



Designation: D6357 – 21

Standard Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Absorption Spectrometry¹

This standard is issued under the fixed designation D6357; 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 These test methods pertain to the determination of antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, vanadium, and zinc in coal and coke. These test methods can also be used for the analysis of residues from coal combustion processes. Additionally, there are specific test methods outlined that pertain to the determination of rare earth elements in coal and coal combustion residues.

NOTE 1—These test methods may be applicable to the determination of other trace elements.

NOTE 2—Rare earth elements are understood to include: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, samarium, scandium, terbium, thulium, ytterbium, and yttrium.

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.

1.2.1 All percentages are percent mass fractions unless otherwise noted.

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.*

¹ These test methods are under the jurisdiction of ASTM Committee D05 on Coal and Coke and are the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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2. Referenced Documents

2.1 ASTM Standards:²

- 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
- D7448 Practice for Establishing the Competence of Laboratories Using ASTM Procedures in the Sampling and Analysis of Coal and Coke
- 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 Other Documents:³

- EPA/600/4-91/010 Methods for the Determination of Metals in Environmental Samples

3. Terminology

3.1 *Definitions*—Definitions applicable to these test methods are listed in Terminology D121.

4. Summary of Test Method

4.1 The coal or coke to be analyzed is ashed under controlled conditions, digested by a mixture of aqua-regia and

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 Superintendent of Documents, U.S. Printing Office, Washington, DC 20402.

hydrofluoric acid, and finally dissolved in 1 % nitric acid. An alternative dissolution procedure is provided which is a high-temperature fusion method using a borate fluxing agent to specifically digest samples for rare earth element determination. Combustion residues are digested on an as-received basis. The mass concentration of individual trace elements is determined by either inductively coupled plasma atomic emission spectrometry (ICPAES) or inductively coupled plasma mass spectrometry (ICPMS). Selected elements that occur at mass concentrations below the detection limits of ICPAES can be quantitatively analyzed by graphite furnace atomic absorption spectrometry (GFAAS) or ICPMS.

5. Significance and Use

5.1 Coal contains several elements whose individual mass fractions are generally less than 0.01 %. These elements are commonly and collectively referred to as trace elements. These elements primarily occur as part of the mineral matter in coal. The potential release of certain trace elements from coal combustion sources has become an environmental concern.

5.2 The ash prepared in accordance with these provisional test methods quantitatively retains the elements listed in 1.1 and is representative of their mass fractions in the coal or coke.

6. Apparatus

6.1 *Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES)*—The spectrometer system may be either simultaneous or sequential, vacuum or purged, but must include computer-controlled background correction.

NOTE 3—The abbreviation ICPAES is used throughout this document 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.

6.1.1 *Argon Gas Supply*—Follow manufacturer specifications for purity.

6.1.2 *Mass Flow Controllers*—A mass-flow controller to regulate the nebulizer gas is required. Mass flow controllers on the intermediate and outer torch gas flows are recommended.

6.2 *Inductively Coupled Plasma Mass Spectrometer (ICPMS)*—The spectrometer system must be capable of scanning the mass range of the elements to be analyzed.

6.2.1 *Argon Gas Supply*—Follow manufacturer specifications for purity.

6.2.2 The use of a variable speed peristaltic pump for delivering sample solution to the nebulizer, a mass-flow controller on the gas supply to the nebulizer, and a water-cooled spray chamber are highly recommended.

6.3 *Atomic Absorption Spectrometer with Graphite Furnace (GFAAS)*, having background correction capable of removing nonspecific absorbance.

6.3.1 *Single-Element Hollow Cathode or Single-Element Electrodeless Discharge Lamps*.

6.3.2 *Single-Output Device*, capable of recording and evaluating peak area and peak shape.

6.3.3 *Pyrolytic Coated Graphite Tubes and Platforms*.

6.3.4 *Argon Gas Supply*—Follow manufacturer specifications for purity.

6.3.5 *Autosampler*—Although not specifically required, the use of an autosampler is highly recommended.

6.4 *Muffle Furnace*, with temperature control and with air circulation as specified in 9.1 or, alternatively, for determination of rare earth elements, as specified in 9.3.

6.5 *Analytical Balance*, capable of weighing to 0.1 mg.

6.6 *Teflon Beakers*, 100 mL or 200 mL capacity.

6.7 *Hot Plate*, capable of regulating temperature between 90 °C to 150 °C.

6.8 *Volumetric Flasks*, 10 mL and 100 mL capacity.

