Designation: D 2795 – 95

Standard Test Methods for Analysis of Coal and Coke Ash[1]

This standard is issued under the fixed designation D 2795; 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 cover the analysis of coal and coke ash for the commonly determined major elements.

1.2 The test methods appear in the following order:

	Sections
Silicon Dioxide (SiO_2)	10 to 12
Aluminum Oxide (Al_2O_3)	13 to 15
Ferric Oxide (Fe_2O_3)	16 to 18
Titanium Dioxide (TiO_2)	19 to 22
Phosphorus Pentoxide (P_2O_5)	23 to 25
Calcium Oxide (CaO), and Magnesium Oxide (MgO)	26 to 29
Sodium Oxide (Na_2O) and Potassium Oxide (K_2O)	30 to 33

NOTE 1—Test Methods D 1757 is used for determination of sulfur.

1.3 The values stated in SI units (Practice E 380) shall be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 1757 Test Methods for Sulfur in Ash from Coal and Coke[2]

D 2013 Test Method for Preparing Coal Samples for Analysis[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)[4]

3. Summary of Test Methods

3.1 The coal or coke to be analyzed is ashed under standard conditions and ignited to constant weight. Two solutions are prepared from the ash. Solution A is obtained by fusing the ash with sodium hydroxide (NaOH) followed by a final dissolution of the melt in dilute hydrochloric acid (HCl). Solution B is prepared by decomposition of the ash with sulfuric (H_2SO_4), hydrofluoric (HF), and nitric (HNO_3) acids. Solution A is used for the analysis of SiO_2 and Al_2O_3, and Solution B for the remaining elements.

3.2 The two solutions are analyzed by a combination of methods: (*1*) spectrophotometric procedures are used for SiO_2, Al_2O_3, Fe_2O_3, TiO_2, and P_2O_5; (*2*) chelatometric titration for CaO and MgO; and (*3*) flame photometry for Na_2O and K_2O. See Fig. 1 for a general outline of the methods and procedures used for each determination.

4. Significance and Use

4.1 A compositional analysis of the ash is often useful in the total coal quality description. Knowledge of the ash composition is also useful in predicting the behavior of the ashes and slags in combustion chambers. Utilization of the coal combustion ash by-products sometimes depends on the chemical composition of the ash.

4.2 It should be noted that chemical composition of laboratory prepared coal ash may not exactly represent the composition of mineral matter in the coal, or the composition of the fly ash and slags resulting from the commercial scale burning of the coal.

5. Apparatus

5.1 *Balance*, sensitive to 0.1 mg.

5.2 *Crucibles*—Nickel crucibles of 50-cm^3 capacity shall be used for NaOH fusion of the ash, and platinum crucibles of 30-cm^3 capacity shall be used for decomposition of the ash with HF.

5.3 *Emission Flame Photometer*.

5.4 *Muffle Furnace*—Electrically heated muffle furnace with good air circulation and capable of maintaining a temperature of approximately 750°C.

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[1] These test methods are under the jurisdiction of ASTM Committee D-5 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] *Annual Book of ASTM Standards*, Vol 05.05.

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

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

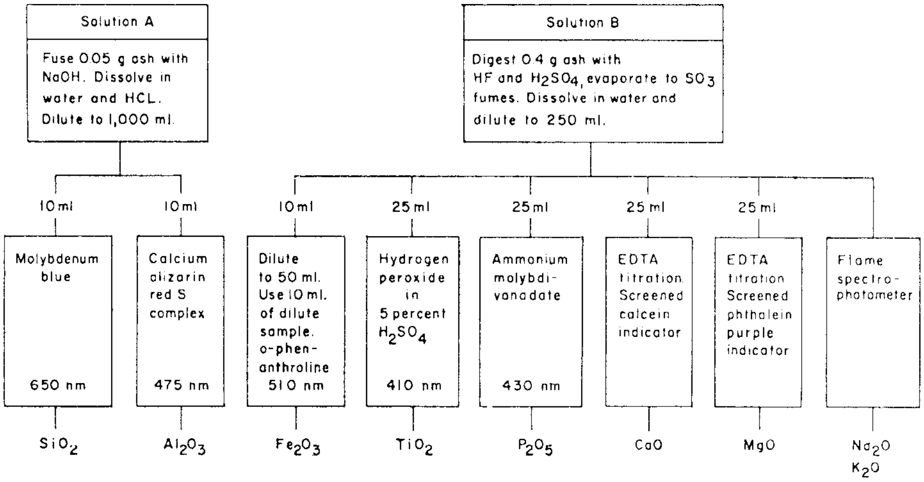

FIG. 1 Outline of Methods for Analysis of Coal Ash

5.5 *Absorption Spectrophotometer*, visible region 380 to 780 nm.

