Designation: D6349 – 09

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[1]

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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 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:*[2]

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
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *ISO Standard:*[3]

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

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 photomutilplier 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

[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 referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from International Organization for Standardization (ISO), 1 rue de Varembé, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

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

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 commerical-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. Sulfur may only be determined if the sample is dissolved by the mixed acid dissolution described in 10.3.2.

5.1.3 Table 2[4] 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 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 100 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.

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

[4] *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 Concentration Equivalents Arising from Interference at the 100-ppm (mg/L) Level[4]

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

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.[5] 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 D1193.

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.

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 HNO_3, 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, $Li_2B_4O_7$, or mixtures of lithium tetraborate ($Li_2B_4O_7$) and anhydrous lithium metaborate ($LiBO_3$).

7.7 *Boric Acids Solution*—1.5 %.

7.8 *Hydrogen Peroxide*—30%

7.9 *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.

7.10 *Standard Solution Diluent*—Use either 7.10.1 or 7.10.2.

7.10.1 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.

7.10.2 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.

[5] *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.

7.11 *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.

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

7.11.2 *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.

7.12 *Initial calibration verification standard(s)* :

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

7.12.2 Where possible the initial calibration verification standard(s) shall be traceable to a primary standard such as a NIST CRM.

7.13 *Periodic calibration verification standard(s)*—The source of these materials can be the same as the calibration materials.

7.14 *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).

7.15 *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).

8. Sample Preparation

8.1 *Coal and Coke*—Prepare the analysis sample in accordance with Practice D2013 (coal) or Practice D346 (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 D3173 or D5142 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 (¼ 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 CO_2, 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 CO_2, 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 HNO_3 (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 0.1g (to the nearest 0.1mg) of the ash sample as prepared in 9.1 or 9.2 into a platinum dish (or crucible) (see Note 2). Weigh 0.4g (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 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 is in a clean 250- or 400-mL beaker. Place a clean TFE-fluorocarbon coated magnetic stirring bar in the platinum dish and add 50 mL of 5 + 95 HNO_3 (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.

NOTE 3—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. The analysis must then be repeated.

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 7.5.4) in a clean 250- or 400-mL beaker containing a Teflon-coated magnetic stirring bar or cool the crucible and transfer the solid pellet to this solution. (It is the analyst's responsibility to ensure that the entire sample is transferred to the nitric acid solution). 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 (see Note 3). 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 ppm with respect to the total sample and contains 4 g/L of fluxing agent.

10.3.2 *Mixed Acid Dissolution*—Weigh 0.1g (to the nearest 0.1 mg) of the ash sample as prepared in 9.1 or 9.2 into a 250-mL polycarbonate bottle with an O-ring seal and screw cap 9see Note 4. The bottle should be capable of withstanding a temperature up to 130°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.)

NOTE 4— Some combustions residues may contain sulfite sulfur. If sulfite is known to be present or is suspected, add 1-mL of 30% H_2O_2 to the digestion bottle before proceeding to 10.3.2.1. The peroxide will oxidize sulfite species to sulfate which is quantitatively retained in the digestion process. If peroxide is added, make the appropriate adjustment to the final sample volume used in the calculation of results in Section 12.

10.3.2.1 Add 5.0 mL of the 70/30 HCl/HF mixed acid solution (7.5.5) and 2.0 mL of HNO_3 to the sample and tighten the screw cap (see Note 5). Heat the bottle at 100 to 130°C in a boiling water bath, on a steam bath, or in an oven for at least 2 h. Remove the bottle from the heat source, and add 93.0 mL of 1.5 % boric acid (H_3BO_3) solution. 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 5—The 70/30 HCl/HF mixed acid solution (see 7.5.5) can be prepared and stored until use, whereas an aqua regia mixture (HCl and HNO_3) is not stable. Using the mixed acid solution and concentrated HNO_3 is equivalent to using aqua regia and HF.

10.3.3 Prepare calibration standards using appropriate values of standard stock solutions (see 7.3). Add 1-mL internal standard solution (see 7.4) per 100-mL volume used. Dilute to the mark with the proper diluents.