6.9 *HDPE Bottles*, 100 mL capacity.

6.10 *Crucibles*, 50 mL quartz or high silica.

6.11 *Hot Block Heater*, capable of heating to 120 °C.

6.12 *Automated Fluxing Equipment*—Although not specifically required, can be used in place of muffle furnace fusion.

6.13 *Fusion Muffle Furnace*, with an operating temperature of 1000 °C to 1100 °C.

6.14 *Stirring Hot Plate*, capable of heating to 80 °C.

6.15 *Teflon, HDPE, or Polypropylene Digestion Vessels*, 50 mL capacity.

6.16 *Glass Beakers*, 100 mL or 250 mL capacity.

6.17 *Graphite Crucibles*, 8 mL or 10 mL capacity.

6.18 *Platinum Crucibles*, 95 % Pt/5 % Au, 25 mL, or 30 mL capacity. If using automated fluxing equipment, use crucibles supplied by the manufacturer.

7. Reagents

7.1 *Purity of Reagents*—All reagents used in these test methods must be trace metal purity grade or equivalent. Redistilled acids are acceptable.

7.2 *Purity of Water*—The purity of the water used in these test methods shall be equivalent to ASTM Type II reagent water of Specification **D1193**.

7.3 *Aqua Regia Solution*—Mix one part concentrated nitric acid (HNO₃, sp. gr. 1.42) and three parts concentrated hydrochloric acid (HCl, sp. gr. 1.9).

7.4 *Hydrofluoric Acid*, concentrated (HF, sp. gr. 1.15).

7.5 *ICP Calibration Standards*—Aqueous multielement solutions made up in 1 % HNO₃ are used for calibration of ICPAES and ICPMS systems. The stock standards may be purchased or prepared from high-purity grade chemicals or metals.

7.5.1 *GFAAS Stock Standard Solution (1000 µg/mL)*—Single-element standards either purchased or prepared from high-purity grade chemicals or metals.

7.5.2 *GFAAS Intermediate Stock Standard Solution (1 µg/mL)*—Add 0.1 mL of stock standard solution (7.5.1) and 1 mL of concentrated nitric acid to a 100 mL volumetric flask. Dilute to volume with water.

NOTE 4—Accuracy of the pipette was not stated in the instructions for the interlaboratory study for the determination of this method's precision, and so it is not stated here; however, the volumetric measurement

accuracy should be considered relative to the repeatability of the method.

7.6 Magnesium Nitrate Solution—Matrix modifier (106 g/L $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) for the determination of arsenic and antimony, equivalent to 10 000 $\mu\text{g}/\text{mL}$ magnesium.

7.6.1 A matrix modifier is used to minimize GFAAS interference effects by selective volatilization of either the analyte or the matrix components. Other matrix modifiers such as nickel nitrate or palladium nitrate can be used. The analyst should compare modifiers to establish optimum performance as outlined in **10.1**.

7.7 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.

7.7.1 Calibration Blank—A 1 % volume fraction nitric acid solution. When using matrix modifiers of GFAAS, the calibration blank shall also contain the same equivalent mass concentration of the matrix modifier.

7.7.2 Method Blank—Consists of all the reagents in the same volumes as used in preparing the samples. The method blank shall be processed through the entire sample digestion scheme.

7.8 Fluxing Agent—Lithium metaborate (LiBO_2) or a mixture of lithium metaborate and lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), anhydrous.

7.9 Nitric Acid (1 + 9)—Dilute 100 mL of concentrated nitric acid to 1000 mL with deionized water.

8. Analysis Sample

8.1 Samples of coal and coke shall be prepared in accordance with Practice **D2013** or Practice **D346**.

8.2 Standard practices for the sampling and preparation of residues from coal utilization processes have not been established. Some of these materials are highly abrasive. The use of high speed pulverizers for size reduction shall be avoided. The use of jaw crushers followed by final preparation in an agate mortar and pestle is recommended to prevent contamination of the sample.

8.3 Analyze separate test portions for moisture content in accordance with Test Methods **D3173** or **D7582** so that calculations to other bases can be made.