5.6 *Sieves*, 150 and 250-µm (No. 100 and No. 60) U.S.A. standard.

6. Purity of Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[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.

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

7. Sample

7.1 Prepare the analysis sample in accordance with Test Method D 2013 or Practice D 346 by pulverizing the material to pass 250 µm (No. 60) sieve.

7.2 Analyze separate test portions for moisture and ash contents in accordance with Test Methods D 3173, D 3174, or D 5142 so that calculations to other bases can be made.

8. Preparation of Coal Ash and Coke Ash

8.1 *Procedure*—Prepare 3 to 5 g of ash from the analysis sample. Spread the coal or coke in a layer not over 6 mm (¼ in.) in depth in a fireclay or porcelain roasting dish. Place 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 to constant weight (± 0.001 g, Note 2), at 750°C. Allow the ash to cool, transfer to an agate mortar, and grind to pass a 150-µm (No. 100) U.S.A. standard sieve. Reignite the ash at 750°C for 1 h, cool rapidly, and immediately weigh portions for analysis. If samples are stored, reignite the ash before weighing or determine loss on ignition at 750°C on a separate sample weighed out at the same time as the analysis sample. Thoroughly mix each sample before weighing.

NOTE 2—Coke may be ignited to constant weight at a temperature not exceeding 950°C if difficulty in ashing is encountered.

9. Preparation of Analysis Solutions (Sample, Standards, and Blank)

9.1 *Reagents and Materials*:

9.1.1 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

9.1.2 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated hydrofluoric acid (HF).

9.1.3 *National Institute of Standards and Technology (NIST) Sample No. 99a Soda Feldspar*. [6]

9.1.4 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

9.1.5 *Sodium Hydroxide* (NaOH) pellets.

9.1.6 *Sulfuric Acid* (1 + 1)—Mix carefully while stirring 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) into 1 volume of water.

9.2 *Procedure*:

9.2.1 The methods described are for typical ash samples; however, different dilutions or aliquots than those specified may be preferable to attain suitable concentrations for proper intensities for various constituents. Colors developed as specified are stable unless otherwise stated. Although the methods are described for a single sample, a group of ten or more can be processed at the same time. Each numbered step should be completed for the group of samples being analyzed before proceeding to the next step.

9.2.2 *Solution A for SiO_2 and Al_2O_3 Determination*— Weigh 0.0500 g of sample and transfer to a 50-mL nickel crucible.

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[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[6] National Institute of Standards and Technology Sample No. 99a, soda feldspar contains 65.2 % SiO_2 and 20.5 % Al_2O_3. This reagent is used for standardization purposes only.

Add 1.5 g of NaOH, cover the crucible, and heat in a gas flame to melt the NaOH. Swirl gently to ensure that no particles of sample float on the surface of the melt. Continue fusion for about 5 min at dull red heat; then remove the crucible from the flame and swirl the melt, while cooling, to coat the crucible wall. Add about 25 mL of water to the melt and let stand for at least 1 h or overnight if convenient. Pour the contents of the crucible into a 600-mL beaker containing 400 mL of water and 20 mL of HCl (1 + 1). (Do not allow the nickel crucible to come in contact with the acid.) With a rubber policeman, remove any residue from the crucible and wash it into a beaker. Clean a 1000-mL volumetric flask with HCl (1 + 1), rinse with water, and then transfer the solution in the beaker to it. Dilute with water to the 1000-mL mark and mix.

