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Standard Test Methods for Chemical Analysis of Hydraulic Cement¹

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1. Scope*

1.1 These test methods cover the chemical analyses of hydraulic cements. Any test methods of demonstrated acceptable precision and bias may be used for analysis of hydraulic cements, including analyses for referee and certification purposes, as explained in Section 3. Specific chemical test methods are provided for ease of reference for those desiring to use them. They are grouped as Reference Test Methods and Alternative Test Methods. The reference test methods are long accepted classical chemical test methods which provide a reasonably well-integrated basic scheme of analysis for hydraulic cements. The alternative test methods generally provide individual determination of specific components and may be used alone or as alternates and determinations within the basic scheme at the option of the analyst and as indicated in the individual method.

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1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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. See 6.3.2.1 and 14.4.1 for specific caution statements.*

2. Referenced Documents

- 2.1 *ASTM Standards*:²
- C25 Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
 - D1193 Specification for Reagent Water
 - E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
 - E275 Practice for Describing and Measuring Performance

¹ These test methods are under the jurisdiction of ASTM Committee C01 on Cement and are the direct responsibility of Subcommittee C01.23 on Compositional Analysis.

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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.

*A Summary of Changes section appears at the end of this standard.

of Ultraviolet and Visible Spectrophotometers
E350 Test Methods for Chemical Analysis of Carbon Steel,
 Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and
 Wrought Iron

E617 Specification for Laboratory Weights and Precision
 Mass Standards

E832 Specification for Laboratory Filter Papers

3. Number of Determinations and Permissible Variations

3.1 *Referee Analyses*—When conformance to chemical specification requirements is questioned, perform referee analyses as described in 3.1.1. The reference test methods that follow in Sections 5-20, or other test methods qualified according to 3.3, are required for referee analysis. A cement shall not be rejected for failure to conform to chemical requirements unless all determinations of constituents involved and all necessary separations prior to the determination of any one constituent are made entirely by these methods. When reporting the results of referee analyses, specify which test methods were used.

3.1.1 Referee analyses shall be made in duplicate and the analyses shall be made on different days. If the two results do not agree within the permissible variation given in Table 1, the determination shall be repeated until two or three results agree within the permissible variation. When two or three results do agree within the permissible variation, their average shall be accepted as the correct value. When an average of either two or three results can be calculated, the calculation shall be based on the three results. For the purpose of comparing analyses and calculating the average of acceptable results, the percentages shall be calculated to the nearest 0.01 (or 0.001 in the case of chloroform-soluble organic substances), although some of the average values are reported to 0.1 as indicated in the test methods. When a blank determination (See Note 1) is specified, one shall be made with each individual analysis or with each group of two or more samples analyzed on the same day for a given component.

NOTE 1—A blank determination is a procedure which follows all steps of analysis but in the absence of a sample. It is used for detection and compensation of systematic bias.

3.1.2 Referee analyses or analyses intended for use as a basis for acceptance or rejection of a cement or for manufacturer's certification shall be made only after demonstration of precise and accurate analyses by the test methods in use by meeting the requirements of 3.1.3, except when demonstrated under 3.3.2.1. Such demonstration may be made concurrently with analysis of the cement being tested and must have been made within the preceding two years. The requirements for verification of equipment and personnel are summarized in Table 2. The demonstration is required only for those constituents being used as a basis for acceptance, rejection, or certification of a cement, but may be made for any constituent of cement for which a standard exists.

3.1.3 Initial qualification of the operator/analyst shall be demonstrated by analysis of each constituent of concern in at least one CRM cement (Note 2) no matter what test method is used (for example, gravimetric, instrumental). Duplicate

samples shall be run on different days. The same test methods to be used for analysis of cement being tested shall be used for analysis of the CRM cement. If the duplicate results do not agree within the permissible variation given in Table 1, the determinations shall be repeated, following identification and correction of problems or errors, until a set of duplicate results do agree within the permissible variation.

NOTE 2—The term CRM (Certified Reference Material) samples refers to NIST Hydraulic-Cement Chemical Standard Reference Materials, or other acceptable reference cement as defined in 3.1.6.

3.1.4 The average of the results of acceptable duplicate determinations for each constituent may differ from the CRM assigned value by no more than the value shown in column 2 of Table 1 after correction for minor components when needed.

3.1.5 Qualification data demonstrating that the same operator or analyst making the acceptance determination obtained precise and accurate results with CRM cements as per 3.1.3 shall be made available on request to all parties concerned when there is a question of acceptance of a cement. If the CRM used is not a NIST cement, the traceability documentation of the CRM used shall also be made available on request.

3.1.6 Acceptable reference cements are NIST CRMs (Note 2), or other reference cements traceable to the NIST CRMs. The reference cement must have an assigned value for the analyte being determined. Traceability consists of documentary evidence that the assigned values of the reference cement are compatible with the certified values of NIST CRMs. To demonstrate traceability for a given analyte, perform a referee analysis (as defined in 3.1) on the proposed reference cement, using a NIST CRM for demonstration of precision and accuracy. The reference cement is acceptable if its assigned value agrees with the average referee value within the limits given in column 3 of Table 1. If the reference cement, as supplied, has no documented guarantee of homogeneity, establish its homogeneity by analyzing at least six randomly selected samples. No result shall deviate from the assigned value by more than the limits given in column 2 of Table 1. An acceptable reference cement must be accompanied by a document showing the data produced in demonstrating traceability and homogeneity.

3.2 *Alternative Analyses*—The alternative test methods provide, in some cases, procedures that are shorter or more convenient to use for routine determination of certain constituents than are the reference test methods (Note 3). Longer, more complex procedures, in some instances, have been retained as alternative test methods to permit comparison of results by different procedures or for use when unusual materials are being examined, where unusual interferences may be suspected, or when unusual preparation for analysis is required.

TABLE 1 Maximum Permissible Variations in Results^A

(Column 1) Component	(Column 2) Maximum Difference Between Duplicates ^B	(Column 3) Maximum Difference of Average of Duplicates from SRM Certificate Values ^{C,D,E}
SiO ₂ (silicon dioxide)	0.16	±0.2
Al ₂ O ₃ (aluminum oxide)	0.20	±0.2
Fe ₂ O ₃ (ferric oxide)	0.10	±0.10
CaO (calcium oxide)	0.20	±0.3
MgO (magnesium oxide)	0.16	±0.2
SO ₃ (sulfur trioxide)	0.10	±0.1
LOI (loss on ignition)	0.10	±0.10
Na ₂ O (sodium oxide)	0.03	±0.05
K ₂ O (potassium oxide)	0.03	±0.05
TiO ₂ (titanium dioxide)	0.02	±0.03
P ₂ O ₅ (phosphorus pentoxide)	0.03	±0.03
ZnO (zinc oxide)	0.03	±0.03
Mn ₂ O ₃ (manganic oxide)	0.03	±0.03
S (sulfide sulfur)	0.01	E
Cl (chloride)	0.003	E
IR (insoluble residue)	0.10	E
Cx (free calcium oxide)	0.20	E
CO ₂ (carbon dioxide)	0.12	E, F
Alk _{sol} (water-soluble alkali) ^G	0.75/w	E
Chl _{sol} (chloroform-soluble organic substances)	0.004	E

^A When seven CRM cements are required, as for demonstrating the performance of rapid test methods, at least six of the seven shall be within the prescribed limits and the seventh shall differ by no more than twice that value. When more than seven CRMs are used, as for demonstrating the performance of rapid test methods, at least 77 % shall be within the prescribed limits, and the remainder by no more than twice the value. When a lesser number of CRM cements are required, all of the values shall be within the prescribed limits.