9. Procedure

9.1 Ashing Procedure 1 (Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, and Zn)—Weigh to the nearest 0.1 mg enough of the coal or coke sample that will yield approximately 0.5 g of ash into an open 50 mL quartz or high-silica crucible. Place the crucible in a cold muffle furnace. Adjust the temperature control so that the furnace reaches a temperature of 300 °C in 1 h and then 500 °C in the second hour. Maintain the furnace temperature at 500 °C for a minimum of 2 h, stirring the sample occasionally. Ashing is complete when no visible evidence of carbonaceous material remains. Cool the samples to room temperature under conditions that minimize the absorption of water. Grind the ash to pass a 150 μm (No. 100) U.S.A. standard sieve in an agate mortar, then reignite at

500 °C for 1 h. Allow the ash to cool under conditions that minimize the absorption of water.

NOTE 5—If all the ash from **9.1** is quantitatively transferred for digestion in **9.2**, it is not necessary to sieve and grind the ash. Results from **11.2.3**, **12.3**, or **13.1.4.8** are then mass fraction of the element in the as-determined sample.

9.1.1 If necessary for results calculations, determine the percentage of ash in the analysis sample according to Test Methods **D3174** or **D7582**, modifying the ashing temperatures in those methods to those specified in **9.1** above.

9.2 Dissolution Procedure 1 (Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, and Zn)—Weigh 0.2000 g to 0.5000 g of the thoroughly blended ash prepared according to **9.1** into a 100 mL or 200 mL Teflon beaker. Add 20 mL of aqua regia and 20 mL of concentrated hydrofluoric acid to the beaker. Place the beaker on a hot plate that has been adjusted to 130 °C to 150 °C. Heat the mixture to dryness, but do not bake. After the solution has evaporated, rinse the beaker walls with water and heat this solution to dryness, again being careful not to bake the sample. Remove the beaker from the hot plate and allow it to cool to room temperature. Add 1 mL of concentrated nitric acid and 20 mL of water to the beaker. Heat the contents on a hot plate at 90 °C to 100 °C until the sample is in solution. If a residue remains after 1 h of heating, it may be ignored. The trace elements are considered to be quantitatively extracted at this point. Remove the beaker from the hot plate and allow the solution to cool to room temperature. Quantitatively transfer the cool solution to a 100 mL volumetric flask and dilute to volume with water. If the solution is not to be analyzed immediately, transfer it to a HDPE bottle to avoid adsorption of lead during storage. Prepare a method blank (**7.7.2**) with each batch of samples to be analyzed. To minimize contamination, clean laboratory ware in a volume fraction of 50 % HNO_3 solution followed by a volume fraction of 50 % HCl solution, then rinse thoroughly with water.

9.3 Ashing Procedure 2 (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y)—Weigh to the nearest 0.1 mg enough of the as-received sample that will yield approximately 0.5 g of ash into an open 50 mL quartz or high-silica crucible and record the test portion mass. Place the crucible in a cold muffle furnace. Adjust the temperature control so that the furnace reaches a temperature of 300 °C in 1 h and then 500 °C in the second hour. Maintain the furnace temperature at 500 °C for a minimum of 2 h, stirring the sample occasionally. If following dissolution Procedure 3 below (**9.5**), increase the final ashing temperature to 550 °C. Ashing is complete when no visible evidence of carbonaceous material remains. Allow the samples to cool to room temperature under conditions that minimize the absorption of water. Grind the ash to pass a 150 μm (No. 100) U.S.A. standard sieve in an agate mortar, then reignite at 500 °C for 1 h. If following dissolution Procedure 3 below (**9.5**), grind the ash to pass a 75 μm (No. 200) U.S.A. standard sieve, then reignite at 550 °C for 1 h. Transfer the ash to a desiccator to cool and store it until sampling for analysis. Determine the percentage of ash by analyzing, under the same conditions, a separate portion of the analysis sample.

NOTE 6—If all the ash from **9.3** is quantitatively transferred for

digestion in 9.4 or 9.5, it is not necessary to sieve and grind the ash. Results from 11.2.3, 12.3, or 13.1.4.8 are then the mass fraction ($\mu\text{g/g}$) of the element in the as-determined sample.

