Designation: D6357 – 21b

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[1]

This standard is issued under the fixed designation D6357; 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 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. Additionally, there are specific test methods outlined that pertain to the determination of rare earth elements in coal and coal combustion residues.

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

NOTE 2—Rare earth elements are understood to include: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, samarium, scandium, terbium, thulium, ytterbium, and yttrium.

1.2 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.2.1 All percentages are percent mass fractions unless otherwise noted.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D121 Terminology of Coal and Coke

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

D3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal

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

D7448 Practice for Establishing the Competence of Laboratories Using ASTM Procedures in the Sampling and Analysis of Coal and Coke

D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis

D8146 Guide for Evaluating Test Method Capability and Fitness for Use

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Documents:*[3]

EPA/600/4-91/010 Methods for the Determination of Metals in Environmental Samples

3. Terminology

3.1 *Definitions*—Definitions applicable to these test methods are listed in Terminology D121.

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

[1] These test methods are under the jurisdiction of ASTM Committee 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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[2] 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.

[3] Available from Superintendent of Documents, U.S. Printing Office, Washington, DC 20402.

hydrofluoric acid, and finally dissolved in 1 % nitric acid. An alternative dissolution procedure is provided which is a high-temperature fusion method using a borate fluxing agent to specifically digest samples for rare earth element determination. Combustion residues are digested on an as-received basis. The mass concentration of individual trace elements is determined by either inductively coupled plasma atomic emission spectrometry (ICPAES) or inductively coupled plasma mass spectrometry (ICPMS). Selected elements that occur at mass concentrations below the detection limits of ICPAES can be quantitatively analyzed by graphite furnace atomic absorption spectrometry (GFAAS) or ICPMS.

5. Significance and Use

5.1 Coal contains several elements whose individual mass fractions 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 mass fractions 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.

NOTE 3—The abbreviation ICPAES is used throughout this document to refer to Inductively Coupled Plasma Atomic Emission Spectrometry and it is understood that some manufacturers will instead use the abbreviation ICPOES. In all cases, it is understood that ICPAES and ICPOES refer to the same technique.

6.1.1 *Argon Gas Supply*—Follow manufacturer specifications for purity.

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*—Follow manufacturer specifications for purity.

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 (GFAAS),* 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*—Follow manufacturer specifications for purity.

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 or, alternatively, for determination of rare earth elements, as specified in 9.3.

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

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

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

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

6.9 *HDPE Bottles,* 100 mL capacity.

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

6.11 *Hot Block Heater,* capable of heating to 120 °C.

6.12 *Automated Fluxing Equipment*—Although not specifically required, can be used in place of muffle furnace fusion.

6.13 *Fusion Muffle Furnace,* with an operating temperature of 1000 °C to 1100 °C.

6.14 *Stirring Hot Plate,* capable of heating to 80 °C.

6.15 *Teflon, HDPE, or Polypropylene Digestion Vessels,* 50 mL capacity.

6.16 *Glass Beakers,* 100 mL or 250 mL capacity.

6.17 *Graphite Crucibles,* 8 mL or 10 mL capacity.

6.18 *Platinum Crucibles,* 95 % Pt/5 % Au, 25 mL, or 30 mL capacity. If using automated fluxing equipment, use crucibles supplied by the manufacturer.

7. Reagents

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

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 D1193.

7.3 *Aqua Regia Solution*—Mix one part concentrated nitric acid (HNO_3, sp. gr. 1.42) and three parts concentrated hydrochloric acid (HCl, sp. gr. 1.9).

7.4 *Hydrofluoric Acid,* concentrated (HF, sp. gr. 1.15).

7.5 *ICP Calibration Standards*—Aqueous multielement solutions made up in 1 % HNO_3 are used for calibration of ICPAES and ICPMS systems. The stock standards may be purchased or prepared from high-purity grade chemicals or metals.

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

7.5.2 *GFAAS Intermediate Stock Standard Solution (1 µg/mL)*—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.

NOTE 4—Accuracy of the pipette was not stated in the instructions for the interlaboratory study for the determination of this method's precision, and so it is not stated here; however, the volumetric measurement