



Designation: D 4606 – 03

## Standard Test Method for Determination of Arsenic and Selenium in Coal by the Hydride Generation/Atomic Absorption Method<sup>1</sup>

This standard is issued under the fixed designation D 4606; 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 This test method<sup>2</sup> covers the determination of total arsenic and selenium in coal.

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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 121 Terminology of Coal and Coke<sup>3</sup>

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>3</sup>

D 2013 Method of Preparing Coal Samples for Analysis<sup>3</sup>

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke<sup>3</sup>

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases<sup>3</sup>

D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures<sup>3</sup>

### 3. Summary of Test Method

3.1 Arsenic and selenium are determined by mixing a weighed coal sample with Eschka mixture and igniting at 750°C. The mixture is dissolved in hydrochloric acid and the gaseous hydride of each element is generated from the appropriate oxidation state and determined by atomic absorption spectrophotometry.

<sup>1</sup> 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 of Coal.

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<sup>2</sup> For information concerning experimental work on which this test method is based see: Bosshart, R. E., Price, A. A., and Ford, C. T., "Evaluation of the Effect of Coal Cleaning on Fugitive Elements, Phase II Final Report, Part II Analytical Methods," *ERDA Report No. C00-44727-35*, 1980, pp. 94–102; Fernandez, F. J., "Atomic Absorption Determination of Gaseous Hydrides Utilizing Sodium Borohydride Reduction," *Atomic Absorption Newsletter*, Vol 12, No. 4, 1973, pp. 93–97; and Brodie, K. G., "A Comparative Study—Determining Arsenic and Selenium by AAS," *American Laboratory*, March 1977, pp. 73–78.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.06.

### 4. Significance and Use

4.1 This test method permits measurement of the total arsenic and selenium content of coal for the purpose of evaluating these elements where they can be of concern, for example, in coal combustion. When coal samples are prepared for analysis in accordance with this test method, the arsenic and selenium are quantitatively retained and are representative of the total amounts in the coal.

### 5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, with background correction system and peak profile recording device.

5.2 *Hydride Generation Apparatus*, for producing the hydrides of arsenic and selenium.

5.3 *Burner or Heated Quartz Cell*, for thermal decomposition of the hydrides.

5.4 *Hotplate*, capable of maintaining a temperature of a solution at 60 to 90°C.

5.5 *Ignition Crucibles*—Porcelain crucible of 30-mL capacity. Do not use porcelain crucible in which the glaze is flaked.

5.6 *Analytical Balance*, capable of weighing to 0.0001 g.

### 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.<sup>4</sup>

6.2 *Purity of Water*—Use high-purity, conductivity water, prepared by passing distilled water (or equivalent) through an ion exchange resin.

6.3 *Eschka Mixture*—Thoroughly mix two parts by weight of light calcined magnesium oxide (MgO) with one part by weight anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). The mixture shall be as free as possible from arsenic and selenium.

<sup>4</sup> *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.

6.4 *Hydrochloric Acid Concentrated* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

6.5 *Hydrochloric Acid (1 + 4)*—Mix one volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with four volumes of deionized water.

6.6 *Potassium Iodide Solution 20 %* (weight per volume)—Dissolve 20 g of potassium iodide (KI) in 100 mL of deionized water.

6.7 *Sodium Borohydride (Pellets or Solution) 3 %* (weight per volume)—To a 1 % (weight per volume) sodium hydroxide (NaOH) solution, add sodium borohydride ( $\text{NaBH}_4$ ) to give a solution 3 % (weight per volume) sodium borohydride ( $\text{NaBH}_4$ ). Prepare fresh daily.

6.8 *Arsenic Stock Solution* (1000-ppm Arsenic)—Certified commercially available standard solution or prepared from primary standard arsenic trioxide ( $\text{As}_2\text{O}_3$ ).

6.9 *Selenium Stock Solution* (1000-ppm Selenium)—Certified commercially available standard solution or prepared from selenium metal (99.99 %).

## 7. Analysis Sample

7.1 Obtain the sample for coal in accordance with Method D 2013 and the sample for coke in accordance with Practice D 346. Prepare the analysis sample by pulverizing the material to pass a 250- $\mu\text{m}$  (No. 60) U.S. standard sieve.

7.2 A separate portion of the analysis sample shall be analyzed concurrently for moisture content in accordance with Test Method D 3173 or Test Methods D 5142.