9.4 Dissolution Procedure 2 (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y)—Weigh to the nearest 0.1 mg, approximately 0.05 g to 0.2 g of the thoroughly blended ash prepared according to 9.3 into a 100 mL or 200 mL Teflon beaker and record the test portion mass. For a nominal 0.2 g test portion mass, add 20 mL of aqua regia and 20 mL of concentrated hydrofluoric acid to the beaker. If a lower test portion mass is used, proportionately reduce the sample masses and acid volumes, and use smaller digestion vessels. Place the beaker on a hot plate (or hot block) that has been adjusted to 130 °C to 150 °C. Heat the mixture to dryness, but do not bake. After the solution has evaporated, rinse the beaker walls with deionized water and heat this solution to dryness, again being careful not to bake the sample. Remove the beaker from the hot plate and allow it to cool to room temperature. Add 1 mL of concentrated nitric acid and 20 mL of deionized water to the beaker. Heat the contents on a hot plate (or hot block) at 90 °C to 100 °C until the sample is in solution. Remove the beaker from the hot plate (or hot block) and allow the solution to cool to room temperature. Quantitatively transfer the cool solution to a 100 mL volumetric flask and dilute to volume with deionized water. If the solution is not to be analyzed immediately, transfer to a HDPE bottle. Prepare a method blank (7.7.2) with each batch of samples to be analyzed. To minimize contamination, clean laboratory ware in a volume fraction of 50 % HNO_3 solution followed by a volume fraction of 50 % HCl solution then rinse thoroughly with deionized water.

NOTE 7—The results of ILS 1591 showed, if residue remains in the final solution, low recovery of rare earth elements can occur. Measures to minimize or eliminate residue are reducing test portion mass and occasionally mixing the beaker's or digestion vessel's contents during the acid digestion.

9.5 Dissolution Procedure 3 (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y)—Weigh to the nearest 0.1 mg, approximately 0.05 g to 0.2 g of the thoroughly blended ash prepared according to 9.3 into a platinum or graphite crucible and record the test portion mass. Weigh 0.4 g (to the nearest 0.5 mg) of the fluxing agent and add to the ash sample. Mix the ash and fluxing agent thoroughly. If using graphite crucibles, it is recommended to weigh the ash and fluxing agent in a separate vessel, mix thoroughly, and then quantitatively transfer the contents to the crucible to avoid introducing graphite particles into the mixture. Place crucibles in a muffle furnace and heat to 1000 °C to 1100 °C for 20 min. Turn off furnace and allow samples to cool to room temperature. If using graphite crucibles, a small glass bead will have formed, which can be easily removed and transferred to a 100 mL glass or Teflon beaker. Place a clean PTFE-coated magnetic stirring bar in the beaker with the glass bead and add 30 mL 1+9 volume fraction of HNO_3 . Place on stirring hot plate, set at 50 °C to 70 °C, and stir until glass pellet is completely dissolved. Other than traces of graphite particles from the crucible, no residue should remain. If using platinum crucibles, carefully rinse the bottom and outside of the crucible with deionized water to remove possible contamination, then

place entire crucible in a clean 150 mL or 250 mL beaker. Place a clean PTFE coated magnetic stirring bar in the platinum crucible and add 30 mL of 1 + 9 volume fraction of HNO_3 . Stir until fused sample is completely dissolved. Alternatively, follow manufacturer's instructions if using automated fluxing equipment. No sample residue should remain after dissolution. Quantitatively transfer the digest solution to a 100 mL volumetric vessel and dilute to volume with deionized water. Samples will require further dilution with 1 % volume fraction of HNO_3 prior to analysis to reduce matrix interferences from high dissolved solids. For ICPMS analysis, 20X to 100X dilution is recommended to obtain optimal internal standard recovery and element detection. Prepare a method blank (7.7.2) with each batch of samples to be analyzed.

10. Analysis

10.1 Difference between various makes and models of instruments will occur, so instrumental operating instructions cannot be provided. Instead, the analyst shall refer to the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, linear dynamic range, interference effects, and appropriate background correction shall be investigated and established for each individual analyte on that particular instrument.

11. Test Method A—Inductively Coupled Plasma Atomic Emission Spectrometry

11.1 **Table 1** shows the elements listed in 1.1 along with some suggested wavelengths for inductively coupled plasma atomic emission spectrometry (ICPAES). Other wavelengths may be substituted if they can provide the needed sensitivity and are treated according to the provisions of 10.1. Also shown are estimated detection limits.

TABLE 1 Suggested Wavelengths for ICPAES

Element	Wavelength, nm	Estimated Detection Limit, $\mu\text{g/L}^A$
As ^B	189.042, 228.812, 193.759	53
Be	313.042	0.3
Cd ^B	226.502	4
Co	228.616	7
Cr	267.716, 205.552	7
Cu	324.754	6
Mn	257.610	30
Mo	202.030, 203.844	8
Ni	231.604	15
Pb	220.353	42
Sb ^B	217.581, 206.833	32
V	292.402, 292.464	8
Zn	213.856	2

^A Detection limits are given for informational purposes only and represent the lowest mass concentration that produces an instrumental response statistically different from an aqueous blank solution. Detection limits should not be confused with quantitation limits. Detection limits are sample and matrix dependent. They will vary from instrument to instrument and should be established by each user of these test methods. These values (3 sigma) are based on data contained in EPA/600/4-91/010, Method 200.7 Revision 5.4 (1994).