9.2.2.1 *Standard Solution for SiO_2 and Al_2O_3 Determination*—Prepare duplicate standard solutions in the same manner (see 9.2.2) using 0.0500-g portions of NIST Sample No. 99a, soda feldspar.[6] Also prepare a blank solution as in 9.2.2, but omit the soda feldspar. Store the standard and blank solutions in plastic bottles.

9.2.3 *Solution B for Fe_2O_3, TiO_2, P_2O_5, CaO, MgO, Na_2O, and K_2O Determinations*—Treat 0.400 ± 0.0005 g of sample in a 30-mL platinum crucible with 3 cm^3 of H_2SO_4(1 + 1) and 10 mL of HF. Evaporate on an air bath until most of the HF is removed then add 1 mL of HNO_3, and continue heating until strong fumes of sulfur trioxide (SO_3) evolve. Cool the crucible and contents, add water to dissolve the residue, and digest on an air bath for ½ h. Transfer the contents of the crucible to a 250-mL volumetric flask. Cool to room temperature then dilute to the 250-mL mark and mix (Note 3). Also prepare a blank Solution B (8.2.3), omitting the sample. Because of the possibility of alkali contamination from the glass from which the flask is made, determine sodium and potassium the same day that Solution B is prepared, or withdraw 25 mL with a pipet and store in a plastic bottle.

NOTE 3—Although some calcium sulfate ($CaSO_4$) from samples high in calcium may not dissolve during digestion in the crucible, it normally will dissolve on further dilution. A small quantity of insoluble barium sulfate ($BaSO_4$) may still remain with some samples. This will settle to the bottom of the flask and not interfere in determining the main constituents. If appreciable insoluble residue is present, the solution can be filtered into another 250-mL flask before finally diluting to the mark.

SILICON DIOXIDE (SiO_2)

10. Reagents

10.1 *Ammonium Molybdate Solution* (7.5 g/100 mL)—Dissolve 7.5 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 75 mL of water. Add 10 mL H_2SO_4 (1 + 1) and dilute to 100 mL. Store in a plastic bottle.

10.2 *Reducing Solution*—Dissolve 0.7 g of sodium sulfite ($Na_2SO_3\cdot 7H_2O$) in 10 cm^3 of water. Add 0.15 g of 1-amino-2-naphthol-4-sulfonic acid and stir until dissolved. Dissolve 9.0 g of sodium metabisulfite ($Na_2S_2O_5$) in 90 mL of water, and add this solution to the solution above and mix. Store in a plastic bottle. *Unless this solution is freshly prepared, check the reducing properties of the solution against a known standard.*

10.3 *Tartaric Acid Solution* (10 % in water)—Store in a plastic bottle.

11. Procedure

11.1 Pipet a 10-mL aliquot of blank solution and 10 mL of each standard solution and Sample Solution A into separate 100-mL volumetric flasks. Dilute each solution to 50 or 60 mL with water and mix. Add 1.5 mL of ammonium molybdate solution with a measuring pipet, mix, and let stand 10 min. Pipet 4 mL of tartaric acid solution followed immediately by 1 mL of reducing solution into the first flask, mixing during the additions. Dilute contents of this flask immediately to the 100-mL mark and mix before proceeding to the next flask. Let each solution stand 1 h; then determine its absorbance at 650 nm, using the blank solution as a reference, assumed to have zero absorbance.

12. Calculation

12.1 Compute factors f_1 and f_2 for each standard solution as follows:

$$f_1 = C_s / A_1 \text{ and } f_2 = C_s / A_2 \quad (1)$$

where:

C_s = concentration of SiO_2 in the standard sample, %, and

A_1 and A_2 = absorbances for replicate standard solution each containing 50 mg of standard sample.

12.2 Calculate the percent of silica in the ash as follows:

$$SiO_2, \% = FA \quad (2)$$

where:

F = $(f_1 + f_2)/2$, and

A = absorbance of the sample solution containing 50 mg of ash.

ALUMINUM OXIDE (Al_2O_3)

13. Reagents

13.1 *Acetic Acid, Glacial* (CH_3COOH).

13.2 *Alizarin Red-S Solution* (0.1 % in water).

