



Designation: D6349 – 21

# 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 Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D6349; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 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.

NOTE 1—There are two interlaboratory studies associated with this test method. The first was conducted in 1997 (RR:D05-1035)<sup>2</sup> and the second was conducted in 2007 (RR:D05-1032).<sup>3</sup> Sulfur trioxide was only included in the 2007 study, and that study only included combustion residues derived from ash and no combustion residues derived from coke.

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.

1.3 *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.*

<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> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1035. Contact ASTM Customer Service at service@astm.org.

<sup>3</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1032. Contact ASTM Customer Service at service@astm.org.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>4</sup>

- 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
- D7348 Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues
- 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 ISO Standard:<sup>5</sup>

- ISO/IEC Guide 99:2007 International vocabulary of metrology -- Basic and general concepts and associated terms (VIM)

## 3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D121.

## 4. Summary of Test Method

4.1 The sample to be analyzed is ashed under standard conditions and ignited to constant mass. The ash is fused with

<sup>4</sup> 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.

<sup>5</sup> Available from International Organization for Standardization (ISO), 1 rue de Varembe, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

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.

## 5. Significance and Use

5.1 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 mass fraction 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.

5.2 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.

## 6. Interferences

6.1 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.

6.1.1 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 mass 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

**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                            |
| Sulfur      | 182.04                            |
| Titanium    | 337.280, 350.50, 334.941          |

that could occur in a sample but for which there is no channel in the instrument array.

6.1.2 **Table 1** lists the elements determined by this method and the recommended wavelengths using conventional nebulization. Sulfur may only be determined if the sample is dissolved by the mixed acid dissolution described in **10.3.2**.

6.1.3 **Table 2**<sup>6</sup> lists some interference effects for the recommended wavelengths given in **Table 1**. The data in **Table 2** are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between mass 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.

6.1.4 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. Humidifying 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.

6.1.5 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 (such as, incident power, gas flows, observation height, and sample uptake rate), by buffering of the sample, matrix matching, and standard addition procedures. These types of

<sup>6</sup> *Methods for Chemical Analysis of Water and Wastes*, (EPA-600/4-79-020), Metals-4, Method 200.7 CLP-M.

**TABLE 2 Examples of Analyte Mass Concentration Equivalents (mg/L) Arising from Interference at the 100 mg/L Level<sup>6</sup>**

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

| 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 |

interferences can be highly dependent on matrix type and the specific analyte element.

## 7. Apparatus

7.1 *Ashing Furnace*, with an adequate air circulation and capable of having its temperature regulated at 500 °C and 750 °C.

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

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

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

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

7.6 *Polycarbonate Bottles*, 250 mL capacity with an O-ring seal and screw cap, capable of withstanding temperatures of 100 °C to 130 °C, the pressure that is developed during the digestion, and resistant to oxidation. Other types of bottles or vials may be used provided they are capable of withstanding the temperatures and pressures developed during the digestion.

7.7 *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.

NOTE 2—The abbreviation ICPAES is used throughout this test method 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.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent 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.<sup>7</sup> 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined by Specification **D1193**.

8.3 *Standard Stock Solutions*—Stock solutions of 1000 mg/L for each element are needed for preparation of dilute standards in the range from < 0.1 mg/L to 100 mg/L. Prepare standard stock solutions from 99.99 % purity metals or salts. Alternatively, one can use commercially available stock solutions specifically prepared for ICP-AES spectroscopy.

8.3.1 If multi-element stock standards are prepared, care should be taken to take into account contamination present for other elements of interest in each single element stock solution. It is recommended that multi-element stocks be purchased from a reputable standards vendor and include a certification of the major element mass concentrations as well as a table of contaminant elements and mass concentrations.

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

### 8.5 Acids:

8.5.1 *Hydrochloric Acid*—Concentrated hydrochloric acid, 12 N, specific gravity 1.19.

8.5.2 *Hydrofluoric Acid*—Concentrated hydrofluoric acid, 29 N, specific gravity 1.17.

8.5.3 *Nitric Acid*—Concentrated nitric acid, 16 N, specific gravity 1.42.

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

<sup>7</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.

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

8.6 *Fluxing Agents*—Lithium tetraborate,  $\text{Li}_2\text{B}_4\text{O}_7$ , or mixtures of lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) and anhydrous lithium metaborate ( $\text{LiBO}_3$ ).

8.7 *Boric Acids Solution*—1.5 %.

8.8 *Hydrogen Peroxide*—30 %.