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) shall be followed.

11.2.1.2 The 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.

11.2.1.4 Select peak wavelengths to minimize/eliminate spectral interferences.

11.2.1.5 Inter-element interference corrections (spectral interferences) 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 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_4O_7 and acids) to the sample solutions.

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

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

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

(3) The low standard should be approximately one-tenth (1⁄10) of the middle standard.

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

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

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 7.12 and 7.13.

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

11.2.4 *Periodic calibration verification*:

11.2.4.1 The calibration shall be verified after every 10th 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 7.12 and 7.13.

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

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

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 standard. 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[6] 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 a weight percent of the sample. The undetermined content shall not exceed 5% when all major and minor analytes and SO3 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 percentage (by weight) of each element in the ash using the following equation:

$$\% E = (C \times V)/W \times D \times 100 \tag{1}$$

where:

E = element analyzed,
C = concentration in mg/L (ppm or g/g) of M in the analyzed solution,
V = volume (in litres) of sample solution prepared in Section 10,
W = weight of sample in milligrams, and
D = dilution factor; = final volume of analyzed solution divided by the amount of the prepared solution (see Section 10) used for the dilution.

12.2 Use Practice D3180 to calculate as-determined results to other bases.

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

$$C = A \times B/100 \tag{2}$$

where:

C = percent of element in the dry sample,
A = percent of element determined in the ash, and
B = % ash in the dry sample.

[6] *Manual of Presentation of Data and Control Chart Analysis*, ASTM MNL7A, ASTM International, 2002.

TABLE 3 Concentration Ranges and Limits for Repeatability and Reproducibility for Major and Minor Elemental Oxides in Ash from Coal, Coke, and Solid Combustion Residues

NOTE—The precision and bias study for SO3 was performed only by the mixed acid dissolution (10.3.2) and does not include data from fusion and dissolution (10.3.1).

Elemental Oxide	Concentration Range	Repeatability Limit (*r*)	Reproducibility Limit (*R*)
SiO_2	2.04–73.73 %	−0.13 + 0.09 $\bar{x}^A$	2.00 + 0.10 $\bar{x}^A$
Al_2O_3	1.04–29.54 %	0.17 + 0.06 $\bar{x}^A$	0.86 + 0.07 $\bar{x}^A$
Fe_2O_3	0.39–47.94 %	0.13 $\bar{x}^A$	0.23 $\bar{x}^A$
MgO	0.40–7.29 %	0.02 + 0.08 $\bar{x}^A$	0.11 + 0.11 $\bar{x}^A$
CaO	1.04–44.03 %	0.11 $\bar{x}^A$	0.25 $\bar{x}^A$
TiO_2	0.06–1.47 %	0.02 + 0.07 $\bar{x}^A$	0.05 + 0.12 $\bar{x}^A$
K_2O	0.09–2.53 %	0.06 + 0.11 $\bar{x}^A$	0.14 + 0.30 $\bar{x}^A$
P_2O_5	0.10–1.34 %	0.01 + 0.18 $\bar{x}^A$	0.11 + 0.31 $\bar{x}^A$
Na_2O	0.17–7.44 %	0.06 + 0.09 $\bar{x}^A$	0.10 + 0.17 $\bar{x}^A$
MnO_2	198–834 ppm	0.16 $\bar{x}^A$	0.42 $\bar{x}^A$
BaO	266–950 ppm	0.07 $\bar{x}^A$	190 ppm
BaO	0.13–3.00 %	0.17 $\bar{x}^A$	0.30 $\bar{x}^A$
SrO	285–10460 ppm	33 + 0.076 $\bar{x}^A$	73 + 0.164 $\bar{x}^A$
$SO_3{}^B$	0.14–10.0	0.03 $\bar{x}$+0.06	0.08 $\bar{x}$+0.06

[A]Where $\bar{x}$ is the average of two single test results.
[B]SO_3 vales are applicable to mixed acid dissolution only. See 10.3.