13.3 *Calcium Chloride Solution* ($CaCl_2$) (7 g/500 mL)—Transfer 7 g of calcium carbonate ($CaCO_3$) to a 250-mL beaker. Add about 50 mL of water and HCl (1 + 1) in drops until the $CaCO_3$ is dissolved. Boil the solution for 1 to 2 min, cool, and dilute with water to 500 mL.

13.4 *Buffer Solution*—Dissolve 70 g of sodium acetate ($CH_3COONa\cdot 3H_2O$) in water, add 30 mL of CH_3COOH, and dilute to 500 mL.

13.5 *Hydroxylamine Hydrochloride Solution* (10 % in water)—Prepare fresh.

13.6 *Thioglycollic Acid* (5 %)—Dilute 5 mL of thioglycollic acid to 100 mL with water. Prepare fresh.

14. Procedure

14.1 Pipet a 10-mL aliquot of Sample Solution A, 20 mL of each Standard Solution A, and 20 mL of blank solution into separate 100-mL volumetric flasks. Then pipet 10 mL of blank solution to the flask containing 10 mL of sample solution to maintain correct pH. For ash samples that contain less than 20 % Al_2O_3 take a 20-mL aliquot directly from Sample Solution A. Add from pipets, in the following order, mixing thoroughly after addition of each reagent, 1 cm^3 of $CaCl_2$

solution, 1 mL of hydroxylamine hydrochloride solution, and 1 mL of thioglycollic acid solution. From a graduated cylinder add 10 mL of buffer solution to each flask and allow to stand 10 min. Add 5 mL of alizarin red-S solution with a pipet, dilute to 100 mL, and mix. Allow each solution to stand for 1 h, and measure absorbance at 475 nm using the blank solution as a reference, assumed to have zero absorbance.

15. Calculation

15.1 Compute factors f_1 and f_2 for each standard test as follows:

$$f_1 = C_A/A_1 \text{ and } f_2 = C_A/A_2 \qquad (3)$$

where:

C_A = concentration of Al_2O_3 in standard feldspar sample, %, and

A_1 and A_2 = absorbances for replicate standard solutions.

15.2 Calculate the percent Al_2O_3 as follows:

For 10-mL aliquot of Sample Solution A:

$$Al_2O_3\text{, \% in ash} = 2\,FA \qquad (4)$$

For 20-mL aliquot of Sample Solution A:

$$Al_2O_3\text{, \% in ash} = FA \qquad (5)$$

where:

F = $(f_1 + f_2)/2$, and

A = absorbance of sample solution.

FERRIC OXIDE (Fe_2O_3)

16. Reagents

16.1 *Hydroxylamine Hydrochloride Solution* (10 %)—Prepare a 10 % solution of hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) in water.

16.2 *Orthophenanthroline* (0.1 %)—Prepare a 0.1 % solution in water.

16.3 *Sodium Citrate* (10 %)—Prepare a 10 % solution of sodium citrate ($Na_3C_8H_5O_7\cdot 2H_2O$) in water.

16.4 *Iron, Standard Solution* (1 mL = 0.1 mg Fe_2O_3)—Dissolve 0.2455 ± 0.0005 g of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ in water, add 3 mL of H_2SO_4(1 + 1), and dilute to 500 mL.

17. Procedure

17.1 Dilute 10 mL of Sample Solution B to 50 mL in a volumetric flask. Pipet 10 cm^3 of diluted sample solution into a 100-mL volumetric flask, pipet 5 cm^3 of standard iron solution into another 100-mL flask, and add nothing to a third flask for reagent blank. Add 5 mL of hydroxylamine hydrochloride solution with a graduated cylinder to each flask, and allow to stand for 10 min. Then add 10 mL of orthophenanthroline solution with a graduated cylinder to each flask and mix. Finally, add 10 mL of sodium citrate solution with a graduated cylinder to each flask, dilute to 100 mL with water, and mix. After 1 h measure absorbance at 510 nm, using the reagent blank as reference, assumed to have zero absorbance.

18. Calculation

18.1 Calculate the percent Fe_2O_3 as follows:

$$Fe_2O_3\text{, \%} = (AC_F/A_1B) \times 100 \qquad (6)$$

where:

A = absorbance of sample solution.