^B As, Cd, and Sb are typically present in coal at mass fractions that are below the detection limits of ICPAES.

11.2 *Calibration Procedure*—Calibrate the instrument according to the procedure recommended by the manufacturer using a calibration blank and aqueous multielement standards made up in a volume fraction of 1 % trace metal grade HNO₃. All calibration solutions must also contain an internal standard (see Note 8). Records for all calibrations must be in accordance with Practice D7448. Internal standards need to be added to all analytical solutions, samples, calibration standards, and quality control samples. Addition of an internal standard can be done either online or manually.

NOTE 8—An internal standard is needed to compensate for:

1. Differences in physical properties (such as viscosity) between the calibration standard and the test samples,
 2. Drift caused by thermal changes in the laboratory which will affect the instrument optics, and
 3. Drift caused by changes in the sample introduction system, including tubing wear and nebulizer performance.
- An appropriate internal standard element should:
- (i) not be naturally present in the test samples in appreciable mass fractions,
 - (ii) not present spectral interferences with any analyte,
 - (iii) be a strong emitter so that its relative mass concentration can be kept low, and
 - (iv) be as chemically similar to the analyte as possible.

11.2.1 *Initial Calibration Verification*—Before analyzing test samples, analyze the method blank and verify the proper calibration of the instrument by analyzing a reference material that has traceability to an internationally recognized certifying agency such as NIST. Results for the reference material must be within the stated uncertainty limits or the calibration procedure must be repeated.

11.2.2 *Periodic Calibration Verification and Recalibration*—In accordance with Practice D7448, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits or all results obtained since the last successful control check of that element must be rejected and the calibration procedure repeated.

11.2.3 *Calculation*—Calculate the mass fraction of the element (dry basis) in the ash as follows:

$$w_a = \left(\frac{cVD}{m} \right) \quad (1)$$

where:

- w_a = mass fraction of the element in the ash (dry basis), µg/g,
- c = mass concentration of the element in solution, µg/mL,
- V = final volume of the 100 mL flask containing the dissolved solution of the ash, mL,
- D = analytical dilution factor (if used), dimensionless, and
- m = mass of the ash sample, g.

12. Test Method B—Inductively Coupled Plasma Mass Spectrometry

12.1 Table 2 shows the elements listed in 1.1, the isotope, and its abundance used for ICPMS determinations. Also shown are some potential molecular interferences. Most elements, and especially the lanthanides, require kinetic energy discrimination (KED) mode to get the most accurate and reproducible results.

TABLE 2 Isotopes Used for ICPMS Trace and Rare Earth Element Determinations

Element	Isotope	Abundance	Interferant	Estimated Detection Limit, µg/L ^A
As	75	100	⁴⁰ Ar ³⁵ Cl+	0.9
Be	9	100		0.1
Cd	114	28.8	⁹⁶ Mo ¹⁶ O+	0.1
Co	59	100		0.03
Cr	52	83.8		0.07
Cu	63	69.1	⁴⁷ Ti ¹⁶ O+	0.03
Mn	55	100		0.1
Mo	98	23.8		0.1
Ni	60	26.1		0.2
Pb	206	52.4		0.08
Sb	121	57.3		0.08
V	51	99.8	³⁵ Cl ¹⁶ O+	0.02
Zn	68	18.6	³⁶ S ¹⁶ O ¹⁶ O+	0.2
Ce	140	88.5		
Dy	163	24.9		
Er	166	33.6		
Eu	153	52.2		
Gd	157	15.6		
Ho	165	100		
La	139	99.9		
Lu	175	97.4		
Nd	146	17.2		
Pr	141	100		
Sm	147	15.0		
Sc	45	100		
Tb	159	100		
Tm	169	100		
Yb	172	21.9		
Y	89	100		

^A Detection limits are given for informational purposes only and represent the lowest mass concentration that produces an instrument response statistically different from an aqueous blank solution. Detection limits should not be confused with quantitation limits. Detection limits are sample and matrix dependent. They will vary from instrument to instrument and should be established by each user of these test methods. The values (3 sigma) are based on data contained in EPA/600/4-91/010, Table 1, Method 200.8, Revision 5.4 (1994). The rare earth elements are not included in the EPA method table referenced.