8.9 *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.

8.10 *Standard Solution Diluent*—Use either 8.10.1 or 8.10.2.

8.10.1 Transfer 4 g, determined to the nearest 0.0001 g, of fluxing agent (see 8.6) into a clean 1000 mL beaker containing a magnetic stirring bar. Add 500 mL of 5 + 95 nitric acid (see 8.5.4) 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 3). 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.

8.10.2 Transfer 4 g, determined to the nearest 0.0001 g, of fluxing agent (see 8.6) 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 8.5.4) 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 3). 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 3—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.

8.11 *Blank Solutions*—All of the test methods in this standard require two types of blank solutions. A calibration blank that is used to establish the analytical calibration curve and a method blank which is used to evaluate possible contamination and assess spectral background. The calibration blank is also used initially and periodically to verify the baseline of the calibration has not changed significantly.

8.11.1 *Calibration Blank*—The same solution as the Standard Solution Diluent.

8.11.2 *Method Blank*—The method blank shall be processed through the same digestion procedure as the samples and consist of all the reagents in the same volumes as used in preparing the samples.

8.12 *Initial Calibration Verification Standard(s)*:

8.12.1 Where possible the initial calibration verification standard(s) shall be from alternate producers or different lot numbers from the calibration standard(s).

8.12.2 Where possible the initial calibration verification standard(s) shall be traceable to a primary standard such as a National Institute of Technology Standard Reference Material (NIST SRM).

8.13 *Periodic Calibration Verification Standard(s)*—The source of these materials can be the same as the calibration materials.

8.14 *Primary Control Sample*—A material that is processed following the same procedure as an analytical sample and is a measurement standard whose quantity value and measurement uncertainty are established without relation to another measurement standard for a quantity of the same kind (see ISO/IEC Guide 99:2007 International Vocabulary of Basic and General Terms in Metrology).

8.15 *Secondary Control Sample*—A material that is processed following the same procedure as an analytical sample and is a measurement standard whose quantity value and measurement uncertainty are assigned through calibration against, or comparison with, a primary measurement standard for a quantity of the same kind (see ISO/IEC Guide 99:2007 International Vocabulary of Basic and General Terms in Metrology).

## 9. Sample Preparation

9.1 *Coal and Coke*—Prepare the analysis sample in accordance with Practice D2013 for coal or Practice D346 for coke by pulverizing the material to pass a 250  $\mu\text{m}$  (No. 60) U.S.A. standard sieve.

9.1.1 Analyze separate test portions for moisture and ash contents in accordance with Test Methods D3173, D3174, or D7582 so that calculation to other bases can be made.

9.2 *Laboratory Ashing of Coal and Coke Analysis Sample*—Prepare the ash from a thoroughly mixed analysis sample of coal or coke (see 9.1). Spread the coal and coke in a layer not over 6 mm 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  $\pm$  10 °C at the end of 1 h. Continue the gradual heating until the temperature rises from 500 °C  $\pm$  10 °C to 750 °C  $\pm$  15 °C at the end of 1 h. Maintain the 750 °C temperature until the test specimen reaches a constant mass or for an additional 2 h. Allow the dish to cool, transfer to an agate mortar, and grind to pass a 75  $\mu\text{m}$  (No. 200) U.S.A. standard sieve. Reignite the ash at 750 °C for 1 h, allow to cool to room temperature, and determine the mass of portions for analysis.

9.3 *Solid Combustion Residue*—Dry a representative portion of the solid residue to constant mass at 107 °C  $\pm$  3 °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 75  $\mu\text{m}$  (No. 200) U.S.A. standard sieve. Use a mill that minimizes metal contamination.

9.4 *Ashing Solid Combustion Residue*—Spread an appropriate amount of the prepared sample 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  $500\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$  at the end of 1 h. Continue the gradual heating until the temperature rises from  $500\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$  to  $750\text{ }^{\circ}\text{C} \pm 15\text{ }^{\circ}\text{C}$  at the end of 1 h. Maintain the  $750\text{ }^{\circ}\text{C}$  temperature until the combustion residue reaches a constant mass or for an additional 2 h. Cool the test specimen, grind to pass a  $75\text{ }\mu\text{m}$  (No. 200) U.S.A standard sieve, and reignite at  $750\text{ }^{\circ}\text{C}$  for 1 h.

