



Standard Test Methods for Chemical Analysis of Hydraulic Cement¹

This standard is issued under the fixed designation C 114; 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 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 wet 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.

1.2 Contents:

Section	Subject
2	Referenced Documents
3	Number of Determinations and Permissible Variations
3.1	Referee Analyses
3.2	Optional Analyses
3.3	Performance Requirements for Rapid Test Methods
3.4	Precision and Bias
4	General
4.1	Interferences and Limitations
4.2	Apparatus and Materials
4.3	Reagents
4.4	Sample Preparation
4.5	General Procedures
4.6	Recommended Order for Reporting Analyses
	Reference Test Methods
5	Insoluble Residue
6	Silicon Dioxide
6.2	Cements with Insoluble Residue Less Than 1 %
6.3	Cements with Insoluble Residue Greater Than 1 %
7	Ammonium Hydroxide Group
8	Ferric Oxide
9	Phosphorus Pentoxide
10	Titanium Dioxide
11	Zinc Oxide
12	Aluminum Oxide
13	Calcium Oxide
14	Magnesium Oxide

15	Sulfur
15.1	Sulfur Trioxide
15.2	Sulfide
16	Loss On Ignition
16.1	Portland Cement
16.2	Portland Blast-Furnace Slag Cement and Slag Cement
17	Sodium and Potassium Oxides
17.1	Total Alkalis
17.2	Water-Soluble Alkalis
18	Manganic Oxide
19	Chloride
20	Chloroform-Soluble Organic Substances
	Alternative Test Methods
21	Calcium Oxide
22	Magnesium Oxide
23	Loss on Ignition
23.1	Portland Blast-Furnace Slag Cement and Slag Cement
24	Titanium Dioxide
25	Phosphorus Pentoxide
26	Manganic Oxide
27	Free Calcium Oxide
Appendices	Title
Appendix X1	Example of Determination of Equivalence Point for the Chloride Determination
Appendix X2	CO ₂ Determinations in Hydraulic Cements

1.3 The values stated in SI units are to be regarded as the 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 Note 43 for specific caution statements.

2. Referenced Documents

2.1 ASTM Standards:²

- C 25 Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
- C 183 Practice for Sampling and the Amount of Testing of Hydraulic Cement
- C 595 Specification for Blended Hydraulic Cements
- D 1193 Specification for Reagent Water
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

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.

Current edition approved Jan. 1, 2004. Published March 2004. Originally approved in 1934. Last previous edition approved in 2003 as C 114–03.

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.

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers

E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron

E 617 Specification for Laboratory Weights and Precision Mass Standards

E 832 Specification for Laboratory Filter Papers

3. Number of Determinations and Permissible Variations

3.1 Referee Analyses— The reference test methods that follow in Sections 5-20, or other test methods qualified according to 3.3, are required for referee analysis in those cases where conformance to chemical specification requirements are questioned. In these cases, 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 reference test methods prescribed in the appropriate sections of this test method or by other qualified test methods, except when specific test methods are prescribed in the standard specification for the cement in question. The test methods actually used for the analysis shall be designated.

3.1.1 Referee analyses, when there is a question regarding acceptance, 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 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.

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 1) no matter what test method is used (for example, gravimetric, instrumental). Duplicate

TABLE 1 Maximum Permissible Variations in Results^A

(Column 1) Component	(Column 2) Maximum Difference Between Duplicates ^B	(Column 3) Maximum Difference of the 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 Interlelement 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.

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.

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 1—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 Data demonstrating that precise and accurate results were obtained with CRM cements by the same analyst making the acceptance determination 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 1), 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. An acceptable reference cement must be accompanied by a document showing the data produced in demonstrating traceability.

3.2 *Optional 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 2). 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. 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 5-27 requires method qualification in accordance with 3.3.

NOTE 2—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 3 for examples of procedures.

NOTE 3—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 1). 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 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

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

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. The standardization, if needed, used for qualification and for analysis of each constituent shall be determined by valid curve-fitting procedures. The qualification testing shall be conducted with newly prepared specimens.

NOTE 4—An actual drawing of a curve is not required if such curve is not needed for the method in use. 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.

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 E 617. 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 E 617. 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 F₁ 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 E 832, 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 $\pm 25^{\circ}\text{C}$, 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 D 1193.