12.2 *Calibration*—In conjunction with 11.2, calibrate the instrument by analyzing a blank consisting of water and appropriate internal standards in a volume fraction of 1 % solution of HNO₃ containing 0 ng/mL of the elements to be analyzed and internal standards. Continue the calibration by analyzing three solutions that cover the expected mass concentration range of the elements to be analyzed. The mass concentrations of the calibration standards should bracket the expected mass concentrations of the analytes. Suggested mass concentration ranges are 10 ng/mL, 50 ng/mL, and 250 ng/mL.

12.2.1 *Internal Standards*—Internal standards are needed for the reasons stated in 11.2. Drift associated with ICPMS instruments can in part be mass dependent. Therefore, it is recommended that the analyst use a series of internal standards that covers the mass range and ionization potentials of the elements to be analyzed. Elements used as internal standards should not be present in the samples to be analyzed in appreciable quantities. Refer to the manufacturer for recommendations of internal standards for the list of elements in 1.1. If Li is used as an internal standard, an enriched (95 % or better) ⁶Li must be used because of the significant mass fraction of naturally occurring ⁷Li in most coals. Because they

are not present in coal in appreciable mass fractions, isotopes of Ge, In, and Bi may be used.

12.2.2 *Initial Calibration Verification*—Before analyzing test samples, analyze the method blank and verify the proper calibration of the instrument by analyzing a reference material that has traceability to an internationally recognized certifying agency such as NIST. Results for the reference material must be within the stated uncertainty limits or the calibration procedure must be repeated.

12.2.3 *Periodic Calibration Verification and Recalibration*—In accordance with Practice D7448, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits or all results obtained since the last successful control check for that element must be rejected and the calibration procedure repeated.

12.3 *Calculation*—Calculate the mass fraction of the element in the ash according to Eq 1 in 11.2.3.

13. Test Method C—Graphite Furnace Atomic Absorption Spectrometry

13.1 Calibration and Sample Solution Preparation:

13.1.1 Use the intermediate stock standard solution (7.5.2) to prepare at least five working standards to cover the optimum mass concentration ranges specified by the instrument manufacturer for the element to be analyzed. Add an aliquot of concentrated nitric acid to obtain a final volume fraction of 1 % HNO₃. When preparing arsenic or antimony working standards, add 2 mL of magnesium nitrate solution (7.6) per 10 mL of working standard solution.

13.1.2 *Sample Aliquot*—Add an aliquot of the sample solution (9.2 or 9.4) in the optimum mass concentration range for the element to be determined to a 10 mL volumetric flask. To estimate the aliquot of sample solution, it may be necessary to analyze the original sample solution (9.2 or 9.4). In some cases, only by trial and error can the correct aliquot of sample be determined. Alternatively, ICPAES can be used to screen samples to determine which elements may require analysis by GFAAS.

13.1.3 Add nitric acid so that the 10 mL of solution will have a final volume fraction of 1 % nitric acid. The determination of arsenic and antimony require the addition of 2 mL of magnesium nitrate solution (7.6) per 10 mL of working standard solution. Dilute to volume with water.

13.1.4 *Instrument Parameters*—As stated in 10.1, because of differences in equipment, it is impossible to specify instrument operating parameters (for example, wavelength, slit, lamp power, drying, ashing and atomization temperatures, and so forth). Instead, the analyst shall initially program the system according to the instrument manufacturer’s instructions for a particular analyte. Optimize instrument performance for each analyte according to the following sections.

13.1.4.1 *Drying Temperature*—Make an injection of both a sample and a working standard solution according to 13.1.4. Use a mirror to observe the samples through the introduction port. The drying temperature should be high enough to evaporate the sample smoothly but not so hot that the sample begins to boil or spatter.

13.1.4.2 *Ashing Temperature*—As the ashing step begins, no sizzle or popping sounds should be heard. The ashing temperature should be high enough to eliminate most of the background but not so hot as to volatilize the analyte. A high flow rate of inert gas is required during the ashing stage to sweep the furnace of unwanted background material.

13.1.4.3 *Atomization Temperature*—Adjust the atomization temperature as necessary to eliminate low, broad, misshapen, or doublet peaks. Adjustments should be made in 100 °C increments. Peak shape may also dictate the mode of measurement (peak height or peak area) and the choice of graphite tube and platforms. Graphite platforms significantly improve instrument performance for the determination of Cd, Pb, As, and Sb. It is strongly recommended that they be tried as part of optimizing instrument performance for each element to be determined.