A_1 = absorbance of standard iron solution,

B = sample contained in the final dilution of Solution B (9.23 and Section 17), mg, and

C_F = Fe_2O_3 in aliquot taken for standard iron solution, mg.

NOTE 4—For the dilutions given, 5 mL of standard iron solution contains 0.5 mg of Fe_2O_3 (C_F) and the diluted sample solution contains 3.2 mg of sample (B). For samples containing more than 15 % of Fe_2O_3, take a 5-mL aliquot of the diluted sample solution which contains 1.6 mg of sample.

TITANIUM DIOXIDE (TiO_2)

19. Reagents

19.1 *Hydrogen Peroxide* (3 %)—Prepare a 3 % solution of hydrogen peroxide (H_2O_2) in water.

19.2 *Titanium, Standard Solution* (1 mL = 0.20 mg TiO_2)—Transfer 0.2008 ± 0.0005 g of NIST Sample No. 154a (99.6 % TiO_2) or the appropriate amount of reagent TiO_2 of known composition to a platinum crucible. Fuse with potassium pyrosulfate (in the ratio of about 4 + 1). Dissolve the melt in 50 mL of H_2SO_4 (1 + 1) cool, and dilute to 1000 mL in a volumetric flask.

20. Calibration

20.1 Transfer 5.0 mL of standard titanium solution to a 50-mL volumetric Flask No. 1, and add about 25 mL of water. Add 25 mL of water to Flask No. 2. To each flask, add 5 mL of H_2SO_4 (1 + 1) and cool to room temperature. Add 5 mL of H_2O_2 to Flask No. 1, fill both flasks to the 50-mL mark with water, and mix. Measure the absorbance of the solution from Flask No. 1 at 410 nm and use the reagent blank in Flask No. 2 as the reference, assumed to have zero absorbance.

21. Procedure

21.1 Pipet a 25-mL portion of Sample Solution B (see 9.2.3) into a 50-mL volumetric flask (No. 1) and for the reference solution pipet a second 25-mL portion of Solution B to another 50-mL flask (No. 2). Add 5 cm of H_2SO_4 (1 + 1) to each flask, mix, and cool to room temperature. Then add 5 mL of H_2O_2 to Flask No. 1. Fill both flasks to the 50-mL mark with water and mix. Measure absorbance at 410 nm of solution from Flask No. 1 using the solution from Flask No. 2 as the reference, assumed to have zero absorbance.

22. Calculation

22.1 Calculate the percent TiO_2 as follows:

$$TiO_2\text{, \%} = (AC_T/A_1B) \times 100 \qquad (7)$$

where:

A = absorbance of sample solution,

A_1 = absorbance of standard titanium solution,

B = sample contained in final dilution of Solution B, mg, and

C_T = TiO_2 in aliquot taken for standard titanium solution, mg.

NOTE 5—For the dilutions given, C_T = 1 mg TiO_2 and B = 40 mg of sample. Using these figures the above equation reduces to:

$$TiO_2, \% = 2.5\ A/A_1 \quad (8)$$

PHOSPHORUS PENTOXIDE (P_2O_5)

23. Reagents

23.1 *Molybdivanadate Solution*—Dissolve 0.625 g of ammonium metavanadate (NH_4VO_3) in 200 mL HNO_3 (1 + 1) (1 volume of HNO_3, sp gr 1.42, and 1 volume of water). Dissolve 25 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 200 mL of water. Pour the ammonium molybdate solution into the metavanadate solution while stirring and dilute to 500 mL with water.

23.2 *Phosphorus Pentoxide, Standard Concentrated Stock Solution*—Dissolve 0.3835 ± 0.0005 g of potassium dihydrogen phosphate (KH_2PO_4), which has been dried at 110°C, in water, and dilute to 1000 mL with water.

23.3 *Phosphorus Pentoxide, Standard Working Solution*—Dilute 50 mL of concentrated stock solution to 500 mL with water. Each 25 mL of this solution contains 0.50 mg of P_2O_5.