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.

4.3.5 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* $\text{Na}_2\text{S}_2\text{O}_3$ solution or $\text{K}_2\text{Cr}_2\text{O}_7$ (1 mL = 0.004 g Fe_2O_3). 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 non-standardized 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

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.

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 multiplying or dividing, where possible, retain the equivalent of 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.

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 E 29.⁵

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).

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

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 $\text{NH}_4\text{NO}_3/\text{L}$).

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 NH_4NO_3 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 (SiO_2) 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 SiO₂ thus obtained, which will contain small amounts of impurities, in the crucible with 1 or 2 mL of water, 2 drops of H₂SO₄ (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 SiO₂. Consider the weighed residue remaining after the volatilization of SiO₂ 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 (Na₂S₂O₇ or K₂S₂O₇) 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 SiO₂ to the nearest 0.1 multiplying the mass in grams of SiO₂ 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)).

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 (SiO₂) 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 SiO₂.

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 Na₂CO₃ by grinding in an agate mortar. Place a thin layer of Na₂CO₃ on the bottom of a platinum crucible of 20 to 30-mL capacity, add the cement-Na₂CO₃ mixture, and cover the mixture with a thin layer of Na₂CO₃. 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 NH_4OH (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 (NH_4NO_3 , 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 SiO_2 , 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 cm^2 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 NH_4OH used to precipitate the hydroxides must be free of contamination with carbon dioxide (CO_2).

NOTE 19—It usually takes 1 drop of NH_4OH (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 ($\text{Fe}(\text{OH})_3$) is precipitated without aluminum hydroxide ($\text{Al}(\text{OH})_3$) being completely precipitated. In such a case, the color changes may be better observed. However, if the content of Fe_2O_3 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 NH_4OH (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 NH_4NO_3 solution in the wash bottle, followed by NH_4OH (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 NH_4OH (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 NH_4NO_3 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 to the nearest 0.01 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 Fe_2O_3 content of the cement is determined on a separate portion of the cement by reducing the iron to the ferrous state with stannous chloride (SnCl_2) and titrating with a standard solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). 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 ($\text{K}_2\text{Cr}_2\text{O}_7$) 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 1), 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 ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) 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 LiBO₂ using a mortar and pestle, and transfer to a previously fired 8-mL carbon crucible that has 0.1 g LiBO₂ sprinkled in the bottom (Note 23). Cover with 0.1 g LiBO₂ 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 LiBO₂. 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 SnCl₂ 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 (HgCl₂) solution. Stir the solution vigorously for 1 min by swirling the beaker and add 10 mL of H₃PO₄ (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 K₂Cr₂O₇ 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 K₂Cr₂O₇ solution.

8.3.4 *Blank*—Make a blank determination following the same procedure and using the same amounts of reagents. Record the volume of K₂Cr₂O₇ 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 K₂Cr₂O₇ solution, record the blank as zero.

8.4 *Calculation*:

8.4.1 Calculate the percentage of Fe₂O₃ to the nearest 0.01 % (to be reported to the nearest 0.1) as follows:

$$\text{Fe}_2\text{O}_3, \% = E(V - B) \times 100/W \quad (2)$$

where:

E = Fe₂O₃ equivalent of the K₂Cr₂O₇ solution, g/mL,

V = millilitres of K₂Cr₂O₇ solution required by the sample determination,

B = millilitres of K₂Cr₂O₇ solution required by the blank determination, and

W = mass of sample within 0.1 mg.

9. Phosphorus Pentoxide (Reference Test Method)

9.1 *Summary of Test Method*—This colorimetric test method is applicable to the determination of P₂O₅ 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 E 275.

9.3 *Reagents*:

9.3.1 *Ammonium Molybdate Solution*—Into a 1-L volumetric flask introduce 500.0 mL of 10.6 N H₂SO₄ (9.3.7). Dissolve 25.0 g of ammonium molybdate ((NH₄)₆Mo₇O₂₄ · 4H₂O) in about 250 mL of warm water and transfer to the flask containing the H₂SO₄, 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 $\pm$ 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 $\pm$ 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 (KH₂PO₄) 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 (Ba(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 CO₂ 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 ($10.6 \pm 0.1 N$)—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 $10.6 \pm 0.1 N$ 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 to the nearest 0.01.