^B Where no value appears in Column 3, CRM certificate values do not exist. In such cases, only the requirement for differences between duplicates shall apply.

^C Inter-element corrections may be used for any oxide standardization provided improved accuracy can be demonstrated when the correction is applied to all seven CRM cements.

^D Where an CRM certificate value includes a subscript number, that subscript number shall be treated as a valid significant figure.

^E Not applicable. No certificate value given.

^F Demonstrate performance by analysis, in duplicate, of at least one Portland cement. Prepare three standards, each in duplicate: Standard A shall be selected Portland cement; Standard B shall be Standard A containing 2.00 % Certified CaCO₃ (such as NIST 915a); Standard C shall be Standard A containing 5.00 % Certified CaCO₃. Weigh and prepare two separate specimens of each standard. Assign the CO₂ content of Standard A as the average of the two values determined, provided they agree within the required limit of Column 2. Assign CO₂ values to Standards B and C as follows: Multiply the Certified CaCO₃ value (Y) for CO₂ (from the certificate value) by the mass fraction of Certified CaCO₃ added to that standard (percentage added divided by 100); multiply the value determined for Standard A by the mass fraction of Standard A in each of the other standards (that is, 0.98 and 0.95 for Standards B and C, respectively); add the two values for Standard A and for Standard B, respectively; call these values B and C.

Example:

$$B = 0.98A + 0.02Y.$$

$$C = 0.95A + 0.05Y.$$

Where for Certified CaCO₃, if Y = 39.9 %

$$B = 0.98A + 0.80 \% \text{ by mass.}$$

$$C = 0.95A + 2.00 \% \text{ by mass.}$$

Maximum difference between the duplicate CO₂ values for Standards B and C, respectively, shall be 0.17 and 0.24 % by mass. Averages of the duplicate values for Standards B and C shall differ from their assigned values (B and C) by no more than 10 % of those respective assigned values.

^G w = weight, in grams, of samples used for the test.

Test results from alternative test methods may be used as a basis for acceptance or rejection when it is clear that a cement does or does not meet the specification requirement. Any change in test method procedures from those procedures listed in Sections 5-28 requires method qualification in accordance with 3.3.

TABLE 2 Minimum Number of CRMs Required for Qualification of Chemical Testing

	Method Type	
	Reference ^A	Other ^B
Equipment Qualification	None	7
Operator Qualification ^C	1	1

^AReference Methods are those outlined in Sections 5-20.

^BThese may be any test method as described in 3.2 or any instrumental or rapid test method, which must be qualified in accordance with 3.3.

^CEach operator performing acceptance or reference analyses must be qualified in accordance with 3.1.3 at a frequency of two years. If qualification of the instrument is completed by a single operator, the operator has demonstrated individual qualifications per 3.1.3.

NOTE 3—It is not intended that the use of reference test methods be confined to referee analysis. A reference test method may be used in preference to an alternative test method when so desired. A reference test method must be used where an alternative test method is not provided.

3.2.1 Duplicate analyses and blank determinations are not required when using the alternative test methods. If, however, a blank determination is desired for an alternative test method, one may be used and it need not have been obtained concurrently with the analysis. The final results, when corrected for blank values, should, in either case, be so designated.

3.3 Performance Requirements for Rapid Test Methods:³

3.3.1 *Definition and Scope*—Where analytical data obtained in accordance with this test method are required, any test method may be used that meets the requirements of 3.3.2. A test method is considered to consist of the specific procedures, reagents, supplies, equipment, instrument, etc. selected and used in a consistent manner by a specific laboratory. See Note 4 for examples of procedures.

NOTE 4—Examples of test methods used successfully by their authors for analysis of hydraulic cement are given in the list of references. Included are test methods using atomic absorption X-ray spectrometry, and spectrophotometry-EDTA.

3.3.1.1 If more than one instrument, even though substantially identical, is used in a specific laboratory for the same analyses, use of each instrument shall constitute a separate test method and each must be qualified separately.

3.3.2 *Qualification of a Test Method*—Prior to use for analysis of hydraulic cement, each test method (see 3.3.1) must be qualified individually for such analysis. Qualification data, or if applicable, requalification data, shall be made available pursuant to the Manufacturer's Certification Section of the appropriate hydraulic cement specification.

3.3.2.1 Using the test method chosen, make single determinations for each oxide under consideration on at least seven CRM samples (Note 2). Complete two rounds of tests on different days repeating all steps of sample preparations. Calculate the differences between values and averages of the values from the two rounds of tests.

3.3.2.2 When seven CRMs are used in the qualification procedure, at least six of the seven differences between duplicates obtained of any single component shall not exceed the limits shown in Column 2 of Table 1 and the remaining

³ Gebhardt, R. F., "Rapid Methods for Chemical Analysis of Hydraulic Cement," ASTM STP 985, 1988.

differences by no more than twice that value. When more than seven CRMs are used, the values for at least 77 % of the samples shall be within the prescribed limits, while the values for the remainder shall differ by no more than twice that value.

3.3.2.3 For each component and each CRM, the average obtained shall be compared to the certified concentrations. Where a certificate value includes a subscript number, that subscript shall be assumed to be a significant number. When seven CRMs are used in the qualification procedure, at least six of the seven averages for each component (oxide) shall not differ from the certified concentrations by more than the value shown in Column 3 of **Table 1**, and the remaining average by more than twice that value. When more than seven CRMs are used in the qualification procedure, at least 77 % of the averages for each component (oxide) shall not differ from the certified concentrations by more than the value shown in Column 3 of **Table 1**, and the remaining average(s) by more than twice that value.

3.3.2.4 The standardization, if needed, used for qualification and for analysis of each constituent shall be determined by valid curve-fitting procedures. A point-to-point, saw-tooth curve that is artificially made to fit a set of data points does not constitute a valid curve-fitting procedure. A complex polynomial drawn through the points is similarly not valid. For the same reason, empirical inter-element corrections may be used, only if $\leq (N - 3)/2$ are employed, where N is the number of different standards used. The qualification testing shall be conducted with specimens newly prepared from scratch, including all the preparation stages applicable for analysis of an unknown sample, and employing the reagents currently in use for unknown analyses.

3.3.3 *Partial Results*—Test Methods that provide acceptable results for some components but not for others may be used only for those components for which acceptable results are obtained.

3.3.4 *Report of Results*—Chemical analyses obtained by qualified rapid test methods and reported pursuant to the Manufacturer's Certification Section of the appropriate hydraulic cement specification shall be indicated as having been obtained by rapid methods and the type of test method used shall be designated.

3.3.5 *Rejection of Material*—See **3.1** and **3.2**.

3.3.6 *Requalification of a Test Method*:

3.3.6.1 Requalification of a test method shall be required upon receipt of substantial evidence that the test method may not be providing data in accordance with **Table 1** for one or more constituents. Such requalification may be limited to those constituents indicated to be in error and shall be carried out prior to further use of the method for analysis of those constituents.