24. Procedure

24.1 Pipet a 25-mL aliquot from Sample Solution B, 25 mL of standard working solution, and 25 mL of the blank solution into separate 50-mL volumetric flasks. With a pipet add 10 mL of molybdivanadate solution to each flask, dilute with water to the mark, and allow to stand for 5 min. Measure the absorbance at 430 nm, using the reagent blank as the reference, assumed to have zero absorbance.

25. Calculation

25.1 Calculate the percent P_2O_5 as follows:

$$P_2O_5, \% = (AC_P/A_1B) \times 100 \quad (9)$$

where:

A = absorbance of the sample solution,
A_1 = absorbance of the standard phosphorus solution,
B = sample contained in final dilution of Solution B, mg, and
C_P = P_2O_5 in the aliquot taken for the standard phosphorus solution, mg.

NOTE 6—For the dilutions given, $C_P = 0.50$ mg and $B = 40$ mg of sample. Using these figures the above equation reduces to:

$$P_2O_5, \% = 1.25\ A/A_1 \quad (10)$$

CALCIUM OXIDE (CaO) AND MAGNESIUM OXIDE (MgO)

26. Reagents

26.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

26.2 *Calcein Indicator*—Mix 0.2 g of calcein, 0.12 g of thymolphthalein, and 20 g of finely ground potassium chloride (KCl).

26.3 *EDTA Solution*—Dissolve 3.720 g of the disodium salt of ethylenediaminetetraacetic acid (EDTA) in water and dilute to 1000 mL. Standardize against the standard calcium solution using calcein or phthalein purple indicator.

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

26.5 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

26.6 *Phthalein Purple Indicator*—Mix 0.1 g of phthalein purple, 0.005 g of methyl red, and 0.05 g of naphthol green B with 10 g of finely ground KCl.

26.7 *Potassium Hydroxide Solution* (224.4 g/L)—Dissolve 224.4 g of potassium hydroxide (KOH 85 %) in water and dilute to 1000 mL. Store in a plastic bottle.

26.8 *Calcium Standard Solution* (1.000 g/L) (1 mL = 0.00056 g CaO)—Dissolve 1.000 g of calcium carbonate ($CaCO_3$) in water with 4 mL of HCl (1 + 1). Heat to boiling to expel carbon dioxide (CO_2), cool, and dilute to 1000 mL.

26.9 *Triethanolamine Solution*—Dilute 500 mL of triethanolamine with water to 1000 mL and mix.

27. Procedure for CaO

27.1 Pipet 25 mL of Sample Solution B and 25 mL of the blank solution into separate 500-mL Erlenmeyer flasks. Dilute with water to approximately 100 mL. Add 20 drops of concentrated HCl, 5 mL of the triethanolamine solution, 5 mL of NH_4OH, and 10 mL of KOH solution in that order, mixing after addition of each reagent. Dilute with water to about 200 mL. Add approximately 40 mg of calcein indicator and titrate with standard EDTA solution until the color changes from a green fluorescence to purple. Observe the color change in diffused light looking down through the flask to a black surface.

28. Procedure for MgO

28.1 Pipet 25 mL of Sample Solution B and 25 mL of blank solution into separate 500-mL Erlenmeyer flasks. Dilute with water to about 100 mL. Add 20 drops of concentrated HCl, 20 mL of triethanolamine solution, and 25 mL of NH_4OH, mixing after addition of each reagent. Dilute with water to approximately 200 mL. Add a volume of standard EDTA solution slightly less than the calcium titer; then add about 40 mg of phthalein purple indicator. Continue the titration until the color changes from pale purple to colorless or pale grey. A slight excess of EDTA solution produces a green coloration. Observe the color change in diffused light looking down through the flask to a white surface.

29. Calculations

29.1 Calculate the percent CaO as follows:

$$\text{CaO}, \% = \frac{V_1 \times F(250/A)}{W} \times 100 \quad (11)$$

where:

V_1 = volume of EDTA solution required for the calcium titration, minus the volume of EDTA solution required for the blank titration, mL,
F = grams of CaO = 1 mL EDTA,
W = grams of sample, and
A = volume of aliquot, mL.

NOTE 7—If $W = 0.4$ g, $F = 0.0056$ g, and $A = 25$ mL, then percent of CaO = 1.4 V_1.