7.3 Use certified reference materials, such as the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) coals. SRM 1632b and SRM 1635 are two different coal samples which are currently available and have certified values for both arsenic and selenium. Results obtained by analyzing these coals for arsenic and selenium using the test methods described herein can be used for checking analytical technique and test method accuracy. At least one SRM coal sample should be analyzed as a control when a set of coal samples are analyzed.

## 8. Sample Preparation and Solution

8.1 To minimize the potential for contamination, clean all labware thoroughly with dilute HCl solution (1 + 9) and rinse with deionized water. The hydride generation apparatus shall be kept equally clean.

8.2 Weigh approximately 1 g of coal into a preweighed 30-mL crucible. Record the weight to the nearest 0.0001 g. Thoroughly mix the sample with 1.5 g of Eschka mixture and cover the mixture with an additional 1.5 g of Eschka mixture. Place the sample in a cold muffle furnace. Set the temperature control to 500°C. Heat the sample for 1 h. Increase the furnace temperature to 750°C. Continue heating at this temperature for 3 h. Remove the sample and allow to cool to room temperature.

8.3 Add 20 to 30 mL of hot deionized water to a 150-mL beaker. Transfer the contents of the crucible from 8.2 to the beaker. Add 5 mL of concentrated HCl to the crucible. Then slowly and carefully, with the aid of a stirring rod, transfer the HCl to the beaker. Rinse any remaining material in the crucible into the beaker with deionized water. Add 15-mL concentrated HCl in three 5-mL portions to the crucible and transfer to the

beaker. Swirl the contents until the Eschka has dissolved (Note 1). Cool the solution and transfer it to a 100-mL polypropylene volumetric flask. Dilute to volume with deionized water.

NOTE 1—Some residue can remain.

## 9. Blank

9.1 Weigh 15 g of Eschka mixture into a crucible. Heat as described in 8.2. Add 100- to 150-mL hot deionized water to a 500-mL beaker. Transfer the contents of the crucible to the beaker. Add 25-mL concentrated HCl to the crucible. Then slowly and carefully, with the aid of a stirring rod, transfer the HCl to the beaker. Rinse any remaining material in the crucible into the beaker with deionized water. Add 75-mL concentrated HCl in three 25-mL portions to the crucible and transfer to the beaker. Swirl the contents until the Eschka has dissolved (Note 1). Cool the solution and transfer to a 500-mL polypropylene volumetric flask. Dilute to volume with deionized water.

## 10. Procedure for Arsenic

10.1 The solutions and preparations described are typical for North American coals. Different solution concentrations can be required to establish suitable analytical results for those elements with concentrations outside the typical range. Each analyst shall determine the sensitivity and optimum method of calibration of their own equipment and choose standards with concentration ranges compatible with the samples and instruments specific to their work. Twenty millilitres is a normal working volume for batch hydride generation systems. If a hydride generation system is designed to accommodate other than 20 mL (sample + acid), a different volume can be used and all reagents and sample volumes can be ratioed accordingly.

10.2 Prepare an intermediate arsenic standard 1 to 10  $\mu\text{g}/\text{mL}$  from the stock solution. Prepare fresh daily. Prepare a working standard (Note 2) by adding 1 mL of the intermediate standard to a 100-mL polypropylene volumetric flask. Dilute to volume with blank (Section 9).

NOTE 2—Five millilitres of the working standard should produce a signal approximately in the middle of the linear dynamic range for the atomic absorption operating conditions chosen.

10.3 Prepare three calibration standards by combining volumes of the working standard and blank solution which yield a total volume equivalent to the analytical volume ( $A_v$ ) (see Annex A1) in a reaction flask. Dilute to 20 mL with HCl (1 + 4).

10.4 Prepare a reagent blank by adding a volume of blank solution equivalent to the analytical volume ( $A_v$ ) (see Annex A1) to a reaction flask and dilute to 20 mL with HCl (1 + 4).

10.5 Add 2 mL of potassium iodide solution to the calibration standards and blank. Allow the solutions to sit at ambient temperature for 30 min.

10.6 Use an arsenic hollow cathode or electrodeless discharge lamp and set the monochromator for 193.7 nm. Adjust instrument parameters to optimum for the particular instrument used.

10.7 Attach the reaction flask to the sampling system and introduce either sodium borohydride pellets or solution and read out the peak response for the blank and each calibration standard. Either peak height or peak area can be used. The