9.5 If previously-ignited samples are stored and the absorption of moisture, or  $\text{CO}_2$ , or both, is in question, reignite the ash at  $750\text{ }^{\circ}\text{C}$  before use. Alternatively, determine loss on ignition using Test Method [D7348](#) on a separate sample whose mass is determined 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 mass concentrations for those elements varying outside the range of the typical sample. Analysts must determine the sensitivity and linear range of calibration of their own equipment and choose mass 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 (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 tabletops, 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: fusion and mixed acid. 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 mass 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*—Transfer 0.1 g (determined to the nearest 0.1 mg) of the ash sample as prepared in [9.5](#) or [9.4](#) into a platinum dish (or crucible) (see [Note 4](#)). Transfer 0.4 g (determined to nearest 0.5 mg) of the fluxing agent and add to the ash sample. Mix the ash and fluxing agent thoroughly and heat to melting at  $1000\text{ }^{\circ}\text{C}$  to  $1200\text{ }^{\circ}\text{C}$  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  $1000\text{ }^{\circ}\text{C}$ ; 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 mL or 400 mL beaker. Place a clean TFE-fluorocarbon coated magnetic stirring bar in the platinum dish and add 50 mL of (5 + 95) nitric acid (see [8.5.4](#)) 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. Constantly stir and heat the solution, and repeat the analysis if precipitate is formed (see [Note 5](#)). 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 mg/L with respect to the total sample and contains 4 g/L of fluxing agent. Prepare a method blank using the above procedure.

**NOTE 4**—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.

**NOTE 5**—If the stirring is not constantly maintained, some of the constituents may precipitate, primarily silicic acid, as a result of heating in the highly acidic solution.

10.3.1.2 If a flame is used for heating, rotate the platinum dish in the flame until a clear melt is obtained. If automated fusion equipment is being used, follow the manufacturer's programmed steps. If the crucible is inserted manually into the flame using platinum-tipped tongs, stir by swirling for at least 5 min. When a clear melt is obtained, either pour the hot melt into 50 mL of (5 + 95) nitric acid (see [8.5.4](#)) in a clean 250 mL or 400 mL beaker containing a TFE-fluorocarbon magnetic stirring bar or cool the crucible and transfer the solid pellet to this solution. If it cannot be completely transferred, the sample should be discarded and re-prepared. Immediately place the beaker on a stirring hot plate. Stir and heat the solution to just below boiling and maintain the near boiling condition until the pellet is dissolved or for not more than 30 min. Constantly stir and heat the solution, and repeat the analysis if precipitate is formed (see [Note 5](#)). Transfer the solution quantitatively 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 mg/L with respect to the total ash sample and contains 4 g/L of fluxing agent. Prepare a method blank using the above procedure.

10.3.2 *Mixed Acid Dissolution*—Transfer 0.1 g (determined to the nearest 0.1 mg) of the ash sample as prepared in [9.5](#) or [9.4](#) into a 250 mL polycarbonate bottle with an O-ring seal and screw cap. The bottle should be capable of withstanding a temperature up to  $130\text{ }^{\circ}\text{C}$ , the pressure developed during digestion, and resistant to oxidation. (**Warning**—With repeated use the polycarbonate bottles will become brittle and develop cracks. They should be inspected before each use. A convenient way to do this is to hold them up to a light source. If any evidence of cracks is noted, the bottle should be discarded.)

10.3.2.1 If sulfite is known to be present or is suspected, add 1 mL of 30 % peroxide to the digestion bottle (see [Note 4](#))

before proceeding to 10.3.2.2. If 30 % peroxide is added, make the appropriate adjustment to the final sample volume (for example, 101 mL versus 100 mL) used in the calculation of results in Section 12.

NOTE 6—The peroxide will oxidize sulfite species to sulfate which is quantitatively retained in the digestion process.

10.3.2.2 Add 5.0 mL of the 70/30 HCl/HF mixed acid solution (8.5.5) and 2.0 mL of concentrated HNO<sub>3</sub> to the sample and tighten the screw cap (see Note 7). Heat the bottle at 100 °C to 130 °C in a boiling water bath, on a steam bath, or in an oven at 100 °C to 130 °C for at least 2 h. Remove the bottle from the heat source, and add 1.0 mL of internal standard and 92.0 mL of 1.5 % boric acid (H<sub>3</sub>BO<sub>3</sub>) solution. Tighten the screw cap. Return the bottle to the heat source and continue heating for 1 h. Cool the solution to room temperature before analysis. If the samples are not analyzed immediately, they may be stored in their original digestion bottles or transferred to polyethylene bottles. Prepare a method blank using the above procedure.

