



Designation: D 6349 – 01

Standard Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma—Atomic Emission Spectrometry¹

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1. Scope

1.1 This test method covers a procedure for the analysis of the commonly determined major and minor elements in coal, coke, and solid residues from combustion of coal and coke. These residues may be laboratory ash, bottom ash, fly ash, flue gas desulfurization sludge, and other combustion process residues.

1.2 The values stated in SI units are to 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:

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis²

D 1193 Specification for Reagent Water³

D 2013 Method of Preparing Coal Samples for Analysis²

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases²

D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures²

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

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 *Annual Book of ASTM Standards*, Vol 05.06.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

3. Summary of Test Method

3.1 The sample to be analyzed is ashed under standard conditions and ignited to constant weight. The ash is fused with a fluxing agent followed by dissolution of the melt in dilute acid solution. Alternatively, the ash is digested in a mixture of hydrofluoric, nitric, and hydrochloric acids. The solution is analyzed by inductively coupled plasma-atomic emission spectrometry (ICP) for the elements. The basis of the method is the measurement of atomic emissions. Aqueous solutions of the samples are nebulized, and a portion of the aerosol that is produced is transported to the plasma torch where excitation and emission occurs. Characteristic line emission spectra are produced by a radio-frequency inductively coupled plasma. A grating monochromator system is used to separate the emission lines, and the intensities of the lines are monitored by photomultiplier tube or photodiode array detection. The photocurrents from the detector are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of elements. Background must be measured adjacent to analyte lines of samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured.

4. Significance and Use

4.1 A compositional analysis of coal and coke and their associated combustion residues are often useful in assessing their quality. Knowledge of the elemental composition of the associated residues is also useful in predicting the elemental enrichment/depletion compositional behavior of ashes and slags in comparison to the concentration levels in the parent coal. Utilization of the ash by-products and hazardous potential may also depend on the chemical composition and leachability of the inorganic constituents of the coal ash.

4.2 The chemical composition of laboratory-prepared ash may not exactly represent the composition of mineral matter in coal or the composition of fly ash and slag resulting from commercial-scale burning of the coal.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of major and minor elements. The analyst should follow the manufacturer's operating guide to develop and apply correction factors to compensate for the interferences. The interferences can be classified as spectral, physical, and chemical.

5.1.1 Spectral interferences can be categorized as overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

5.1.2 Table 1 lists the elements determined by this method and the recommended wavelengths using conventional nebulization.

TABLE 1 Recommended Wavelengths for Elements Determined by ICP

Element	Wavelengths, nm
Aluminum	396.152, 256.80, 308.215, 309.271
Barium	455.403, 493.41, 233.53
Calcium	317.93, 315.887, 364.44, 422.67
Iron	259.940, 271.44, 238.204
Magnesium	279.553, 279.08, 285.21, 277.983
Manganese	257.610, 294.92, 293.31, 293.93
Phosphorous	178.287, 214.900
Potassium	766.491, 769.896
Silicon	212.412, 288.16, 251.611
Sodium	588.995, 589.592
Strontium	421.55
Titanium	337.280, 350.50, 334.941

5.1.3 Table 2⁵ lists some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are

⁵ *Methods for Chemical Analysis of Water and Wastes*, (EPA-600/4-79-020), Metals-4, Method 200.7 CLP-M.

intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The analyst should follow the manufacturer's operating guide to develop and apply correction factors to compensate for the interferences.

5.1.4 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples that may contain high dissolved solids or acid concentrations, or both. The use of a peristaltic pump is recommended to lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample or utilization of standard addition techniques, or both. Another problem that can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon before nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate, particularly nebulizer flow, improves instrument precision. This is accomplished with the use of mass flow controllers.

5.1.5 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique. However, if such effects are observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, matrix matching, and standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

6. Apparatus

6.1 *Ashing Furnace*, with an adequate air circulation (two to four volume changes per minute) and capable of having its temperature regulated between 700 and 750°C.

6.2 *Fusion Furnace*, with an operating temperature of 1000 to 1200°C.

6.3 *Meeker-Type Burner*, with inlets for fuel gas (propane or natural gas) and compressed air, capable of flame temperatures of 1000 to 1200°C.

6.4 *Platinum Dishes or Crucibles*, 35- to 85-mL capacity. Graphite crucibles with 10- to 15-mL capacity may also be used.

6.5 *Stirring Hotplate and Bars*, with operating temperature up to 200°C.

6.6 *Polycarbonate Bottles*, 250-mL capacity with an O-ring seal and screw cap, capable of withstanding temperatures of

TABLE 2 Examples of Analyte Concentration Equivalents Arising from Interference at the 100-ppm (mg/L) Level⁵

NOTE 1—Dashes indicate that no interference was observed even when interferents were introduced at the following levels: Al, Ca, and Fe = 1000 ppm, Mn = 200 ppm, and Mg = 100 ppm.