13.1.4.4 Refer to the instrument manufacturer’s instructions for further information on optimizing performance.

13.1.4.5 Repeat the steps in 13.1 through 13.1.4 for each element to be determined.

13.1.4.6 *Initial Calibration Verification*—Before analyzing test samples, analyze the method blank and verify the proper calibration of the instrument by analyzing a reference material that has traceability to an internationally recognized certifying agency such as NIST. Results for the reference material must be within the stated uncertainty limits or the calibration procedure must be repeated.

NOTE 9—**Caution:** Matrix problems are prevalent when analyzing the types of samples described in 1.1 by GFAAS. If the sample matrix varies significantly from that of the reference material, validation of the test methods with the reference material may lead to an incorrect assumption that the test methods are applicable to other matrices.

13.1.4.7 *Periodic Calibration, Verification, and Recalibration*—In accordance with Practice D7448, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits or all results obtained since the last successful control check for that element must be rejected and the calibration procedure repeated.

13.1.4.8 *Calculation*—Calculate the mass fraction of the element according to Eq 1 in 11.2.3.

TABLE 3 Mass Fraction Range and Limits for Repeatability and Reproducibility for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues

Priority Element	Mass Fraction Range, µg/g	Repeatability Limit, <i>r</i>	Reproducibility Limit, <i>R</i>
Sb	0.17 to 5.71	$-0.06 \bar{x} + 0.29 \bar{x}^A$	$0.08 \bar{x} + 0.44 \bar{x}^A$
As	0.56 to 138.79	$0.42 \bar{x} + 0.13 \bar{x}^A$	$1.73 \bar{x} + 0.23 \bar{x}^A$
Be	0.42 to 13.11	$0.08 \bar{x} + 0.08 \bar{x}^A$	$0.14 \bar{x} + 0.30 \bar{x}^A$
Cd	0.02 to 0.84	$0.03 \bar{x} + 0.16 \bar{x}^A$	$0.04 \bar{x} + 0.43 \bar{x}^A$
Co	0.76 to 47.18	$0.28 \bar{x} + 0.11 \bar{x}^A$	$1.26 \bar{x} + 0.18 \bar{x}^A$
Cr	2.37 to 221	$1.03 \bar{x} + 0.09 \bar{x}^A$	$1.50 \bar{x} + 0.18 \bar{x}^A$
Cu	3.43 to 107.06	$0.62 \bar{x} + 0.10 \bar{x}^A$	$-0.31 \bar{x} + 0.28 \bar{x}^A$
Mn	11.69 to 419.61	$0.98 \bar{x} + 0.10 \bar{x}^A$	$8.12 \bar{x} + 0.15 \bar{x}^A$
Mo	0.40 to 20.52	$0.23 \bar{x} + 0.11 \bar{x}^A$	$0.80 \bar{x} + 0.18 \bar{x}^A$
Ni	2.00 to 113.32	$0.35 \bar{x} + 0.13 \bar{x}^A$	$1.26 \bar{x} + 0.19 \bar{x}^A$
Pb	1.57 to 66.99	$0.26 \bar{x} + 0.16 \bar{x}^A$	$0.13 \bar{x} + 0.30 \bar{x}^A$
Zn	3.76 to 202.31	$0.70 \bar{x} + 0.10 \bar{x}^A$	$2.98 \bar{x} + 0.18 \bar{x}^A$
V	4.50 to 293.17	$0.75 \bar{x} + 0.13 \bar{x}^A$	$2.02 \bar{x} + 0.21 \bar{x}^A$

^A Where \bar{x} is the average of two single test results.

TABLE 4 Comparison of Certified Values ($\mu\text{g/g}$) for Standard Reference Material SRM 1632b with Interlaboratory Study Values for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues^A

Elemental Oxide	RR:D05-1029 Value	SRM Value	Bias, %	Significant (95 % Confidence Level)
As	3.64 ± 0.21	3.72 ± 0.09	-2.15	no
Cd	0.065 ± 0.01	0.057 ± 0.0027	14.04	yes
Co	2.18 ± 0.15	2.29 ± 0.17	-4.80	no
Cu	6.31 ± 0.36	6.28 ± 0.30	0.48	no
Mn	11.7 ± 0.64	12.4 ± 1.0	-5.65	no
Ni	6.20 ± 0.37	6.10 ± 0.27	1.64	no
Pb	3.74 ± 0.33	3.67 ± 0.26	1.91	no
Zn	11.30 ± 0.52	11.89 ± 0.78	-4.96	no

^A The ± values associated with the RR:D05-1029 values are the values for *r*.