NOTE 7—The 70/30 HCl/HF mixed acid solution (see 8.5.5) can be prepared and stored until use, whereas an aqua regia mixture (HCl and HNO<sub>3</sub>) is not stable. Using the mixed acid solution and concentrated HNO<sub>3</sub> is equivalent to using aqua regia and HF.

10.3.3 Prepare calibration standards using appropriate values of standard stock solutions (see 8.3). Add 1 mL internal standard solution (see 8.4) per 100 mL volume used. Dilute to the mark with the proper matrix-matched diluents (see 11.2.2.2).

10.3.4 If instrumentation is capable of continuous addition of internal standard to both samples and standards, then samples and standards can be prepared without the internal standard so long as volumes are correctly accounted for in subsequent calculations of mass concentration.

## 11. Instrument Operation

11.1 Consult the manufacturer's instructions for operation of the ICP spectrometer. The present method assumes that good operating procedures are followed. Design differences among instruments and different selected analytical wavelengths for individual spectrometers make it impractical to list detailed conditions.

11.2 To ensure the validity of the data obtained from an ICP analysis, the following QC elements shall be considered the minimum for each analyte wavelength.

11.2.1 Initial and periodic instrument performance verification (also to be performed after major maintenance):

11.2.1.1 All manufacturer specified spectral alignment practices (such as Mercury lamp alignment and viewing alignment procedures) shall be followed.

11.2.1.2 The alignment reference peak intensity shall be monitored following the manufacturer recommendations. A manganese solution is often used for this purpose.

11.2.1.3 The minimum detectable limit shall be verified every 6 months for analytes previously determined to be within ten times the minimum detectable limit. The minimum detectable limit must be less than or equal to the reporting limit.

**TABLE 3 Examples of Calibration Standard Mass Concentrations to Prepare Based on Estimated Ash Sample Mass Concentrations**

| Analyte  | Calcium                                | Silicon                          |
|--|--|----------------------------------|
| Estimated sample mass concentration            | Calcium 10 mg/L to 20 mg/L in solution | 180 mg/L to 230 mg/L in solution |
| Recommended middle standard mass concentration | 15 mg/L                                | 200 mg/L                         |
| Recommended high standard mass concentration   | 30 mg/L                                | 400 mg/L                         |
| Recommended low standard mass concentration    | 1.5 mg/L                               | 20 mg/L                          |

11.2.1.4 Select peak wavelengths to minimize/eliminate spectral interferences.

11.2.1.5 Inter-element interference corrections and other types of corrections for spectral interferences (such as schematic models used for correction of spectral overlaps) and background point corrections shall be verified every 3 months according to manufacturer specifications.

### 11.2.2 Calibration:

11.2.2.1 All analysis results must fall within the mass concentration range of the calibration standards. If a sample result occurs above the high calibration standard, dilute the sample and reanalyze for that element.

11.2.2.2 All calibration solutions shall be matrix matched (in relation to the dissolution background such as LiB<sub>4</sub>O<sub>7</sub> and acid type and concentrations) to the ash sample solutions. See Note 8

NOTE 8—In order to compensate for physical interferences such as viscosity differences between calibration standards and samples that may affect intensities of the elements being analyzed, the use of an internal standard is permitted. The internal standard should be added to all calibration blanks, standards, QC samples, and samples at the same mass concentration and should be an element not present in any sufficient quantity in the samples. Elements such as Sc, In, and Y are routinely used. The internal standard can either be spiked into each solution or alternatively added online through the use of a mixing tee just prior to the sample solution entering the nebulizer.

11.2.2.3 The calibration shall include a minimum of a calibration blank and three calibration standard mass concentrations, assuming a linear calibration. See examples in Table 3. The recommended relative mass concentrations for the calibration standards are:

(1) The middle standard should be near the mid-point of the expected sample mass concentration range.

(2) The high standard should be approximately two times the middle standard.

(3) The low standard should be approximately one-tenth (<sup>1</sup>/<sub>10</sub>) of the middle standard.

(4) The linear correlation of the calibration regression shall be 0.995 or greater.

### 11.2.3 Initial Calibration Verification:

11.2.3.1 A successful calibration shall be verified with an initial calibration verification standard(s) and the calibration blank prior to the analysis of any samples.

