Designation: D4606 – 15

Standard Test Method for Determination of Arsenic and Selenium in Coal by the Hydride Generation/Atomic Absorption Method[1]

This standard is issued under the fixed designation D4606; 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] covers the determination of total arsenic and selenium in coal.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:*[3]

D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis
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
D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis

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.

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 °C to 90 °C.

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

5.6 *Analytical Balance,* capable of weighing to a resolution of 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.[4]

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[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 of Coal.

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[2] 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.

[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.

[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.

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*—Prepare (with thorough mixing) a mixture that has a mass fraction of 67 % light calcined magnesium oxide (MgO) and 33 % anhydrous sodium carbonate (Na_2CO_3). The mixture shall be as free as possible from arsenic and selenium.

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

6.5 *Hydrochloric Acid* (1 + 4) —Prepare a solution of dilute HCl in water with a volume fraction of 20 % of concentrated hydrochloric acid (HCl, sp gr 1.19).

6.6 *Potassium Iodide Solution* 0.2 g/mL—Dissolve 20 g of potassium iodide (KI) in 100 mL of water.

6.7 *Sodium Borohydride (Pellets or Solution)* 0.03 g/mL—To dilute sodium hydroxide (NaOH) solution (0.01 g/mL), add sodium borohydride ($NaBH_4$) to give a solution that is 0.03 g/mL sodium borohydride ($NaBH_4$). Prepare fresh daily.

6.8 *Arsenic Stock Solution* (1000 mg/L Arsenic)—Certified commercially available standard solution or prepared from primary standard arsenic trioxide (As_2O_3).

6.9 *Selenium Stock Solution* (1000 mg/L 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 D2013 and the sample for coke in accordance with Practice D346. Prepare the analysis sample by pulverizing the material to pass a 250 µm (No. 60) U.S.A. standard sieve.

7.2 A separate portion of the analysis sample shall be analyzed concurrently for moisture content in accordance with Test Method D3173 or Test Methods D7582.

7.3 Use certified reference materials, such as the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) coals. SRM 1632d and SRM 163a5 are two different coal samples that 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 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 mass 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 it to cool to room temperature.

8.3 Add 20 mL to 30 mL of hot 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 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). Allow the solution to cool to room temperature and transfer it to a 100 mL polypropylene volumetric flask. Dilute to volume with 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 mL 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 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). Allow the solution to cool to room temperature and transfer to a 500 mL polypropylene volumetric flask. Dilute to volume with 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 mass fractions 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 mL to 10 µg/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 that yield a total volume equivalent to the analytical volume (*Av*) (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 (*Av*) (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 operator shall select the response that gives the maximum response per microgram of arsenic.

10.8 Establish a calibration curve of micrograms of arsenic in the reaction flask versus peak response.

10.9 Samples should be analyzed within 24 h of preparation. Take an aliquot of sample solution that contains less arsenic than the highest concentration calibration standard and more arsenic than the lowest concentration calibration standard. Dilute to the analytical volume (*Av*) (see Annex A1) with blank solution and then to 20 mL with HCl (1 + 4) to a reaction flask. Treat as in 10.5 – 10.7. Read out the peak response and establish micrograms of arsenic in the aliquot of solution analyzed from the calibration curve.

11. Procedure for Selenium

11.1 Prepare an intermediate selenium standard taking note of the provisions stated in 10.1 and using the same procedure as described for arsenic in 10.2.

11.2 Prepare three calibration standards by combining volumes of the working standard and blank solution that yield a total volume equivalent to the analytical volume (*Av*) (see Annex A1) in a 150 mL beaker.

11.3 Prepare a reagent blank by adding a volume of blank solution equivalent to the analytical volume (*Av*) (see Annex A1) to a 150mL beaker.

11.4 Add 10 mL of concentrated hydrochloric acid (HCl) to the beakers. The solution temperature shall be maintained between 60 °C and 90 °C. To monitor the solution temperature, place a thermometer in a beaker containing a volume of water equivalent to the solution volume in the other beakers. Place the beakers covered with watch glasses on a hot plate and heat for 1 h. Allow the solutions to cool to room temperature. Transfer by rinsing with concentrated HCl where necessary to reaction flasks so that the final volume of solution in the reaction flask is 20 mL.

11.5 Use a selenium hollow cathode or electrodeless discharge lamp and set the monochromator for 196.0 nm. Adjust instrument parameters to optimum for the particular instrument used.

11.6 Analyze the sample using the procedure described for arsenic in 10.7.

11.7 Calibrate using the same procedure as described for arsenic in 10.8.

11.8 Samples should be analyzed within 24 h of preparation. Take an aliquot of sample solution that contains less selenium than the highest concentration calibration standard and more selenium than the lowest concentration calibration standard. Dilute to the analytical volume (*Av*) (see Annex A1) with blank solution in a 150 mL beaker. Treat the solution as in 11.4 – 11.6. Establish micrograms of selenium in the aliquot of sample solution analyzed from the calibration curve.

12. Calculations

12.1 Calculation of arsenic mass fraction:

$$\mathrm{As}\,(\mu\mathrm{g/g\ coal\ db}) = (S \times 100)/(V \times W) \tag{1}$$

where:

As = arsenic µg/g coal dry basis;
S = arsenic in aliquot of solution analyzed, µg;
100 = volume of solution from which aliquot was taken, mL;
V = volume of sample aliquot analyzed, mL; and
W = mass of dried coal, g.