3.3.6.2 Substantial evidence that a test method may not be providing data in accordance with **Table 1** shall be considered to have been received when a laboratory is informed that analysis of the same material by Reference Test Methods run in accordance with **3.1.1**, the final average of a CCRL sample, a certificate value of an NIST CRM, the assigned value of an alternate CRM, or an accepted value of a known secondary standard differs from the value obtained by the test method in

question by more than twice the value shown in Column 2 of **Table 1** for one or more constituents. When indirect test methods are involved, as when a value is obtained by difference, corrections shall be made for minor constituents in order to put analyses on a comparable basis prior to determining the differences. (See **Note 5**.) For any constituents affected, a test method also shall be requalified after any substantial repair or replacement of one or more critical components of an instrument essential to the test method.

NOTE 5—Instrumental analyses can usually detect only the element sought. Therefore, to avoid controversy, the actual procedure used for the elemental analyses should be noted when actual differences with reference procedures can exist. For example, P_2O_5 and TiO_2 are included with Al_2O_3 in the usual wet test method and sulfide sulfur is included in most instrumental procedures with SO_3 .

3.3.6.3 If an instrument or piece of equipment is replaced, even if by one of identical make or model, or is significantly modified, a previously qualified test method using such new or modified instrument or equipment shall be considered a new method and must be qualified in accordance with **3.3.2**.

3.4 *Precision and Bias*—Different analytical test methods are subject to individual limits of precision and bias. It is the responsibility of the user to demonstrate that the test methods used at least meet the limits of precision and bias shown in **Table 1**.

4. General

4.1 *Interferences and Limitations*:

4.1.1 These test methods were developed primarily for the analysis of portland cements. However, except for limitations noted in the procedure for specific constituents, the reference test methods provide for accurate analyses of other hydraulic cements that are completely decomposed by hydrochloric acid, or where a preliminary sodium carbonate fusion is made to ensure complete solubility. Some of the alternative test methods may not always provide accurate results because of interferences from elements which are not removed during the procedure.

4.1.2 When using a test method that determines total sulfur, such as most instrumental test methods, sulfide sulfur will be determined with sulfate and included as such. In most hydraulic cements, the difference resulting from such inclusion will be insignificant, less than 0.05 weight %. In some cases, notably slags and slag-containing cements but sometimes other cements as well, significant levels of sulfide may be present. In such cases, especially if there is a question of meeting or not meeting a specification limit or when the most accurate results are desired, analytical test methods shall be chosen so that sulfate and sulfide can be reported separately.

4.2 *Apparatus and Materials*:

4.2.1 *Balance*—The analytical balance used in the chemical determinations shall conform to the following requirements:

4.2.1.1 The balance shall be capable of reproducing results within 0.0002 g with an accuracy of ± 0.0002 g. Direct-reading balances shall have a sensitivity not exceeding 0.0001 g (**Note 6**). Conventional two-pan balances shall have a maximum sensibility reciprocal of 0.0003 g. Any rapid weighing device that may be provided, such as a chain, damped motion, or heavy riders, shall not increase the basic inaccuracy by more

than 0.0001 g at any reading and with any load within the rated capacity of the balance.

NOTE 6—The sensitivity of a direct-reading balance is the weight required to change the reading one graduation. The sensibility reciprocal for a conventional balance is defined as the change in weight required on either pan to change the position of equilibrium one division on the pointer scale at capacity or at any lesser load.

4.2.2 Weights—Weights used for analysis shall conform to Types I or II, Grades S or O, Classes 1, 2, or 3 as described in Specification **E617**. They shall be checked at least once a year, or when questioned, and adjusted at least to within allowable tolerances for Class 3 weights (**Note 7**). For this purpose each laboratory shall also maintain, or have available for use, a reference set of standard weights from 50 g to 10 mg, which shall conform at least to Class 3 requirements and be calibrated at intervals not exceeding five years by the National Institute of Standards and Technology (NIST). After initial calibration, recalibration by the NIST may be waived provided it can be shown by documented data obtained within the time interval specified that a weight comparison between summations of smaller weights and a single larger weight nominally equal to that summation, establishes that the allowable tolerances have not been exceeded. All new sets of weights purchased shall have the weights of 1 g and larger made of stainless steel or other corrosion-resisting alloy not requiring protective coating, and shall meet the density requirements for Grades S or O.

NOTE 7—The scientific supply houses do not presently list weights as meeting Specification **E617**. They list weights as meeting NIST or OIML standards. The situation with regard to weights is in a state of flux because of the trend toward internationalization. Hopefully this will soon be resolved.

NIST Classes S and S-1 and OIML Class F_1 weights meet the requirements of this standard.

4.2.3 Glassware and Laboratory Containers—Standard volumetric flasks, burets, and pipets should be of precision grade or better. Standard-taper, interchangeable, ground-glass joints are recommended for all volumetric glassware and distilling apparatus, when available. Wherever applicable, the use of special types of glassware, such as colored glass for the protection of solutions against light, alkali-resistant glass, and high-silica glass having exceptional resistance to thermal shock is recommended. Polyethylene containers are recommended for all aqueous solutions of alkalis and for standard solutions where the presence of dissolved silica or alkali from the glass would be objectionable. Such containers shall be made of high-density polyethylene having a wall thickness of at least 1 mm.

4.2.4 Desiccators—Desiccators shall be provided with a good desiccant, such as magnesium perchlorate, activated alumina, or sulfuric acid. Anhydrous calcium sulfate may also be used provided it has been treated with a color-change indicator to show when it has lost its effectiveness. Calcium chloride is not a satisfactory desiccant for this type of analysis.

4.2.5 Filter Paper—Filter paper shall conform to the requirements of Specification **E832**, Type II, Quantitative. When coarse-textured paper is required, Class E paper shall be used, when medium-textured paper is required, Class F paper shall be used, and when retentive paper is required, Class G shall be used.

4.2.6 Crucibles—Platinum crucibles for ordinary chemical analysis should preferably be made of pure unalloyed platinum and be of 15 to 30-mL capacity. Where alloyed platinum is used for greater stiffness or to obviate sticking of crucible and lid, the alloyed platinum should not decrease in weight by more than 0.2 mg when heated at 1200 °C for 1 h.

4.2.7 Muffle Furnace—The muffle furnace shall be capable of operation at the temperatures required and shall have an indicating pyrometer accurate within ± 25 °C, as corrected, if necessary, by calibration. More than one furnace may be used provided each is used within its proper operating temperature range.

4.3 Reagents:

4.3.1 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.⁴ 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.

4.3.2 Unless otherwise indicated, references to water shall mean water conforming to the numerical limits for Type II reagent water described in Specification **D1193**.

4.3.3 Concentration of Reagents:

4.3.3.1 Prepackaged Reagents—Commercial prepackaged standard solutions or diluted prepackaged concentrations of a reagent may be used whenever that reagent is called for in the procedures provided that the purity and concentrations are as specified. Verify purity and concentration of such reagents by suitable tests.

4.3.3.2 Concentrated Acids and Ammonium Hydroxide—When acids and ammonium hydroxide are specified by name or chemical formula only, it shall be understood that concentrated reagents of the following specific gravities or concentrations by weight are intended:

Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$)	99.5 %
Hydrochloric acid (HCl)	sp gr 1.19
Hydrofluoric acid (HF)	48 %
Nitric acid (HNO_3)	sp gr 1.42
Phosphoric acid (H_3PO_4)	85 %
Sulfuric acid (H_2SO_4)	sp gr 1.84
Ammonium hydroxide (NH_4OH)	sp gr 0.90

4.3.3.3 The desired specific gravities or concentrations of all other concentrated acids shall be stated whenever they are specified.