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 3. The precision characterized by the repeatability (S_r, *r*) and reproducibility (S_R, *R*) is described in Table A1.1 in the Annex A1.

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 standard reference material (1633b-coal fly ash) from the National Institute for Standards and Technology (NIST) was included in the ICP interlaboratory study to ascertain possible bias between reference material values and those determined by the new method. A comparison of the NIST values and those obtained in the interlaboratory study are given in Table 4. The results show a very small (positive) bias for the reported values for iron.

TABLE 4 Comparison of Certified Values for Standard Reference Material 1633b with Interlaboratory Study Values for Major and Minor Elemental Oxides in Ash from Coal, Coke, and Solid Combustion Residues

Elemental Oxide	ICP-RR Value	NIST Value
SiO_2	50.47 ± 1.21	49.25 ± 0.17
Al_2O_3	29.00 ± 0.63	28.44 ± 0.51
Fe_2O_3	11.92 ± 0.35	11.12 ± 0.33
MgO	0.81 ± 0.027	0.80 ± 0.01
CaO	2.28 ± 0.16	2.11 ± 0.08
TiO_2	1.32 ± 0.037	1.32 ± 0.02
K_2O	2.33 ± 0.067	2.35 ± 0.04
P_2O_5	0.61 ± 0.036	0.53^A
Na_2O	0.27 ± 0.04	0.27 ± 0.004
$MnO_2{}^B$	207.3 ± 5.6	208.6 ± 2.7
BaO^B	821 ± 38	792 ± 30
SrO^B	1237 ± 54	1231 ± 17
SO_3	0.51 ± 0.02	0.52 ± 0.01

[A]Noncertified value.
[B]Value in ppm.

13.3 An interlaboratory study, designed consistent with Practice E691, was conducted in 1997, and twelve labs participated.[7]

13.4 A second interlaboratory study, designed consistent with Practice E691, was conducted in 2003. The purpose of the interlaboratory study was to include sulfur in the suite of elements analyzed by ICP-AES. The details of the study and supporting data are given in a Research Report filed at ASTM headquarters.[8]

14. Keywords

14.1 coal; coal ash; inductively coupled plasma-atomic emission spectrometry; major and minor element

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1035.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1032.

ANNEX

(Mandatory Information)

A1. PRECISION STATISTICS

A1.1 The precision of this test method, characterized by repeatability (S_r, r) and reproducibility (S_R, R) has been determined for the materials described in Table A1.1.

A1.2 *Repeatability Standard Deviation (S_r)*—The standard deviation of test results obtained under repeatability conditions.

A1.3 *Reproducibility Standard Deviation (S_R)*—The standard deviation of test results obtained under reproducibility conditions.

TABLE A1.1 Repeatability (S_r, r) and Reproducibility (S_R, R) Parameters Used for Calculation of Precision Statement