Analyte Elements	Wavelengths, nm	Interferents					
		Al	Ca	Fe	Mg	Mn	Ti
Aluminum	308.215	---	---	---	---	0.21	---
Barium	455.103	---	---	---	---	---	---
Calcium	317.933	---	---	0.01	0.01	0.04	0.03
Iron	259.940	---	---	---	---	0.12	---
Magnesium	279.079	---	0.02	0.13	---	0.25	0.07
Manganese	257.610	0.005	---	0.002	0.002	---	---
Silicon	288.148	---	---	---	---	---	---
Sodium	588.995	---	---	---	---	---	0.08

100 to 130°C, the pressure that is developed during the digestion, and resistant to oxidation.

6.7 *Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP)*, either a sequential or simultaneous spectrometer is suitable. Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument's linear range in which correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements of this method and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents

7.1 *Purity of Reagents*—Reagents grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society in which such specifications are available.⁶ 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined by Specification D 1193.

7.3 *Standard Stock Solutions*—Stock solutions of 1000 ppm (mg/L) for each element are needed for preparation of dilute standards in the range from <0.1 to 100 ppm. Prepare standard stock solutions from 99.999 % purity metals or salts. Alternatively, one can use commercially available stock solutions specifically prepared for ICP-AES spectroscopy.

⁶ *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.

7.4 *Internal Standard Solution*—Stock solution of 1000 ppm (mg/L) of yttrium (Y), scandium (Sc), indium (In), or other suitable element not found in significant concentrations in the test samples.

7.5 Acids:

7.5.1 *Hydrochloric Acid*—Concentrated HCl, sp gr 1.19.

7.5.2 *Hydrofluoric Acid*—Concentrated HF, sp gr 1.17.

7.5.3 *Nitric Acid*—Concentrated HNO₃, sp gr 1.42.

7.5.4 *Nitric Acid (5 + 95)*—Dilute 50 mL of concentrated nitric acid to 1000 mL.

7.5.5 *Mixed Acid Solution, 70/30 HCl/HF*—Mix seven parts concentrated hydrochloric acid and three parts concentrated hydrofluoric acid.

7.6 *Fluxing Agents*—Lithium tetraborate, Li₂B₄O₇, or mixtures of lithium tetraborate (Li₂B₄O₇) and anhydrous lithium metaborate (LiBO₃).

7.7 *Boric Acids Solution*—1.5 %.

7.8 *Wetting Agents*—Approximately 0.1 g of reagent grade lithium iodide (LiI) or other suitable wetting agent may be added to the flux to facilitate pooling of the melt and removal of the melt of cooled pellet.

7.9 *Standard Solution Diluent*—Use either 7.9.1 or 7.9.2.

7.9.1 Weigh 4 g, to the nearest 0.0001 g, of fluxing agent (see 7.6) into a clean 1000-mL beaker containing a magnetic stirring bar. Add 500 mL of 5 + 95 nitric acid (see 7.5.4) to the beaker and place on a stirring hot plate. Heat the mixture to just below boiling and maintain this temperature with constant stirring until the fluxing agent dissolves. This dissolution process should take about 30 min or less (see Note 1). Quantitatively transfer the warm solution to a 1000-mL volumetric flask. After the solution cools to room temperature, dilute to 1000 mL with reagent grade water.

7.9.2 Weigh 4 g, to the nearest 0.0001 g, of fluxing agent (see 7.6) into a platinum dish (or crucible). Heat to 1000°C to form a liquid and cool. Carefully rinse the bottom and outside of the platinum dish to remove possible contamination. Place the cooled platinum dish containing the flux and a magnetic stirring bar into a clean 1000-mL beaker. Add 500 mL of 5 + 95 nitric acid (see 7.5.4) to the beaker and place immediately on the stirring hotplate. Heat the mixture to just below the boiling temperature and maintain this temperature with constant stirring until the melt dissolves. This dissolution process should take about 30 min (see Note 1). After dissolution remove the platinum dish after rinsing with reagent water and

collecting the washings in the acid solution. Quantitatively transfer the warm solution to a 1000-mL volumetric flask. After the solution cools to room temperature, dilute to 1000 mL with reagent grade water.

NOTE 1—This time and temperature are sufficient to dissolve the melt completely. If stirring is not maintained constantly, some of the material may not dissolve, and the final solution must be filtered before use.

8. Sample Preparation

8.1 *Coal and Coke*—Prepare the analysis sample in accordance with Method D 2013 (coal) or Practice D 346 (coke) by pulverizing the material to pass a 250- μm (No. 60) sieve.

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

8.2 *Solid Combustion Residue*—Dry a representative portion of the solid residue to constant weight at 110 to 115°C. Determine the moisture loss during this drying step if it is desirable to calculate results to an as-received basis. Crush the dried portion of the sample to pass a No. 200 (75- μm) sieve. Use a mill that minimizes metal contamination.