4.3.4 Diluted Acids and Ammonium Hydroxide—Concentrations of diluted acids and ammonium hydroxide, except when standardized, are specified as a ratio stating the number of volumes of the concentrated reagent to be added to a given number of volumes of water, for example: HCl (1+99) means 1 volume of concentrated HCl (sp gr 1.19) added to 99 volumes of water.

⁴ *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. Pharmacopeia Convention, Inc. (USPC), Rockville, MD.

4.3.5 *Standard Solutions*—Concentrations of standard solutions shall be expressed as normalities (*N*) or as equivalents in grams per millilitre of the component to be determined, for example: 0.1 *N* Na₂S₂O₃ solution or K₂Cr₂O₇ (1 mL = 0.004 g Fe₂O₃). The average of at least three determinations shall be used for all standardizations. When a material is used as a primary standard, reference has generally been made to the standard furnished by NIST. However, when primary standard grade materials are otherwise available they may be used or the purity of a salt may be determined by suitable tests.

4.3.6 *Nonstandardized Solutions*—Concentrations of nonstandardized solutions prepared by dissolving a given weight of the solid reagent in a solvent shall be specified in grams of the reagent per litre of solution, and it shall be understood that water is the solvent unless otherwise specified, for example: NaOH solution (10 g/L) means 10 g of NaOH dissolved in water and diluted with water to 1 L. Other nonstandardized solutions may be specified by name only, and the concentration of such solutions will be governed by the instructions for their preparation.

4.3.7 *Indicator Solutions:*

4.3.7.1 *Methyl Red*—Prepare the solution on the basis of 2 g of methyl red/L of 95 % ethyl alcohol.

4.3.7.2 *Phenolphthalein*—Prepare the solution on the basis of 1 g of phenolphthalein/L of 95 % ethyl alcohol.

4.4 *Sample Preparation:*

4.4.1 Before testing, pass representative portions of each sample through a No. 20 (850- μ m) sieve, or any other sieve having approximately 20 openings/1 in., in order to mix the sample, break up lumps, and remove foreign materials. Discard the foreign materials and hardened lumps that do not break up on sieving or brushing.

4.4.2 By means of a sample splitter or by quartering, the representative sample shall be reduced to a laboratory sample of at least 50 g. Where larger quantities are required for additional determinations such as water-soluble alkali, chloride, duplicate testing, etc., prepare a sample of at least 100 g.

4.4.3 Pass the laboratory sample through a U.S. No. 100 sieve (sieve opening of 150 μ m). Further grind the sieve

residue so that it also passes the No. 100 sieve. Homogenize the entire sample by again passing it through the sieve.

4.4.4 Transfer the sample to a clean, dry, glass container with an airtight lid and further mix the sample thoroughly.

4.4.5 Expedite the above procedure so that the sample is exposed to the atmosphere for a minimum time.

4.5 *General Procedures:*

4.5.1 *Weighing*—The calculations included in the individual test methods assume that the exact weight specified has been used. Accurately weighed samples, that are approximately but not exactly equal to the weight specified, may be used provided appropriate corrections are made in the calculations. Unless otherwise stated, weights of all samples and residues should be recorded to the nearest 0.0001 g.

4.5.2 *Tared or Weighed Crucibles*—The tare weight of crucibles shall be determined by preheating the empty crucible to constant weight at the same temperature and under the same conditions as shall be used for the final ignition of a residue and cooling in a desiccator for the same period of time used for the crucible containing the residue.

4.5.3 *Constancy of Weight of Ignited Residues*—To definitely establish the constancy of weight of an ignited residue for referee purposes, the residue shall be ignited at the specified temperature and for the specified time, cooled to room temperature in a desiccator, and weighed. The residue shall then be reheated for at least 30 min, cooled to room temperature in a desiccator, and reweighed. If the two weights do not differ by more than 0.2 mg, constant weight is considered to have been attained. If the difference in weights is greater than 0.2 mg, additional ignition periods are required until two consecutive weights agree within the specified limits. For ignition loss, each reheating period shall be 5 min.

4.5.4 *Volatilization of Platinum*—The possibility of volatilization of platinum or alloying constituents from the crucibles must be considered. On reheating, if the crucible and residue lose the same weight (within 0.2 mg) as the crucible containing the blank, constant weight can be assumed. Crucibles of the same size, composition, and history shall be used for both the sample and the blank.

4.5.5 *Calculation*—In all operations on a set of observed values such as manual multiplication or division, retain the equivalent of at least two more places of figures than in the single observed values. For example, if observed values are read or determined to the nearest 0.1 mg, carry numbers to the nearest 0.001 mg in calculation. When using electronic calculators or computers for calculations, perform no rounding, except in the final reported value.

4.5.6 *Rounding Figures*—Rounding of figures to the number of significant places required in the report should be done after calculations are completed, in order to keep the final results substantially free of calculation errors. The rounding procedure should follow the principle outlined in Practice E29.⁵ In assessing analyst- and method-qualification in accordance with Section 3, the individual duplicate results, the difference between them, the average of duplicates on CRMs,

TABLE 3 Rounding of Reported Results

Component	Decimal Places
SiO ₂ (silicon dioxide)	1
Al ₂ O ₃ (aluminum oxide)	1
Fe ₂ O ₃ (ferric oxide)	2
CaO (calcium oxide)	1
MgO (magnesium oxide)	1
SO ₃ (sulfur trioxide)	2
Loss (loss on ignition)	1
Na ₂ O (sodium oxide)	2
K ₂ O (potassium oxide)	2
SrO (strontium oxide)	2
TiO ₂ (titanium dioxide)	2
P ₂ O ₅ (phosphorous pentoxide)	2
ZnO (zinc oxide)	2
Mn ₂ O ₃ (manganic oxide)	3
S (sulfide sulfur)	2
Cl (chloride)	3
IR (insoluble residue)	2
FL (free calcium oxide)	1
CO ₂ (carbon dioxide)	1
Water-soluble Alkali	2
Chloroform-soluble Organic Substances	3

⁵ See also the *ASTM Manual on Presentation of Data and Control Chart Analysis, STP 15D, 1976.*

and the difference of this average from the certificate value shall be left un-rounded for comparison with the required limits. Round results for reporting as shown in **Table 3**.

NOTE 8—The rounding procedure referred to in **4.5.6**, in effect, drops all digits beyond the number of places to be retained if the next figure is less than 5. If it is more than 5, or equal to 5 and subsequent places contain a digit other than 0, then the last retained digit is increased by one. When the next digit is equal to 5 and all other subsequent digits are 0, the last digit to be retained is unchanged when it is even and increased by one when it is odd. For example 3.96 (50) remains 3.96 but 3.95 (50) becomes 3.96.

4.6 Recommended Order for Reporting Analyses—The following order is recommended for reporting the results of chemical analysis of portland cement:

Major Components:

- SiO₂(silicon dioxide)
- Al₂O₃(aluminum oxide)
- Fe₂O₃(ferric oxide)
- CaO (calcium oxide)
- MgO (magnesium oxide)
- SO₃(sulfur trioxide)
- Loss on ignition

Minor Components:

- Na₂O (sodium oxide)
- K₂O (potassium oxide)
- TiO₂(titanium dioxide)
- P₂O₅(phosphorus pentoxide)
- ZnO (zinc oxide)
- Mn₂O₃(manganic oxide)
- Sulfide sulfur

Separate Determinations:

- Insoluble residue
- Free calcium oxide
- CO₂(Carbon Dioxide)
- Water-soluble alkali
- Chloroform—soluble organic substances

REFERENCE TEST METHODS

5. Insoluble Residue (Reference Test Method)

5.1 Summary of Test Method:

5.1.1 In this test method, insoluble residue of a cement is determined by digestion of the sample in hydrochloric acid followed, after filtration, by further digestion in sodium hydroxide. The resulting residue is ignited and weighed (**Note 9**).