			SiO_2						Al_2O_3		
Material	Average	*Sr*	*SR*	*r*	*R*	Material	Average	*Sr*	*SR*	*r*	*R*
SL 16	2.04	0.1757	0.9016	0.4919	2.5245	SL 16	1.04	0.1176	0.2075	0.3293	0.5811
FBC 9	24.96	0.8585	1.3907	2.4039	3.8941	FBC 9	9.30	0.4087	0.5491	1.1445	1.5376
91three	25.34	0.8172	1.4299	2.2883	4.0036	1635	12.80	0.2692	0.6918	0.7537	1.9371
89one	27.76	0.7742	2.0337	2.1677	5.6943	89one	13.58	0.4246	1.0916	1.189	3.056
WAL 1	30.49	0.7935	1.537	2.2219	4.3036	90five	15.88	0.3715	0.625	1.0402	1.7501
WAL 6	30.78	0.7847	1.6418	2.197	4.5971	91three	17.28	0.471	1.0166	1.3188	2.8464
90five	34.69	1.2085	2.1835	3.3837	6.1137	WAL 7	18.37	0.5599	0.7047	1.5678	1.9731
1635	35.17	0.8463	2.4193	2.3695	6.7741	WAL 1	19.38	0.3037	0.5593	0.8505	0.5661
2776	47.49	1.819	2.2528	5.0931	6.3078	WAL 6	19.69	0.2795	0.5646	0.7825	1.5809
1632c	49.31	1.6403	2.5153	4.5927	7.0429	WAL 4	23.06	0.2947	0.7231	0.825	2.0246
1633b	50.47	1.2066	1.8074	3.3785	5.0608	1632c	24.08	0.4669	0.8512	1.3073	2.3834
WAL 4	55.66	1.3734	2.9156	3.8455	8.1638	2776	28.20	0.9721	1.5042	2.722	4.2117
89ten	58.28	2.1858	2.7337	6.1201	7.6545	1633b	29.00	0.6332	0.918	1.773	2.5703
WAL 7	63.73	2.1713	3.2922	6.0797	9.2183	89ten	29.54	0.8364	0.9418	2.3419	2.637
			Fe_2O_3						MgO		
Material	Average	*Sr*	*SR*	*r*	*R*	Material	Average	*Sr*	*SR*	*r*	*R*
SL 16	0.39	0.0494	0.0873	0.1382	0.2445	91three	0.40	0.022	0.055	0.061 46	0.153 88
89ten	4.21	0.2511	0.449	0.7031	1.2572	SL 16	0.52	0.0221	0.0299	0.061 94	0.083 77
90five	4.98	0.2102	0.3113	0.5886	0.8716	89one	0.60	0.0271	0.0406	0.075 9	0.113 54
WAL 7	5.02	0.1823	0.2039	0.5105	0.571	1632c	0.79	0.0346	0.0557	0.096 93	0.155 81
WAL 4	5.03	0.1993	0.2765	0.5581	0.7743	1633b	0.82	0.0271	0.0388	0.075 9	0.108 52
WAL 6	5.30	0.1498	0.2647	0.4195	0.741	89ten	0.83	0.0324	0.056	0.090 76	0.156 80
FBC 9	5.91	0.2782	0.4979	0.779	1.394	2776	1.03	0.0395	0.116	0.110 48	0.324 89
WAL 1	6.46	0.2527	0.3738	0.7075	1.0467	WAL 7	2.03	0.0742	0.2447	0.207 73	0.685 13
1635	7.23	0.239	0.3593	0.6692	1.0061	WAL 4	2.47	0.0483	0.1237	0.135 36	0.346 29
91three	9.45	0.4187	0.6115	1.1723	1.7122	1635	3.27	0.104	0.1369	0.291 18	0.383 42
1633b	11.92	0.3534	1.2383	0.9896	3.4673	FBC 9	3.34	0.1144	0.2105	0.320 34	0.589 36
2776	12.54	0.4945	0.7811	1.3845	2.1872	90five	5.65	0.1819	0.2096	0.509 21	0.586 84
1632c	14.92	0.5103	0.9565	1.4289	2.6781	WAL 6	6.29	0.1806	0.285	0.505 62	0.798 05
89one	47.94	2.2709	4.1201	6.3584	11.536	WAL 1	7.29	0.2194	0.3344	0.614 23	0.936 40

TABLE A1.1 *Continued*

CaO

Material	Average	*Sr*	*SR*	*r*	*R*
89ten	1.0375	0.0299	0.1413	0.0838	0.3957
1633b	2.2183	0.167	0.2047	0.4677	0.5732
1632c	2.8042	0.0657	0.2025	0.1838	0.5671
89one	3.2775	0.145	0.3509	0.4061	0.9825
2776	3.4013	0.0814	0.4155	0.228	1.1634
WAL 7	5.9115	0.2381	0.4895	0.6665	1.3707
WAL 4	8.3385	0.3049	0.5893	0.8538	1.6502
1635	17.2344	0.4056	0.9246	1.1358	2.5888
WAL 6	20.0223	0.6715	1.2675	1.8801	3.549
90five	21.6719	0.5909	0.9488	1.6544	2.6567
WAL 1	22.8144	0.6572	1.0275	1.8402	2.877
91three	32.459	0.8782	1.7329	2.4588	4.852
SL 16	38.3577	1.9973	6.2295	5.5923	17.443
FBC 9	44.0321	0.2669	3.7107	6.3473	10.39