TABLE 5 Comparison of Certified Values ($\mu\text{g/g}$) for Standard Reference Material SRM 1635 with Interlaboratory Study Values for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues^A

Elemental Oxide	RR:D05-1029 Value	SRM Value	Bias, %	Significant (95 % Confidence Level)
As	0.56 ± 0.11	0.42 ± 0.15	33.3	no
Cd	0.03 ± 0.01	0.03 ± 0.01	0.0	no
Cr	2.4 ± 0.2	2.5 ± 0.3	-4.00	no
Cu	3.4 ± 0.3	3.6 ± 0.3	-5.56	no
Mn	20.4 ± 1.2	21.4 ± 1.5	-4.67	no
Ni	2.00 ± 0.28	1.74 ± 0.10	14.94	no
Pb	1.6 ± 0.1	1.9 ± 0.2	-15.79	yes
V	4.5 ± 0.2	5.2 ± 0.5	-13.46	yes
Zn	5.00 ± 0.7	4.7 ± 0.5	6.38	no

^A The ± values associated with the RR:D05-1029 values are the values for *r*.

TABLE 6 Comparison of Certified Values ($\mu\text{g/g}$) for Standard Reference Material SRM 1633b with Interlaboratory Study Values for Priority Trace Elements in Coal, Coke, and Solid Combustion Residues^A

Elemental Oxide	RR:D05-1029 Value	SRM Value	Bias, %	Significant (95 % Confidence Level)
As	138.8 ± 6.5	136.2 ± 2.6	1.91	no
Cd	0.845 ± 0.080	0.784 ± 0.006	7.78	no
Cr	184.1 ± 7.7	198.2 ± 4.7	-7.11	yes
Cu	107.1 ± 3.8	112.8 ± 2.6	-5.05	yes
Mn	130.6 ± 4.2	131.8 ± 1.7	-0.91	no
Ni	113.3 ± 6.0	120.6 ± 1.8	-6.05	yes
Pb	67.0 ± 3.8	68.2 ± 1.1	1.76	no
V	293.2 ± 11.1	295.7 ± 3.6	-0.85	no

^A The ± values associated with the RR:D05-1029 values are the values for *r*.

14. Report

14.1 Convert mass fraction of the element in the ash to the whole coal basis for reporting as follows:

$$w_c = A w_a / 100 \quad (2)$$

where:

- w_c = mass fraction of the element in the coal (dry basis), $\mu\text{g/g}$,
- A = mass fraction of the ash in the coal (dry basis) as determined by Test Methods **D3174** or **D7582**, %,
- w_a = mass fraction of the element in the ash, dry basis, $\mu\text{g/g}$, and,

100 = conversion factor to convert A from % to a dimensionless value, %.

14.2 For reporting analyses to other than the as-determined basis, refer to Practice **D3180**.

15. Precision and Bias

15.1 *Precision*—The precision of this test method for the determination of priority trace elements in 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**.

15.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time on identical test items taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

15.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories, with different operators using different equipment, using identical test items 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 %.

15.2 *Bias*—The NIST standard reference materials SRM 1632b, SRM 1635, and SRM 1633b were included in the priority trace element 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 **Tables 4-6**. Trace element values are not certified for the elements beryllium, molybdenum, and antimony; therefore, bias cannot be determined for these elements at this time.

15.3 An interlaboratory study, designed consistent with Practice **E691**, was conducted in 1997 for the priority trace elements (Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, and Zn). Twelve laboratories participated; however, data from only six labs was used. The details of the study and supporting data are given in ASTM Research Report RR:D05-1029.⁴

15.4 *Precision (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y)*—The precision of this test method for the determination of rare earth elements in coal and solid combustion residues is shown in **Table 7**. The precision characterized by the repeatability (S_r , r) and reproducibility (S_R , R) is described in **Table A2.1**.

15.5 *Bias (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y)*—The NIST standard reference materials SRM 1635a, SRM 1632e, and SRM 1633c, were included in the rare earth element interlaboratory study along with USGS SBC-1 to compare the reference material values and those

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1029. Contact ASTM Customer Service at service@astm.org.