11.2.3.2 The initial calibration verification recovery shall be within 5 % of the known value. See 8.12 and 8.13.

11.2.3.3 The initial calibration blank reported mass concentration shall be below the reporting limit.

11.2.4 *Periodic Calibration Verification:*

11.2.4.1 The calibration shall be verified after every 10<sup>th</sup> analysis and at the end of the batch or shift using a periodic calibration verification standard(s) and a calibration blank.

11.2.4.2 The periodic calibration verification recovery shall be within 10 % of the known value. See 8.12 and 8.13.

11.2.4.3 The periodic calibration blank reported mass concentration shall be below the reporting limit.

11.2.5 If a calibration verification fails to meet the criteria, it shall be re-analyzed once. If it still fails, the calibration is suspect and any samples analyzed after the last acceptable calibration verification shall be re-analyzed after the instrument has been recalibrated.

11.2.6 *Preparation Batch Quality Control Checks:*

11.2.6.1 Various checks are necessary to ensure that the dissolution process applied to the samples provides accurate recovery without contamination.

11.2.6.2 All preparation batch quality control shall be performed once for each batch or for every 40 samples, whichever is more frequent.

11.2.6.3 *Method Blank*—Absolute results for this blank shall be less than the reporting limit.

11.2.6.4 *Preparation Duplicates*—A sample prepared in duplicate following the procedure in section 10 of this standard. If the duplicates fail to meet the repeatability specifications of this test method, reanalyze the sample solution and the duplicate solution once. If these results still fail to meet the repeatability specifications consider the preparation batch in question and investigate the problem.

11.2.6.5 *Secondary Control Sample*—A secondary measurement standard shall be processed following the procedure in Section 10 of this test method. Results for the control sample shall be within the ASTM Reproducibility limits and within the laboratory's process control limits (as defined in ASTM Manual 7<sup>8</sup> or other appropriate process control limit definition).

11.2.6.6 *Primary Control Sample*—A primary measurement standard shall be processed through the entire sample digestion scheme. This sample shall be performed a minimum of once per quarter. Results for the primary control sample shall be within the ASTM Reproducibility limit and within the laboratory's process control limit (as defined in ASTM Manual 7 or other appropriate process control limit definition).

11.2.7 *Secondary QC Verifications*—Post analysis verifications include verification of the sum of the oxides as percent mass fractions of the sample. The undetermined content shall not exceed 5 % when all major and minor analytes and SO<sub>3</sub> are included. If the undetermined value exceeds 5 %, the analysis shall be considered suspect, and verification steps shall be taken when the cause for a high undetermined percent is not already known.

## 12. Calculation or Interpretation of Results

12.1 Calculate the mass fraction of each element in the ash using the following equation:

$$E = \frac{100CVD}{W} \quad (1)$$

where:

- $E$  = mass fraction of element analyzed, %,
- 100 = conversion factor from dimensionless mass fraction to percent, %,
- $C$  = mass concentration of the element in the analyzed solution, mg/L,
- $V$  = volume of sample solution prepared in Section 10, L,
- $W$  = mass of ash sample, mg, and
- $D$  = dilution factor; final volume of analyzed solution divided by the volume of the prepared solution (see 11.2.2.1) used for the dilution.

12.2 Use Practice D3180 to calculate results to other bases.

12.3 Convert mass fractions in the ash to the dry sample basis for reporting as follows:

$$E_0 = \frac{AB}{100} \quad (2)$$

where:

- $E_0$  = mass fraction of elemental oxide in the sample, % dry basis,
- $A$  = mass fraction of elemental oxide determined in the ash sample, %,
- $B$  = mass fraction ash in the sample, % dry basis, and,
- 100 = conversion factor from dimensionless mass fraction to percent, %.

## 13. Precision and Bias

13.1 *Precision*—The precision of this test method for the determination of major and minor elements in ash from coal, coke, and solid combustion residues are shown in Table 4. The precision characterized by the repeatability ( $S_r$ ,  $r$ ) and reproducibility ( $S_R$ ,  $R$ ) is described in Table A1.1 in the Annex A1.

NOTE 9—The precision and bias study for SO<sub>3</sub> was performed only by the mixed acid dissolution (10.3.2) and does not include data from fusion and dissolution (10.3.1). This study did not include combustion residues derived from coke.

13.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results 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 from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

13.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as nearly homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

13.2 *Bias*—A reference material (SRM 1633b Constituent Elements in Coal Fly Ash) from NIST was included in the ICP

<sup>8</sup> Manual of Presentation of Data and Control Chart Analysis, ASTM MNL7A, ASTM International, 2002.