TiO_2

Material	Average	*Sr*	*SR*	*r*	*R*
SL 16	0.06	0.0053	0.0231	0.014 87	0.064 80
FBC 9	0.44	0.0251	0.0304	0.070 39	0.084 99
1635	0.74	0.0181	0.0534	0.050 63	0.149 43
89one	0.79	0.0296	0.0486	0.082 86	0.135 94
WAL 4	0.85	0.0139	0.0761	0.033 89	0.213 13
WAL 7	1.01	0.0332	0.0485	0.092 97	0.135 80
1632c	1.09	0.0274	0.0474	0.076 58	0.132 67
WAL 1	1.17	0.0358	0.0633	0.100 31	0.177 21
90five	1.28	0.0304	0.0821	0.085 07	0.229 77
91three	1.32	0.0504	0.0742	0.141 00	0.207 65
1633b	1.32	0.0374	0.0573	0.104 67	0.160 41
2776	1.32	0.0446	0.2734	0.124 86	0.765 40[A]
WAL 6	1.36	0.0357	0.0641	0.099 88	0.179 49
89ten	1.47	0.0385	0.1046	0.107 68	0.292 92

K_2O

Material	Average	*Sr*	*SR*	*r*	*R*
91three	0.09	0.013 66	0.032 35	0.038 26	0.090 59
SL 16	0.09	0.016 36	0.042 75	0.045 80	0.119 70
90five	0.39	0.042 86	0.084 79	0.120 00	0.237 40
1635	0.45	0.041 81	0.187 20	0.117 08	0.524 16
WAL 1	0.53	0.037 18	0.084 70	0.104 11	0.237 15
WAL 6	0.73	0.054 65	0.131 87	0.153 02	0.386 86
WAL 7	0.93	0.061 62	0.142 25	0.172 55	0.398 31
FBC 9	1.03	0.056 24	0.183 03	0.157 48	0.512 50
WAL 4	1.30	0.050 99	0.126 60	0.142 77	0.354 48
89one	1.49	0.202 06	0.306 53	0.565 76	0.858 27
2776	1.69	1.101 39	0.234 14	0.283 90	0.655 59
1632c	1.74	0.051 26	0.180 40	0.143 53	0.505 13
1633b	2.34	0.067 30	0.241 91	0.188 44	0.677 36
89ten	2.53	0.141 68	0.387 37	0.396 70	1.084 64

P_2O_5

Material	Average	*Sr*	*SR*	*r*	*R*
FBC 9	0.10	0.0193	0.0731	0.053 97	0.243 24
89ten	0.16	0.0195	0.0667	0.054 72	0.186 87
89one	0.19	0.0249	0.097	0.069 73	0.271 71
WAL 6	0.31	0.0251	0.0752	0.070 16	0.210 43
1635	0.35	0.0232	0.0647	0.064 96	0.181 26
WAL 1	0.40	0.0346	0.072	0.096 80	0.201 56
2776	0.40	0.0205	0.0719	0.057 25	0.201 35
1632c	0.53	0.0379	0.0762	0.106 06	0.213 42
1633b	0.61	0.0361	0.1035	0.101 04	0.289 88
WAL 7	0.70	0.035	0.0869	0.097 92	0.243 24
91three	0.76	0.053	0.1032	0.148 38	0.288 94
90five	1.07	0.0776	0.1712	0.217 38	0.479 47
WAL 4	1.34	0.0974	0.2269	0.272 82	0.635 33