NOTE 9—This test method, or any other test method designed for the estimation of an acid-insoluble substance in any type of cement, is empirical because the amount obtained depends on the reagents and the time and temperature of digestion. If the amount is large, there may be a little variation in duplicate determinations. The procedure should be followed closely in order to reduce the variation to a minimum.

5.1.2 When this test method is used on blended cement, the decomposition in acid is considered to be complete when the portland-cement clinker is decomposed completely. An ammonium nitrate solution is used in the final washing to prevent finely-ground insoluble material from passing through the filter paper.

5.2 Reagents:

5.2.1 Ammonium Nitrate Solution (20 g NH₄NO₃/L).

5.2.2 Sodium Hydroxide Solution (10 g NaOH/L).

5.3 Procedure:

5.3.1 To 1 g of the sample (**Note 10**) add 25 mL of cold water. Disperse the cement in the water and while swirling the

mixture, quickly add 5 mL of HCl. If necessary, warm the solution gently, and grind the material with the flattened end of a glass rod for a few minutes until it is evident that decomposition of the cement is complete (**Note 11**). Dilute the solution to 50 mL with hot water (nearly boiling) and heat the covered mixture rapidly to near boiling by means of a high-temperature hot plate. Then digest the covered mixture for 15 min at a temperature just below boiling (**Note 12**). Filter the solution through a medium-textured paper into a 400-mL beaker, wash the beaker, paper, and residue thoroughly with hot water, and reserve the filtrate for the sulfur trioxide determination, if desired (**Note 13**). Transfer the filter paper and contents to the original beaker, add 100 mL of hot (near boiling) NaOH solution (10 g/L), and digest at a temperature just below boiling for 15 min. During the digestion, occasionally stir the mixture and macerate the filter paper. Acidify the solution with HCl using methyl red as the indicator and add an excess of 4 or 5 drops of HCl. Filter through medium-textured paper and wash the residue at least 14 times with hot NH₄ NO₃ solution (20 g/L) making certain to wash the entire filter paper and contents during each washing. Ignite the residue in a weighed platinum crucible at 900 to 1000 °C, cool in a desiccator, and weigh.

NOTE 10—If sulfur trioxide is to be determined by turbidimetry it is permissible to determine the insoluble residue on a 0.5-g sample. In this event, the percentage of insoluble residue should be calculated to the nearest 0.01 by multiplying the weight of residue obtained by 200. However, the cement should not be rejected for failure to meet the insoluble residue requirement unless a 1-g sample has been used.

NOTE 11—If a sample of portland cement contains an appreciable amount of manganic oxide, there may be brown compounds of manganese which dissolve slowly in cold diluted HCl but rapidly in hot HCl in the specified strength. In all cases, dilute the solution as soon as decomposition is complete.

NOTE 12—In order to keep the solutions closer to the boiling temperature, it is recommended that these digestions be carried out on an electric hot plate rather than in a steam bath.

NOTE 13—Continue with the sulfur trioxide determination (**15.1.2.1-15.1.3**) by diluting to 250 or 200 mL as required by the appropriate section.

5.3.2 *Blank*—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

5.4 *Calculation*— Calculate the percentage of the insoluble residue to the nearest 0.01 by multiplying the weight in grams of the residue (corrected for the blank) by 100.

6. Silicon Dioxide (Reference Test Method)

6.1 *Selection of Test Method*—For cements other than portland and for which the insoluble residue is unknown, determine the insoluble residue in accordance with Section 5 of these test methods. For portland cements and other cements having an insoluble residue less than 1 %, proceed in accordance with 6.2. For cements having an insoluble residue greater than 1 % proceed in accordance with 6.3.

6.2 *Silicon Dioxide in Portland Cements and Cements with Low Insoluble Residue:*

6.2.1 *Summary of Test Method*—In this test method silicon dioxide (SiO₂) is determined gravimetrically. Ammonium chloride is added and the solution is not evaporated to dryness.

This test method was developed primarily for hydraulic cements that are almost completely decomposed by hydrochloric acid and should not be used for hydraulic cements that contain large amounts of acid-insoluble material and require a preliminary sodium carbonate fusion. For such cements, or if prescribed in the standard specification for the cement being analyzed, the more lengthy procedure in 6.3 shall be used.

6.2.2 *Reagent*—Ammonium chloride (NH_4Cl).

6.2.3 *Procedure*:

6.2.3.1 Mix thoroughly 0.5 g of the sample and about 0.5 g of NH_4Cl in a 50-mL beaker, cover the beaker with a watch glass, and add cautiously 5 mL of HCl, allowing the acid to run down the lip of the covered beaker. After the chemical action has subsided, lift the cover, add 1 or 2 drops of HNO_3 , stir the mixture with a glass rod, replace the cover, and set the beaker on a steam bath for 30 min (Note 14). During this time of digestion, stir the contents occasionally and break up any remaining lumps to facilitate the complete decomposition of the cement. Fit a medium-textured filter paper to a funnel, transfer the jelly-like mass of silicic acid to the filter as completely as possible without dilution, and allow the solution to drain through. Scrub the beaker with a policeman and rinse the beaker and policeman with hot HCl (1+99). Wash the filter two or three times with hot HCl (1+99) and then with ten or twelve small portions of hot water, allowing each portion to drain through completely. Reserve the filtrate and washings for the determination of the ammonium hydroxide group (Note 15).

NOTE 14—A hot plate may be used instead of a steam bath if the heat is so regulated as to approximate that of a steam bath.

Under conditions where water boils at a lower temperature than at sea level: such as at higher elevations, 30 min may not be sufficient to recover all of the silica. In such cases, increase the time of digestion as necessary to get complete recovery of the silica. In no case should this time exceed 60 min.

NOTE 15—Determine the ammonium hydroxide group in accordance with the procedure described in 7.1-7.3.

6.2.3.2 Transfer the filter paper and residue to a weighed platinum crucible, dry, and ignite, at first slowly until the carbon of the paper is completely consumed without inflaming, and finally at 1100 to 1200 °C for 1 h. Cool in a desiccator and weigh. Reignite to constant weight. Treat the SiO_2 thus obtained, which will contain small amounts of impurities, in the crucible with 1 or 2 mL of water, 2 drops of H_2SO_4 (1+1), and about 10 mL of HF, and evaporate cautiously to dryness. Finally, heat the small residue at 1050 to 1100 °C for 5 min, cool in a desiccator, and weigh. The difference between this weight and the weight previously obtained represents the weight of SiO_2 . Consider the weighed residue remaining after the volatilization of SiO_2 as combined aluminum and ferric oxides and add it to the result obtained in the determination of the ammonium hydroxide group.

6.2.3.3 If the HF residue exceeds 0.0020 g, the silica determination shall be repeated, steps should be taken to ensure complete decomposition of the sample before a silica separation is attempted, and the balance of the analysis (ammonium hydroxide group, CaO, and MgO) determined on the new silica filtrate provided the new silica determination has a HF residue of 0.0020 g or less except as provided in 6.2.3.4 and 6.2.3.5.

