methods D3173 or D5142 so that calculation to other bases can be made.

8. Calibration and Standardization

8.1 Calibration standards are prepared from stock solutions (see 6.5) appropriately diluted so as to finally contain 1.5 % v/v aqua regia solution, 3 % v/v hydrofluoric acid (HF), and 3 % v/v H_3BO_3(Note 4). The corresponding absorbance response for each standard is plotted versus concentration for calibration. Sample responses are compared directly with the calibration curve.

NOTE 4—It is important that the standards closely approximate the sample solution so that errors as a result of matrix differences are minimal.

9. Procedure

9.1 *Ashing*—Ash approximately 6 g (weighed to the nearest 0.1 mg) of the analysis sample in an open 50-mL quartz or high-silica crucible. Place the crucible in a cold muffle furnace and heat gradually at such a rate that the temperature reaches 300°C in about 1 h. Continue heating so that a temperature of 500°C is reached at the end of the second hour. Continue the ashing at 500°C for an additional 2 h. Stir the sample once each hour until no carbonaceous materials remain. After cooling and weighing, finely grind the ash in a clean agate or mullite mortar and then reignite at 500°C for 1 h. Cool and reweigh to calculate the percent ash.

NOTE 5—Coke can be ignited to a constant weight at a temperature not exceeding 950°C if difficulty in ashing is encountered. If a higher ashing temperature is used, it should be recorded with results.

9.2 *Dissolution*—Place ash samples (approximately 0.2 g) in 125-mL plastic bottles with screw caps (Note 7). Bottles should be capable of withstanding temperatures up to 130°C. Add 3 mL of aqua regia solution and 5 mL of HF to the samples, tighten screw caps, and place the bottles on a steam bath for at least 2 h. Add 50 mL of saturated H_3BO_3 solution to the resultant solution (Note 8). If a residue remains, the mixture may be reheated for about 1 h to help dissolve it (Note 9). Cool the solutions to room temperature and adjust their volume to 100 mL by the addition of deionized water. Prepare blanks by using the above procedure. Store samples in polyethylene bottles.

NOTE 6—Avoid the use of sulfates and sulfuric acid (H_2SO_4). They have adverse effects on the flame, and some sulfates have low solubility.

NOTE 7—To minimize contamination, clean laboratory ware in a 10 % solution of hot HCl and rinse thoroughly with deionized water (6.2).

NOTE 8—Boric acid (H_3BO_3) not only complexes F, but it also has been shown to have good flame properties and acts as a flame buffer.

NOTE 9—If a residue persists it can be ignored. The trace elements are considered to be quantitatively extracted at this point.

9.3 *Analysis*—Use conventional atomic absorption procedures and make background corrections for each element. A nitrous oxide/acetylene (N_2O/C_2H_2) flame can be used for beryllium, chromium, and vanadium, while an air/acetylene flame is used for cadmium, copper, manganese, nickel, lead, and zinc. Table 1 summarizes the instrumental parameters to be used.

TABLE 1 Instrument Parameters

Element	Wavelength, nm	Oxidant-Fuel
Be	234.9	N_2O-C_2H_2
Cd	228.8	air-C_2H_2
Cr	357.9	N_2O-C_2H_2
Cu	324.8	air-C_2H_2
Mn	279.5	air-C_2H_2
Ni	232.0	air-C_2H_2
Pb	283.3	air-C_2H_2
V	318.0	N_2O-C_2H_2
Zn	213.9	air-C_2H_2

10. Calculation

10.1 Convert concentrations in the ash to the air-dried coal basis for reporting as follows:

$$C = (AB/100)$$

where:

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

C = ppm (µg/g) in air-dried coal,
A = ppm (µg/g) in ash, and
B = % ash in air-dried coal.

NOTE 10—See Practice D3180 for procedures to convert values to other bases.

11. Precision and Bias [5]

11.1 *Precision*:

11.1.1 *Repeatability Limit (r)*—the value below which the absolute difference between two test results calculated to a dry basis (Practice D3180) 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 homogenous material, may be expected to occur with a probability of approximately 95%. The repeatability limits determined by this test method are listed in Table 2.

11.1.2 *Reproducibility (R)*—the value below which the absolute difference between two test results calculated to a dry basis (Practice D3180) carried out in different laboratories using samples taken at random from a single quantity of material that is as homogenous as possible, may be expected to occur with a probability of approximately 95%. The reproducibility limits determined by this test method are listed in Table 3.

11.2 *Bias*—Standard Reference Material 1632, a National Institute of Standards and Technology (NIST) certified coal sample, was analyzed with the results which are tabulated in Table 4.

NOTE 11—The NIST value for beryllium is not certified and is given for informational purposes only. Values for Test Method D3683 represent the mean of the means from four separate laboratories, each of which made four replicate analyses on four separate samples of the coal standard.

[5] Supporting data are available from ASTM Headquarters. Request RR:D05-1001.

TABLE 2 Repeatability

Element	Air-Dried Coal, ppm (µg/g)	
	Repeatability[A]	Range[B]
Be	0.2	0.5 to 5
Cr	3	5 to 50
Cu	2	5 to 50
Mn	3	10 to 300
Ni	1	<5
Ni	3	5 to 30
Pb	2	10 to 100
V	5	10 to 100
Zn	3	<50
Zn	8	50 to 100

[A] Values should be considered as a general guide for the kinds of repeatability and reproducibility obtainable and not necessarily as values from which no deviation is permissible.
[B] Approximate range of concentrations within which sample results used for statistical evaluation fall.

TABLE 3 Reproducibility

Element	Air-Dried Coal, ppm (µg/g)	
	Reproducibility[A]	Range[B]
Be	0.5	0.5 to 5
Cr	5	5 to 50
Cu	3	5 to 50
Mn	6	<50
Mn	20	50 to 500
Ni	3	<5
Ni	9	9 to 30
Pb	9	10 to 100
V	9	10 to 50
V	20	50 to 100
Zn	4	<50
Zn	17	50 to 100

[A] Values should be considered as a general guide for the kinds of repeatability and reproducibility obtainable and not necessarily as values from which no deviation is permissible.
[B] Approximate range of concentrations within which sample results used for statistical evaluation fall.

12. Keywords

12.1 coal; coal ash; coke ash; trace elements; atomic absorption spectroscopy

TABLE 4 Bias

SRM 1632	Air-Dried Coal, ppm (µg/g)							
	Be	Cr	Cu	Mn	Ni	Pb	V	Zn
NIST	1.5[A]	20.2 ± 0.5	18.2 ± 2	40 ± 3	15 ± 1	30 ± 9	35 ± 3	37 ± 4
D3683	1.5 ± 0.1	20.0 ± 1	17.4 ± 0.6	43.8 ± 3	14.6 ± 3	27.8 ± 4	45.7 ± 4	37 ± 4

[A]Not certified; for information purposes only.