Na_2O

Material	Average	*Sr*	*SR*	*r*	*R*
91three	0.17	0.017 56	0.028 64	0.049 17	0.080 18
FBC 9	0.20	0.020 18	0.045 85	0.056 51	0.128 39
1633b	0.27	0.017 74	0.039 49	0.046 6	0.110 56
89ten	0.29	0.018 76	0.024 74	0.052 5	0.069 28
89one	0.32	0.033 12	0.079 32	0.092 7	0.222 09
WAL 4	0.56	0.091 77	0.108 24	0.257	0.303 08
1632c	0.59	0.023 89	0.053 64	0.066 90	0.150 20
WAL 7	0.64	0.022 73	0.064 14	0.063 6	0.179 60
2776	0.64	0.047 05	0.053 26	0.131 7	0.149 13
90five	1.99	0.118 47	0.152 37	0.331 7	0.426 63
WAL 1	3.80	0.127 63	0.405 17	0.357 4	1.134 7
1635	6.65	0.218 39	0.371 48	0.611 50	1.040 14
WAL 6	7.44	0.256 06	0.488 1	0.717	1.366 69

MnO_2

Material	Average	*Sr*	*SR*	*r*	*R*
89ten	198	7.06	18.52	19.78	51.87
1633b	207	5.62	14.64	15.74	41.00
FBC 9	212	15.27	35.85	42.74	100.39
90five	240	18.89	49.5	52.89	138.60
1632c	275	23.63	38.93	66.16	108.99
WAL 4	463	16.85	60.98	47.18	170.74
2776	471	34.16	86.71	95.66	242.79
WAL 6	565	16.48	100.9	46.14	282.51
89one	622	49.77	90.52	139.35	253.45
1635	653	31.63	104.83	88.58	293.52
WAL 7	699	34.75	90.79	97.30	254.22
91three	770	39.04	142.03	109.32	397.67
WAL 1	834	53.04	99.72	148.50	279.23

BaO

Material	Average	*Sr*	*SR*	*r*	*R*
FBC 9	266	17.1	87.2	47.8	244.1
89one	343	20.6	89.6	57.8	250.9
91three	381	29.7	51.5	83.2	144.2
1632c	645	19.6	43.2	54.8	121.0
1633b	821	38.2	59.9	107.1	167.6
89ten	950	36.9	62.8	103.5	175.9
2776	1 353	141.0	141.0	394.9	394.9
1635	1 898	250.1	321.4	700.3	899.9
WAL 7	3 540	134.5	198.0	376.5	554.3
90five	6 034	321.7	328.9	900.7	921.0
WAL 4	6 899	142.6	400.9	399.4	1122.5
WAL 6	17 120	697.0	1614.9	1951.6	4521.8
WAL 1	30 479	2101.0	3542.7	5882.7	9919.6

SrO

Material	Average	*Sr*	*SR*	*r*	*R*
89one	285	20.8	50.8	58.3	142.3
SL 16	338	36.2	121.4	101.3	340.0
FBC 9	734	58.4	76.3	163.6	213.7
89ten	867	37.9	93.2	106.0	260.9
1632c	1 047	25.3	56.7	70.8	158.8
WAL 7	1 229	52.6	88.7	147.3	248.4
1633b	1 237	53.7	113.8	150.4	318.8
2776	1 670	46.9	116.1	131.2	325.2
91three	1 935	57.2	165.5	160.0	463.5
WAL 4	2 948	57.4	207.4	160.6	580.6
90five	2 959	97.1	167.3	271.9	468.5
1635	3 435	88.4	230.2	247.4	644.5
WAL 6	9 290	290.5	519.9	813.4	1455.6
WAL 1	10 460	285	712	798.0	1993.6

TABLE A1.1 *Continued*

SO_3 Material	Average	Sr	SR	r	R
NIST	0.5062	0.0205	0.0277	0.0574	...
1633b	...	...	...	...	0.0774
APBA	0.1396	0.0288	0.0579	0.0806	0.1621
BD	0.8700	0.0201	0.0692	0.0564	0.1938
PHA	4.6179	0.0586	0.3237	0.1642	0.9064
ESP5	8.7171	0.1419	0.2234	0.3973	0.6256
LP1	3.6971	0.0546	0.0727	0.1528	0.2036
LP2	10.0279	0.0942	0.3698	0.2637	1.0355
SDA	6.0992	0.0992	0.3014	0.2778	0.8439
SFA	4.7088	0.0968	0.0987	0.2709	0.2765

[A]Value-treated as an outlier.