9. Preparation of Ash

9.1 *Ashing of Coal and Coke Analysis Sample*—Prepare the ash from a thoroughly mixed analysis sample of coal or coke (see 8.1) that has been ground to pass a 250- μm (No. 60) U.S.A. standard sieve. Spread the coal and coke in a layer not over 6 mm ($\frac{1}{4}$ in.) in depth in a porcelain, quartz, or fused silica roasting dish. Place the dish in a cold muffle furnace and heat gradually so that the temperature reaches 500°C in 1 h and 750°C in 2 h. Ignite at 750°C until all carbonaceous matter is removed or for an additional 2 h. Allow the dish to cool, transfer to an agate mortar, and grind to pass a 75- μm (No. 200) sieve. Reignite the ash at 750°C for 1 h, cool rapidly, and weigh portions for analysis. If samples are stored and the absorption of moisture or CO₂, or both, is in question, reignite the ash using the 500-750°C staged combustion before use. Alternatively, determine loss on ignition using the 500-750°C staged combustion on a separate sample weighed out at the same time as the test portion and make the necessary corrections. Thoroughly mix each sample before weighing.

9.2 *Ashing of Solid Combustion Residues*—Spread an appropriate amount of the prepared sample from 8.2 in a layer not over 2 mm in a porcelain, quartz, or fused silica roasting dish. Place the dish in a cold muffle furnace and heat gradually so that the temperature reaches 500°C in 1 h and 750°C in 2 h. Ignite the sample at 750°C until all carbonaceous matter is removed. Allow the ash to cool, transfer to an agate mortar, and grind to pass a 75- μm (No. 200) sieve. Reignite the ash for 1 h at 750°C, cool rapidly, and weigh portions for analysis. If samples are stored and the absorption of moisture or CO₂, or both, is in question, reignite the ash using the 500-750°C staged combustion before use. Alternatively, determine loss on ignition using the 500-750°C staged combustion on a separate sample weighed out at the same time as the test portion and make the necessary corrections. Thoroughly mix each sample before weighing.

10. Procedure

10.1 The solutions and proportions described below are the typical ash samples as represented by American coals. Therefore, stronger or weaker dilutions may be required to establish suitable concentrations for those elements of varying percents outside the range of the typical sample. Analysts must determine the sensitivity and linear range of calibration of their own equipment and choose concentration ranges for standards compatible with the samples and instrument specific to their own work.

10.2 To minimize the potential of contamination, platinum ware must be prepared by boiling in dilute HNO₃ (5 + 95) and rinsing thoroughly with reagent-grade water. After this initial cleaning, the platinum ware must be handled with clean tongs and protected from contamination from table tops, and so forth. All glassware used in analyses must be equally clean and protected.

10.3 *Ash Dissolution*—Two methods of dissolving the ash samples are offered for this test method. The analyst may choose the method most appropriate for their laboratory and instrumentation. Laboratories using the fusion method (see 10.3.1) for dissolving the ash should be aware that a considerable amount of sulfur may be lost from the ash during the fusion process. A blank test solution containing the same concentration of reagents used for the ash samples shall be prepared and analyzed with the ash sample solutions.

10.3.1 *Sample Fusion and Dissolution*—Weigh 0.1 ± 0.0001 g of the ash sample as prepared in 9.1 or 9.2 into a platinum dish (or crucible) (see Note 2). Weigh 0.4000 ± 5 mg (to nearest 0.1 mg) of the fluxing agent and add to the ash sample. Mix the ash and fluxing agent thoroughly and heat to melting at 1000 to 1200°C with stirring, according to 10.3.1.1 or 10.3.1.2, until a clear melt is obtained.

10.3.1.1 If a muffle furnace is used for heating, place the platinum dish in a clean silica or refractory tray and place in a muffle furnace preheated to 1000°C; 7 min at this temperature is sufficient to fuse most mixtures completely, but heating should be continued until a clear pellet is obtained. Use platinum-tipped tongs to swirl the melt gently to dissolve the ash. Remove the tray with the dish and cool to room temperature. Carefully rinse the bottom and outside of the platinum dish to remove possible contamination; then place in a clean 250- or 400-mL beaker. Place a clean Teflon® coated magnetic stirring bar in the platinum dish and add 50 mL of 5 + 95 HNO₃ (see 7.5.4) to the melt in the platinum dish. Immediately place the beaker with the dish on the stirring hotplate. Stir and heat the solution to just below boiling and maintain this near boiling condition until the melt is dissolved or for not more than 30 min (see Note 3). Remove the platinum dish from the beaker, rinse the dish with small amounts of reagent water, and quantitatively transfer the solution to a 100-mL volumetric flask. Add 1 mL of internal standard to the flask and dilute to the 100-mL mark with water. This solution is 1000 ppm with respect to the total sample and contains 4 g/L of fluxing agent.

NOTE 2—Graphite crucibles may be used instead of platinum for the fusion. The graphite crucibles are not to be immersed in the digestion solution. Pour the red-hot melt directly from the crucible into the acid solution and proceed with stirring and heating as written above.