6.2.3.4 If two or three repeated determinations of a sample of portland cement consistently show HF residues higher than 0.0020 g, this is evidence that contamination has occurred in sampling or the cement has not been burned properly during manufacture. In such a case, do not fuse the large HF residue with pyrosulfate for subsequent addition to the filtrate from the silica separation. Instead, report the value obtained for the HF residue. Do not ignite the ammonium hydroxide group in the crucible containing this abnormally large HF residue.

6.2.3.5 In the analysis of cements other than portland, it may not always be possible to obtain HF residues under 0.0020 g. In such cases, add 0.5 g of sodium or potassium pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$ or $\text{K}_2\text{S}_2\text{O}_7$) to the crucible and heat below red heat until the small residue of impurities is dissolved in the melt (Note 16). Cool, dissolve the fused mass in water, and add it to the filtrate and washings reserved for the determination of the ammonium hydroxide group.

NOTE 16—A supply of nonspattering pyrosulfate may be prepared by heating some pyrosulfate in a platinum vessel below red heat until the foaming and spattering cease, cooling, and crushing the fused mass.

6.2.3.6 *Blank*—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

6.2.4 *Calculation*— Calculate the percentage of SiO_2 by multiplying the mass in grams of SiO_2 by 200 (100 divided by the mass (see 6.2.3.1) or equivalent mass (see 6.3.2.1) of the sample used (0.5 g)). Round in accordance with Table 3.

6.3 *Silicon Dioxide in Cements with Insoluble Residue Greater Than 1 %*:

6.3.1 *Summary of Test Method*—This test method is based on the sodium carbonate fusion followed by double evaporation to dryness of the hydrochloric acid solution of the fusion product to convert silicon dioxide (SiO_2) to the insoluble form. The solution is filtered and the insoluble siliceous residue is ignited and weighed. Silicon dioxide is volatilized by hydrofluoric acid and the loss of weight is reported as pure SiO_2 .

6.3.2 *Procedure*:

6.3.2.1 Weigh a quantity of the ignited sample equivalent to 0.5 g of the as-received sample calculated as follows:

$$W = [(0.5 (100.00 - I))/100] \quad (1)$$

where:

W = weight of ignited sample, g, and

I = loss of ignition, %.

The ignited material from the loss on ignition determination may be used for the sample. Thoroughly mix the sample with 4 to 6 g of Na_2CO_3 by grinding in an agate mortar. Place a thin layer of Na_2CO_3 on the bottom of a platinum crucible of 20 to 30-mL capacity, add the cement- Na_2CO_3 mixture, and cover the mixture with a thin layer of Na_2CO_3 . Place the covered crucible over a moderately low flame and increase the flame gradually to a maximum (approximately 1100 °C) and maintain this temperature until the mass is quiescent (about 45 min). Remove the burner, lay aside the cover of the crucible, grasp the crucible with tongs, and slowly rotate the crucible so that the molten contents spread over the sides and solidify as a thin shell on the interior. Set the crucible and cover aside to cool. Rinse off the outside of the crucible and place the crucible on

its side in a 300-mL casserole about one third full of water. Warm the casserole and stir until the cake in the crucible disintegrates and can be removed easily. By means of a glass rod, lift the crucible out of the liquid, rinsing it thoroughly with water. Rinse the cover and crucible with HCl (1+3); then add the rinse to the casserole. Very slowly and cautiously add 20 mL of HCl (sp gr 1.19) to the covered casserole. Remove the cover and rinse. If any gritty particles are present, the fusion is incomplete and the test must be repeated, using a new sample.

Warning—Subsequent steps of the test method must be followed exactly for accurate results.

6.3.2.2 Evaporate the solution to dryness on a steam bath (there is no longer a gelatinous appearance). Without heating the residue any further, treat it with 5 to 10 mL of HCl, wait at least 2 min, and then add an equal amount of water. Cover the dish and digest for 10 min on the steam bath or a hot plate. Dilute the solution with an equal volume of hot water, immediately filter through medium-textured paper and wash the separated SiO₂ thoroughly with hot HCl (1+99), then with hot water. Reserve the residue.

6.3.2.3 Again evaporate the filtrate to dryness, and bake the residue in an oven for 1 h at 105 to 110 °C. Cool, add 10 to 15 mL of HCl (1+1), and digest on the steam bath or hot plate for 10 min. Dilute with an equal volume of water, filter immediately on a fresh filter paper, and wash the small SiO₂ residue thoroughly as described in 6.3.2.2. Stir the filtrate and washings and reserve for the determination of the ammonium hydroxide group in accordance with 7.1-7.3.

6.3.2.4 Continue the determination of silicon dioxide in accordance with 6.2.3.2.

7. Ammonium Hydroxide Group (Reference Test Method)

7.1 *Summary of Test Method*—In this test method aluminum, iron, titanium, and phosphorus are precipitated from the filtrate, after SiO₂ removal, by means of ammonium hydroxide. With care, little if any manganese will be precipitated. The precipitate is ignited and weighed as the oxides.

7.2 Procedure:

7.2.1 To the filtrate reserved in accordance with 6.2.3.1 (Note 17) which should have a volume of about 200 mL, add HCl if necessary to ensure a total of 10 to 15 mL of the acid. Add a few drops of methyl red indicator and heat to boiling. Then treat with NH₄OH (1+1) (Note 18), dropwise until the color of the solution becomes distinctly yellow, and add one drop in excess (Note 19). Heat the solution containing the precipitate to boiling and boil for 50 to 60 s. In the event difficulty from bumping is experienced while boiling the ammoniacal solution, a digestion period of 10 min on a steam bath, or on a hot plate having the approximate temperature of a steam bath, may be substituted for the 50 to 60-s boiling period. Allow the precipitate to settle (not more than 5 min) and filter using medium-textured paper (Note 20). Wash, with hot ammonium nitrate (NH₄NO₃, 20 g/L) (Note 21), twice for a small precipitate to about four times for a large one.

NOTE 17—If a platinum evaporating dish has been used for the dehydration of SiO₂, iron may have been partially reduced. At this stage, add about 3 mL of saturated bromine water to the filtrate and boil the filtrate to eliminate the excess bromine before adding the methyl red indicator. If difficulty from bumping is experienced during the boiling, the

following alternate techniques may be helpful: (1) a piece of filter paper, approximately 1 cm² in area, positioned where the bottom and side of the beaker merge and held down by the end of a stirring rod may solve the difficulty, and (2) use of 400-mL beakers supported inside a cast aluminum cup has also been found effective.

NOTE 18—The NH₄OH used to precipitate the hydroxides must be free of contamination with carbon dioxide (CO₂).

NOTE 19—It usually takes 1 drop of NH₄OH (1+1) to change the color of the solution from red to orange and another drop to change the color from orange to yellow. If desired, the addition of the indicator may be delayed until ferric hydroxide (Fe(OH)₃) is precipitated without aluminum hydroxide (Al(OH)₃) being completely precipitated. In such a case, the color changes may be better observed. However, if the content of Fe₂O₃ is unusually great, it may be necessary to occasionally let the precipitate settle slightly so that the color of the supernatant liquid can be observed. If the color fades during the precipitation, add more of the indicator. Observation of the color where a drop of the indicator strikes the solution may be an aid in the control of the acidity. The boiling should not be prolonged as the color may reverse and the precipitate may be difficult to retain on the filter. The solution should be distinctly yellow when it is ready to filter. If it is not, restore the yellow color with more NH₄OH (1+1) or repeat the precipitation.