12.2 Calculation of selenium mass fraction:

$$\mathrm{Se}\,(\mu\mathrm{g/g\ coal\ db}) = (S \times 100)/(V \times W) \tag{2}$$

where:

Se = selenium µg/g coal dry basis;
S = selenium in aliquot of solution analyzed, µg;
100 = volume of solution from which aliquot was taken, mL;
V = volume of sample aliquot analyzed, mL; and
W = mass of dried coal, g.

13. Report

13.1 Report the value of arsenic or selenium obtained using the calculations specified in Section 12.

13.2 Report the test method used for the concurrent moisture determination.

13.3 Report the value obtained, the certified value, and limits for any CRM analyzed concurrently with the samples.

14. Precision and Bias[5]

14.1 The precision of this test method for the determination of Arsenic and Selenium in coal is shown in Table 1.

TABLE 1 Mass Fraction Range and Limits for Repeatability and Reproducibility for Arsenic and Selenium in Coal.

	Mass Fraction Range, µg/g	Repeatability Limit (r)	Reproducibility Limit (R)
Arsenic	0.7 – 12.2	$0.3+0.07\bar{x}$	$0.6+0.1\bar{x}$
Selenium	0.6 – 5.0	$0.31+0.2\bar{x}$	$0.1+0.3\bar{x}$

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1008.

14.1.1 *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 homogeneous material, may be expected to occur with a probability of approximately 95 %.

14.1.2 *Reproducibility Limit (R)*—the value below which the absolute difference between two tests 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 homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

14.2 *Bias*—Statistical analysis of results submitted for NIST SRM 1632a indicate that it is 95% certain that the mean analytical value bases on results submitted by laboratories using the procedures as described in this test method, for both arsenic and selenium on a dry coal basis, are equivalent to the NIST certified values for SRM 1632a.

14.3 Details of the interlaboratory study and supporting data are given in ASTM Research Report RR:D05 1008.[5]

15. Keywords

15.1 arsenic; atomic absorption; Eschka mixture; hydride generation; selenium

ANNEX

(Mandatory Information)

A1. METHOD FOR ESTABLISHING THE ANALYTICAL VOLUME FOR THE DETERMINATION OF ARSENIC AND SELENIUM

A1.1 *Scope*—This procedure establishes the maximum analytical volume (working standard/sample plus blank) that can be added to the reaction flask while ensuring that the contribution to the response from the reagents in the blank is not in excess of that from the amount of analyte in 1 mL of working standard.

A1.2 *Significance and Use*—Because of the different sensitivities of the various AA hydride generation systems (Ar or N_2/H_2 flame versus heated quartz cell), it can be necessary to adjust the volumes of sample and reagents required to optimize performance of the hydride generation system being used.

A1.3 *Analytical Volume*—The analytical volume shall be designated as *Av*. If the *Av* determined as described in A1.4 is greater than 10 mL, then the *Av* shall be taken as 10 mL.

A1.4 *Determination of the Analytical Volume:*

A1.4.1 *Determination of Analytical Volume for Arsenic*—Add a volume of the working standard for arsenic that is expected to produce a peak response in the middle of the linear dynamic range to a reaction flask. Dilute to 20 mL with HCl (1 + 4). Treat as in 10.4 – 10.6. Read peak response (P_T). Repeat the procedure for an equivalent volume of reagent blank prepared in accordance with 10.3 to obtain P_b. The analytical volume, *Av*, is calculated as described in A1.5.

A1.4.2 *Determination of the Analytical Volume for Selenium*—Add a volume of the working standard for selenium that is expected to produce a peak response in the middle of the linear dynamic range to a 150 mL beaker. Treat as in 11.4 – 11.6. Read out the peak response, P_T. Repeat procedure for an equivalent volume of reagent blank prepared in accordance with 11.3 to obtain P_b. The analytical volume, *Av*, is calculated as described in A1.5.

A1.5 *Calculation of Analytical Volume*—Use the following equation to calculate *Av* (units = mL):

$$Av = (P_T - P_b)/P_b \qquad (A1.1)$$

where:

P_T = peak response for the volume of working standard and

P_b = peak response for the reagent blank.

A1.5.1 If the analytical volume is less than 3 mL, then the purity of the reagents used for the determination of the element in question is to be considered suspect.

A1.6 *Examples:*

A1.6.1 *Example*—Analysis of 6 mL of an arsenic working standard produced a peak response of 0.5 units ($P_T = 0.5$). Analysis of 6 mL of blank produced a peak response of 0.02 units ($P_b = 0.02$). Thus,

$$A_v = 0.5 - 0.02/0.02 = 24 \text{ mL} \qquad (A1.2)$$

In accordance with A1.3, the analytical volume for arsenic would be taken as 10 mL.

A1.6.2 *Example*—Analysis of 5 mL of selenium working standard produced a peak response of 0.05 units ($P_T = 0.05$). Analysis of 5 mL of blank produced a peak response of 0.0125 units ($P_b = 0.0125$). Thus,

$$A_v = 0.05 - 0.0125/0.0125 = 3 \text{ mL} \qquad (A1.3)$$

Compared to the net response from selenium for the 5 mL working standard 0.0500 – 0.0125 = 0.0375, the net response from selenium in the 1 mL working standard would be 0.0375/5 = 0.0075.

The signal from the reagents in the calibration standard would be (0.0125/5) × 3 = 0.0075.

Thus for any analytical volume in excess of 3 mL, the signal from the blank reagents would be in excess of the signal from the analyte for a calibration standard prepared from 1 mL of working standard.

The analytical volume for selenium would be 3 mL.

The lowest concentration calibration standard would be prepared by combining 1 mL of working standard with 2 mL of blank.

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