10. Titanium Dioxide (Reference Test Method)

10.1 Summary of Test Method—In this test method titanium dioxide (TiO_2) in portland cement is determined colorimetrically using Tiron reagent. Under the conditions of the test iron is the only constituent of portland cement causing a very slight interference equivalent to 0.01 % for each 1 % of Fe_2O_3 present in the sample.

10.2 Apparatus:

10.2.1 Spectrophotometer (Note 31):

10.2.1.1 The instrument shall be equipped to measure absorbance of solutions at a spectral wavelength of 410 nm.

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

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

10.2.1.4 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 10.4.1-10.4.6 of this test method.

NOTE 31—For the measurement of the performance of the spectrophotometer, refer to Practice E 275.

10.3 Reagents:

10.3.1 Buffer (pH 4.7)—68 g of $NaC_2H_3O_2 \cdot 3H_2O$, plus 380 mL of water, plus 100 mL of 5.0 N CH_3COOH .

10.3.2 Ethylenedinitrilo Tetraacetic Acid Disodium Salt, Dihydrate (0.2 M EDTA)—Dissolve 37.5 g of EDTA in 350 mL of warm water, and filter. Add 0.25 g of $FeCl_3 \cdot 6H_2O$ and dilute to 500 mL.

10.3.3 Hydrochloric Acid (1+6).

10.3.4 Hydrochloric Acid, Standard (6.5 N)—Dilute 540 mL of concentrated HCl (sp gr 1.19) to 1 L with water.

10.3.5 Ammonium Hydroxide (NH_4OH , 1+1).

10.3.6 Potassium Pyrosulfate ($K_2S_2O_7$).

10.3.7 Titanium Dioxide, Stock Solution A—Fuse slowly in a platinum crucible over a very small flame 0.0314 g of NIST SRM 154b ($TiO_2 = 99.74$ %) or its replacements with about 2 or 3 g of $K_2S_2O_7$. Allow to cool, and place the crucible in a beaker containing 125 mL of H_2SO_4 (1+1). Heat and stir until

the melt is completely dissolved. Cool, transfer to a 250-mL volumetric flask, and dilute the solution to volume.

10.3.7.1 *Titanium Dioxide, Dilute Standard Solution B* (1 mL = 0.0125 mg TiO₂)—Pipet 50 mL of stock TiO₂ solution into a 500-mL volumetric flask, and dilute to volume. One millilitre of this solution is equal to 0.0125 mg of TiO₂, which is equivalent to 0.05 % TiO₂ when used as outlined in 10.4.4-10.4.6.

10.3.8 *Sulfuric Acid* (1+1).

10.3.9 *Tiron* (disodium-1,2-dihydroxybenzene-3,5 disulfonate).

10.4 *Procedure:*

10.4.1 Prepare a series of TiO₂ solutions to cover the range from 0 to 1.0 % TiO₂. Prepare each solution in a 50-mL volumetric flask.

NOTE 32—One millilitre of dilute TiO₂ standard solution B per 50 mL (10.3.7.1) is equivalent to 0.05 % TiO₂ for a 0.2500-g cement sample. Aliquots of 0, 5, 10, 15, and 20 mL of dilute TiO₂ standard solution are equivalent to TiO₂ contents in the sample of 0, 0.25, 0.50, 0.75, and 1.0 %. Dilute each to 25 mL with water.

10.4.2 Develop color in accordance with 10.4.4 starting with second sentence. Measure absorbance in accordance with 10.4.5.

10.4.3 Plot absorbance values obtained as ordinates and the corresponding TiO₂ concentrations as abscissas. Draw a smooth curve through the points.

NOTE 33—A suitable paper for plotting the calibration curve is a linear cross section paper having 10 × 10 divisions to 1 cm. A scale division equivalent to 0.002 absorbance and 0.002 % TiO₂ should be used. A separate calibration curve should be made for each spectrophotometer used.

10.4.4 Transfer a 25.0-mL aliquot of the sample solution prepared in 9.4.5 into a 50-mL volumetric flask (Note 34). Add 5 mL tiron and 5 mL EDTA, mix, and then add NH₄OH (1+1) dropwise, mixing thoroughly after each drop, until the color changes through yellow to green, blue, or ruby red. Then, just restore the yellow color with HCl (1+6) added dropwise and mixing after each drop. Add 5 mL buffer, dilute to volume and mix.