NOTE 20—To avoid drying of the precipitate with resultant slow filtration, channeling, or poor washing, the filter paper should be kept nearly full during the filtration and should be washed without delay.

NOTE 21—Two drops of methyl red indicator solution should be added to the NH₄NO₃ solution in the wash bottle, followed by NH₄OH (1+1) added dropwise until the color just changes to yellow. If the color reverts to red at any time due to heating, it should be brought back to yellow by the addition of a drop of NH₄OH (1+1).

7.2.2 Set aside the filtrate and transfer the precipitate and filter paper to the same beaker in which the first precipitation was effected. Dissolve the precipitate with hot HCl (1+2). Stir to thoroughly macerate the paper and then dilute the solution to about 100 mL. Reprecipitate the hydroxides as described in 7.2.1. If difficulty from bumping is experienced while boiling the acid solution containing the filter paper, it may be obviated by diluting the hot 1+2 solution of the mixed oxides with 100 mL of boiling water and thus eliminate the need for boiling. Filter the solution and wash the precipitate with about four 10-mL portions of hot NH₄NO₃ solution (20 g/L) (Note 21). Combine the filtrate and washings with the filtrate set aside and reserve for the determination of CaO in accordance with 13.3.1.

7.2.3 Place the precipitate in a weighed platinum crucible, heat slowly until the papers are charred, and finally ignite to constant weight at 1050 to 1100 °C taking care to prevent reduction, and weigh as the ammonium hydroxide group.

7.2.4 *Blank*—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

7.3 *Calculation*—Calculate the percentage of ammonium hydroxide group by multiplying the weight in grams of ammonium hydroxide group by 200 (100 divided by the weight of sample used (0.5 g)).

8. Ferric Oxide (Reference Test Method)

8.1 *Summary of Test Method*—In this test method, the Fe₂O₃ content of the cement is determined on a separate portion of the cement by reducing the iron to the ferrous state with stannous chloride (SnCl₂) and titrating with a standard

solution of potassium dichromate ($K_2Cr_2O_7$). This determination is not affected by any titanium or vanadium that may be present in the cement.

8.2 Reagents:

8.2.1 Barium Diphenylamine Sulfonate Indicator Solution—Dissolve 0.3 g of barium diphenylamine sulfonate in 100 mL of water.

8.2.2 Potassium Dichromate, Standard Solution (1 mL = 0.004 g Fe_2O_3)—Pulverize and dry primary standard potassium dichromate ($K_2Cr_2O_7$) reagent, the current lot of NIST 136, at 180 to 200 °C to constant weight. Weigh accurately an amount of dried reagent equal to 2.45700 g times the number of litres of solution to be prepared. Dissolve in water and dilute to exactly the required volume in a single volumetric flask of the proper size. This solution is a primary standard and requires no further standardization.

NOTE 22—Where large quantities of standard solution are required, it may be desirable for certain laboratories to use commercially-produced primary standard potassium dichromate for most determinations. Such a material may be used provided that the first solution made from the container is checked, as follows: Using a standard solution of NIST 136, prepared as described in 8.2.2, analyze, in duplicate, samples of a NIST CRM cement (see **Note 2**), by the procedure given in 8.3.1.3 and 8.3.1.4. Repeat using a similar solution prepared from the commercial primary standard dichromate. The average percentages of Fe_2O_3 found by each method should not differ by more than 0.06 %.

8.2.3 Stannous Chloride Solution—Dissolve 5 g of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 10 mL of HCl and dilute to 100 mL. Add scraps of iron-free granulated tin and boil until the solution is clear. Keep the solution in a closed dropping bottle containing metallic tin.

8.3 Procedure—For cements other than portland and for which the insoluble residue is unknown, determine the insoluble residue in accordance with the appropriate sections of these test methods. When insoluble residue is known, proceed in accordance with 8.3.1 or 8.3.2 as is appropriate for the cement being analyzed.

8.3.1 For portland cements and cements having insoluble residue lower than 1 %, weigh 1 g of the sample into a 500-mL Phillips beaker or other suitable container. Add 40 mL of cold water and, while the beaker is being swirled, add 10 mL of HCl. If necessary, heat the solution and grind the cement with the flattened end of a glass rod until it is evident that the cement is completely decomposed. Continue the analysis in accordance with 8.3.3.

8.3.2 For cements with insoluble residue greater than 1 %, weigh a 0.500 g sample, blend with 1 g $LiBO_2$ using a mortar and pestle, and transfer to a previously fired 8-mL carbon crucible that has 0.1 g $LiBO_2$ sprinkled in the bottom (**Note 23**). Cover with 0.1 g $LiBO_2$ that was used to chemically wash the mortar and pestle (**Note 24**). Place the uncovered crucible in a furnace set at 1100 °C for 15 min. Remove the crucible from the furnace and check for complete fusion (**Note 25**). If the fusion is incomplete, return the crucible to the furnace for another 30 min. Again, check for complete fusion. If the fusion is still incomplete, discard the sample and repeat the fusion procedure using 0.250 g sample or a smaller quantity with the same amount of $LiBO_2$. When the fusion is complete, gently swirl the melt and pour into a 150-mL glass beaker containing

10 mL concentrated HCl and 50 mL water. Stir continuously until the fusion product is dissolved, usually 10 min or less (**Note 26**). If a stirring bar is used, remove and rinse the bar. Continue the analysis in accordance with 8.3.3.

NOTE 23—The firing loosens the carbon on the surface, reducing the possibility of the fusion product sticking to the crucible.

NOTE 24—A chemical wash is a dry rinse of the equipment in which the blending was done so that any sample adhering to this equipment will be loosened and transferred to the crucible.

NOTE 25—When fusion is incomplete, the sample may not be completely melted or there may be particles on top of the bead. Usually, if the bead forms a small smooth spherical ball when taken from the furnace and before it is swirled, the sample is completely fused.

NOTE 26—There are usually some carbon particles that are in suspension, undissolved in the solution, but they will not interfere with the completion of the analysis.

8.3.3 Heat the solution to boiling and treat it with the $SnCl_2$ solution, added dropwise while stirring and boiling, until the solution is decolorized. Add 1 drop in excess and cool the solution to room temperature by placing the beaker in a pan of cool water. After cooling and without delay, rinse the inside of the vessel with water, and add all at once 10 mL of a cool, saturated mercuric chloride ($HgCl_2$) solution. Stir the solution vigorously for 1 min by swirling the beaker and add 10 mL of H_3PO_4 (1+1) and 2 drops of barium diphenylamine sulfonate indicator. Add sufficient water so that the volume after titration will be between 75 and 100 mL. Titrate with the standard $K_2Cr_2O_7$ solution. The end point shall be taken as the point at which a single drop causes an intense purple coloration that remains unchanged on further addition of standard $K_2Cr_2O_7$ solution.

8.3.4 Blank—Make a blank determination following the same procedure and using the same amounts of reagents. Record the volume of $K_2Cr_2O_7$ solution required to establish the end point as described in 8.3.3. As some iron must be present to obtain the normal end point, if no definite purple color is obtained after the addition of 4 drops of the standard $K_2Cr_2O_7$ solution, record the blank as zero.

8.4 Calculation:

8.4.1 Calculate the percentage of Fe_2O_3 as follows:

$$Fe_2O_3, \% = E(V - B) \times 100/W \quad (2)$$

where:

E = Fe_2O_3 equivalent of the $K_2Cr_2O_7$ solution, g/mL,

V = millilitres of $K_2Cr_2O_7$ solution required by the sample determination,

B = millilitres of $K_2Cr_2O_7$ solution required by the blank determination, and

W = mass of sample within 0.1 mg.