29.2 Calculate the percent MgO as follows:

$$\text{MgO}, \% = \frac{(V_2 - V_1)(0.719F)(250/A)}{W} \times 100 \quad (12)$$

where:

V_2 = volumes of EDTA required for calcium plus magnesium titration minus volume of EDTA solution required for blank titration, mL, and

$0.719F$ = grams MgO = 1 mL EDTA.

Remaining symbols are the same as for computing percent CaO.

SODIUM OXIDE (Na_2O) AND POTASSIUM OXIDE (K_2O)

30. Reagents

30.1 *Potassium, Concentrated Stock Solution* (100 ppm)—Dissolve 0.2228 ± 0.0005 g of potassium sulfate (K_2SO_4) in water and dilute to 1000 mL.

30.2 *Potassium, Standard Solution* (50 ppm)—Pipet 50 mL of potassium stock solution into a 100-mL volumetric flask. Add 10 mL of synthetic ash solution and 10 mL of sodium stock solution, dilute with water to the mark, and mix. The solution contains 50 ppm of potassium. As the standard 10-ppm sodium solution contains 10 ppm of potassium, use it also for the standard 10-ppm potassium solution. Store in plastic bottles.

30.3 *Sodium, Concentrated Stock Solution* (100 ppm)—Dissolve 0.3088 ± 0.0005 g of dried sodium sulfate (Na_2SO_4) in water and dilute to 1000 mL.

30.4 *Sodium, Standard Solutions* (10 and 50 ppm)—Pipet 10 and 50 mL of sodium stock solution into separate 100-mL volumetric flasks. Add 10 mL of synthetic ash solution and 10 mL of potassium stock solution to each flask, dilute with water to the 100-mL mark, and mix. The solutions contain 10 and 50 ppm of sodium.

30.5 *Ash (Synthetic) Solution*:

30.5.1 Dissolve 2.0 g of iron in 10 mL of sulfuric acid (H_2SO_4) (1 + 1) and 100 mL of water.

30.5.2 Dissolve 1.0 g of aluminum in 10 mL of H_2SO_4 (1 + 1) and 100 mL of water.

30.5.3 Dissolve 1.25 g of $CaCO_3$ in 3 mL of H_2SO_4 (1 + 1) and about 600 mL of water.

30.5.4 Dissolve 1.0 g of magnesium sulfate ($MgSO_4 \cdot 7H_2O$) in water.

30.5.5 Combine the solutions in 30.5.1 through 30.5.4, filter, and dilute with water to 1000 mL.

31. Calibration

31.1 Prepare additional standard sodium solutions containing 1, 4, 20, 30, and 40 ppm of sodium and standard potassium solutions containing 1, 4, 20, 30 and 40 ppm of potassium. These are prepared by taking appropriate aliquots from the concentrated stock solutions (30.1 and 30.3) and proceeding as described in 30.2 and 30.4. Also prepare blank solutions, the sodium blank containing 10 mL of synthetic ash solution and 10 mL of stock potassium solution per 100 mL, and the potassium blank containing 10 mL of synthetic ash solution and 10 mL of sodium stock solution per 100 mL. Rinse each sample cup two times with the solution it is to contain before filling with the test solution. After adjusting the flame spectrophotometer according to the manufacturer's directions, set the wavelength to 589 nm and aspirate the 50-ppm sodium solution. Move the wavelength control slightly back and forth at the sodium wavelength to find the setting for maximum response. Finally, while aspirating the 50-ppm sodium solution, adjust the slit width and sensitivity to achieve a transmittance reading of 80 %. Rinse the aspirator with water, and determine the transmittance reading for the 40-ppm sodium solution. Repeat this operation, checking that the transmittance reads 80 % for the 50-ppm sodium solution, and take readings for the 30, 20, and 10-ppm sodium solutions. Test the blank solution, and subtract the blank reading from each determination. Prepare a working curve for the range from 10 to 50-ppm sodium. Make another working curve for the range from 1 to 10-ppm sodium. To do this, aspirate the 10-ppm sodium solution and increase the slit width sufficiently to obtain a transmittance reading of 80, and then determine readings for the 4 and 1-ppm sodium solutions. Make similar measurements for the standard potassium solutions at a wavelength of 768 nm, and plot the data obtained.