Round in accordance with **Table 3**.

9. Phosphorus Pentoxide (Reference Test Method)

9.1 Summary of Test Method—This colorimetric test method is applicable to the determination of P_2O_5 in portland cement. Under the conditions of the test, no constituent normally present in portland cement will interfere.

9.2 Apparatus:

9.2.1 Spectrophotometer (**Note 27**):

9.2.1.1 The instrument shall be equipped to measure absorbance of solutions at a spectral wavelength of 725 nm.

9.2.1.2 Wavelength measurements shall be repeatable within ± 1 nm or less.

9.2.1.3 In the absorbance range from 0.1 to 1.0, the absorbance measurements shall be repeatable within ± 1 % or less.

9.2.1.4 To establish that the spectrophotometer will permit a satisfactory degree of accuracy, qualify the instrument in accordance with 3.3.2 using the procedure in 9.4.1-9.4.9.

NOTE 27—For the measurement of the performance of the spectrophotometer, refer to Practice E275.

9.3 Reagents:

9.3.1 *Ammonium Molybdate Solution*—Into a 1-L volumetric flask introduce 500.0 mL of 10.6 N H_2SO_4 (9.3.7). Dissolve 25.0 g of ammonium molybdate ($(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) in about 250 mL of warm water and transfer to the flask containing the H_2SO_4 , while swirling the flask. Cool, dilute to 1 L with water, and store in a plastic bottle.

9.3.2 *Ascorbic Acid Powder*—For ease in dissolving, the finest mesh available should be used.

9.3.3 *Hydrochloric Acid, Standard* (6.5 ± 0.1 N)—Dilute 540 mL of concentrated HCl (sp gr 1.19) to 1 L with water. Standardize against standard NaOH solution (9.3.6) using phenolphthalein as indicator. Determine the exact normality and adjust to 6.5 ± 0.1 N by dilution with water. Restandardize to ensure that the proper normality has been achieved.

9.3.4 *Phosphate, Standard Solution A*—Dissolve 0.1917 g of oven-dried potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 L in a volumetric flask.

9.3.5 *Phosphate, Standard Solution B*—Dilute 50.0 mL of phosphate solution A to 500 mL with water.

9.3.6 *Sodium Hydroxide, Standard Solution* (1 N)—Dissolve 40.0 g of sodium hydroxide (NaOH) in water, add 10 mL of a freshly filtered saturated solution of barium hydroxide ($\text{Ba}(\text{OH})_2$), and dilute to 1 L with water that has been recently boiled and cooled. Shake the solution from time to time during a several-hour period, and filter into a plastic bottle. Keep the bottle tightly closed to protect the solution from CO_2 in the air. Standardize against acid potassium phthalate or benzoic acid acidimetric standards furnished by NIST (standard samples 84f and 350), using the test methods in the certificates accompanying the standard samples. Determine the exact normality of the solution.

9.3.7 *Sulfuric Acid, Standard* (10.6 ± 0.1 N)—To a 1-L volumetric flask cooled in water add about 600 mL of water and then, slowly, with caution, 300 mL of concentrated H_2SO_4 (sp gr 1.84). After cooling to room temperature, dilute to 1 L with water. Standardize against the standard NaOH solution (9.3.6) using phenolphthalein as indicator. Determine the normality and adjust to 10.6 ± 0.1 N by dilution with water. Restandardize to ensure that the proper normality has been achieved.

9.4 Procedure:

9.4.1 Prepare a series of phosphate solutions to cover the range from 0 to 0.5 % P_2O_5 . Prepare each solution by adding a suitable volume of standard phosphate solution B and 25.0 mL of the 6.5 N hydrochloric acid to a 250-mL volumetric flask (Note 28). Dilute to the mark with water.

NOTE 28—One millilitre of standard phosphate solution B/250 mL of solution is equivalent to 0.004 % P_2O_5 for a 0.25-g cement sample.

Aliquots of 0, 12.5, 25, 50, 74, 100, and 125 mL are equivalent to P_2O_5 contents in the sample of 0, 0.05, 0.10, 0.20, 0.30, 0.40, and 0.50 %.

9.4.2 Prepare a blank by adding 25.0 mL of the standard HCl to a 250-mL volumetric flask and diluting to 250 mL with water.

9.4.3 Develop colors in the series of phosphate solutions, and in the blank, in accordance with 9.4.6-9.4.8.

9.4.4 Plot the net absorbance (absorbance of standard minus that of the blank) values obtained as ordinates and the corresponding P_2O_5 concentrations as abscissas. Draw a smooth curve through the points.

NOTE 29—A suitable paper for plotting the calibration curve is a 10 by 15-in. (254 by 381-mm) linear cross section paper having 20 by 20 divisions to the inch. The percentage of P_2O_5 can then be plotted on the long dimension using five divisions equal to 0.01 % P_2O_5 . A scale of one division equal to 0.005 absorbance units is suitable as the ordinate (short dimension of the paper). Scales other than this may be used but under no circumstances should a scale division less than $\frac{1}{20}$ in. (1.3 mm) be used for 0.005 units of absorbance or for 0.005 % P_2O_5 . A separate calibration curve should be made for each spectrophotometer used, and the calibration curve checked against standard phosphate solution whenever a new batch of ammonium molybdate reagent is used.

9.4.5 Transfer 0.250 g of the sample to a 250-mL beaker and moisten with 10 mL of cold water to prevent lumping. Add 25.0 mL of the standard HCl and digest with the aid of gentle heat and agitation until solution is complete. Filter into a 250-mL volumetric flask and wash the paper and the separated silica thoroughly with hot water. Allow the solution to cool and then dilute with water to 250 mL.

9.4.6 Transfer a 50.0-mL aliquot (Note 30) of the sample solution to a 250-mL beaker, add 5.0 mL of ammonium molybdate solution and 0.1 g of ascorbic acid powder. Mix the contents of the beaker by swirling until the ascorbic acid has dissolved completely. Heat the solution to vigorous boiling and then boil, uncovered, for 1.5 ± 0.5 min. Cool to room temperature and transfer to a 50-mL volumetric flask. Rinse the beaker with one small portion of water and add the rinse water to the flask. Dilute to 50 mL with water.

NOTE 30—The range of the test can be extended by taking a smaller aliquot of the sample solution. In such instances the decrease in the aliquot volume must be made up by the blank solution (9.4.5) to maintain the proper acidity of the final solution. Thus, if a 25-mL aliquot of the sample solution is taken (instead of the usual 50 mL), a 25-mL aliquot of the blank solution should be added before proceeding with the test. The result of the test must then be calculated accordingly.

9.4.7 Measure the absorbance of the solution against water as the reference at 725.0 nm.

9.4.8 Develop on a 50.0-mL aliquot of the blank solution prepared in 9.4.2 in the same manner as was used in 9.4.6 for the sample solution. Measure the absorbance in accordance with 9.4.7 and subtract this absorbance value from that obtained for the sample solution in 9.4.6 in order to obtain the net absorbance for the sample solution.

9.4.9 Using the net absorbance value found in 9.4.8, record the percentage of P_2O_5 in the cement sample as indicated by the calibration curve. Report the percentage of P_2O_5 rounded in accordance with Table 3