32. Procedure

32.1 Operate the flame spectrophotometer in the manner used for calibration. Rinse a sample cup with the solution it is to contain, and fill separate cups with standard 50 and 10 ppm of sodium solution, Sample Solution B, Blank Solution B, and water. Adjust the instrument for the 10 to 50-ppm range at the sodium wavelength (589 nm), using the standard 50-ppm sodium solution, and determine readings for the sample solution and the blank. When the sample solution contains less than 10 ppm of sodium, make readings in the 1 to 10-ppm range after adjusting the instrument with the 10-ppm sodium solution. For samples rich in sodium, dilute an aliquot of Solution B for the test. Make similar readings at 768 nm for potassium, using the standard 50 and 10-ppm potassium solutions to adjust the spectrophotometer. Subtract the blank reading from the sample reading, and determine the concentration of sodium and potassium (C_N and C_K) in the test solution from the appropriate working curve.

32.2 When using a flame filter photometer for determination of sodium, these spectral interferences should be noted. A 5:1 concentration of potassium-to-sodium and a 10:1 concentration of calcium-to-sodium produce spectral interferences that can result in an apparent increase in sodium content at the 589-nm sodium line.

33. Calculation

33.1 Calculate the percent Na_2O as follows:

$$Na_2O, \% = C_N \times 1.348/16 \tag{13}$$

where:

C_N = ppm sodium when 0.4 g of sample in 250 mL of Solution B is used.

33.2 Calculate the percent K_2O as follows:

$$K_2O, \% = C_K \times 1.2046/16 \tag{14}$$

where:

C_K = ppm potassium when 0.4 g of sample in 250 mL of Solution B is used.

NOTE 8—If $C_N = 10$ ppm, then the sodium contained in 250 mL = 0.0025 g which originally came from 0.4 g ash; that is,

$$[(\text{ppm Na} \times Na_2O/2\text{Na})/\text{ppm of sample}] \times 100 = Na_2O, \% \quad (15)$$

or

$$Na_2O, \% = [(0.0025)(1.348)/0.4] \times 100 = 0.84. \quad (16)$$

The factor 16 used in the above equations was derived from this kind of calculation and permits use of "parts per million" directly without conversion to "grams" of sodium or potassium.

34. Report

34.1 Report the percentages for the elemental oxides in the ash as specified in 12, 15, 18, 22, 25, 29, and 33.

34.2 Report the method used for concurrent moisture and ash determinations, if applicable.

34.3 Use Practice D 3180 for procedures to convert values to other bases.

35. Precision and Bias

35.1 *Precision*:

35.1.1 *Repeatability*—The difference in absolute value between the results of two consecutive tests, carried out on the same ash sample, in the same laboratory, by the same operator, using the same apparatus, should not exceed the repeatability limits for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability limit, there is reason to question one, or both, of the test results. The repeatability limits determined by these test methods are listed in Table 1.

35.1.2 *Reproducibility*—The difference in absolute value of replicate determinations carried out in different laboratories, on representative samples prepared from the same bulk ash sample, should not exceed the reproducibility limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility limit, there is reason to question one, or both, of the test results. The reproducibility limits determined by these test methods are listed in Table 1.

TABLE 1 Repeatability and Reproducibility Limits

Elemental Oxide	Percent of Ash	
	Repeatability	Reproducibility
SiO_2	1.0	2.0
Al_2O_3	0.7	2.0
Fe_2O_3	0.3	0.7
TiO_2	0.10	0.25
P_2O_5	0.05	0.15
CaO	0.2	0.4
MgO	0.3	0.5
Na_2O	0.1	0.3
K_2O	0.1	0.3

35.2 *Bias*—Bias has not been determined.

36. Keywords

36.1 aluminum oxide (Al_2O_3); calcium oxide (CaO); elemental ash composition; ferric oxide (Fe_2O_3); flame photometry; magnesium oxide (MgO); phosphorus pentoxide (P_2O_5); potassium oxide (K_2O); silicon dioxide (SiO_2); sodium oxide (Na_2O); titanium dioxide (TiO_2)