10.4.5 Measure the absorbance of the solution against water as the reference at 410 nm.

NOTE 34—The range of the test can be extended by taking a smaller aliquot. The results of the test must then be calculated accordingly.

10.4.6 Using the absorbance value determined in 10.4.5, record the percentage of TiO₂ in the cement sample as indicated by the calibration curve to the nearest 0.01. Correct for the iron present in the sample to obtain the true TiO₂ as follows: True TiO₂ = measured % TiO₂ - (0.01 × % Fe₂O₃). Report the percent of TiO₂ to the nearest 0.01.

11. Zinc Oxide (Reference Test Method)⁶

11.1 Any test method may be used that meets the requirements of Section 3.3 and Table 1.

⁶ The 1988 revision of these test methods deleted the colorimetric method for determination of ZnO using an extraction with CCl₄. Those interested in this test method should refer to the 1987 *Annual Book of ASTM Standards*, Volume 04.01.

12. Aluminum Oxide (Reference Test Method)

NOTE 35—In the reference test method, Al₂O₃ is calculated from the ammonium hydroxide group by subtracting the separately determined constituents that usually are present in significant amounts in the ammonium hydroxide precipitate. These are Fe₂O₃, TiO₂ and P₂O₅. Most instrumental test methods for Al₂O₃ analysis give Al₂O₃ alone if standardized and calibrated properly.

12.1 Calculation:

12.1.1 Calculate the percentage of Al₂O₃ by deducting the percentage of the sum of the Fe₂O₃, TiO₂, and P₂O₅ from the percentage of ammonium hydroxide group. All determinations shall be by referee test methods described in the appropriate sections herein. All percentages shall be calculated to the nearest 0.01 %. Report the Al₂O₃ to the nearest 0.1 %. For nonreferee analyses, the percentages of Fe₂O₃, TiO₂, and P₂O₅ can be determined by any procedure for which qualification has been shown.

13. Calcium Oxide (Reference Test Method)

13.1 Summary of Test Method:

13.1.1 In this test method, manganese is removed from the filtrate after the determination of SiO₂ and the ammonium hydroxide group. Calcium is then precipitated as the oxalate. After filtering, the oxalate is redissolved and titrated with potassium permanganate (KMnO₄).

NOTE 36—For referee analysis or for the most accurate determinations, removal of manganese in accordance with 13.3.2 must be made. For less accurate determinations, and when only insignificant amounts of manganese oxides are believed present, 13.3.2 may be omitted.

13.1.2 Strontium, usually present in portland cement as a minor constituent, is precipitated with calcium as the oxalate and is subsequently titrated and calculated as CaO. If the SrO content is known and correction of CaO for SrO is desired as, for example, for research purposes or to compare results with CRM certificate values, the CaO obtained by this method may be corrected for SrO. In determining conformance of a cement to specifications, the correction of CaO for SrO should not be made.

13.2 Reagents:

13.2.1 *Ammonium Oxalate Solution* (50 g/L).

13.2.2 *Potassium Permanganate, Standard Solution* (0.18 N)—Prepare a solution of potassium permanganate (KMnO₄) containing 5.69 g/L. Let this solution stand at room temperature for at least 1 week, or boil and cool to room temperature. Siphon off the clear solution without disturbing the sediment on the bottom of the bottle; then filter the siphoned solution through a bed of glass wool in a funnel or through a suitable sintered glass filter. Do not filter through materials containing organic matter. Store in a dark bottle, preferably one that has been painted black on the outside. Standardize the solution against 0.7000 to 0.8000 g of primary standard sodium oxalate, according to the directions furnished with the sodium oxalate and record the temperature at which the standardization was made (Note 37).

13.2.2.1 Calculate the CaO equivalent of the solution as follows:

1 mL of 1 N KMnO₄ solution is equivalent to 0.06701 g of pure sodium oxalate.

Normality of KMnO_4

$$= \frac{\text{weight of sodium oxalate} \times \text{fraction of its purity}}{\text{mL of } \text{KMnO}_4 \text{ solution} \times 0.06701} \quad (3)$$

1 mL of 1 N KMnO_4 solution is equivalent to 0.02804 g of CaO.

$$F = \frac{\text{normality of } \text{KMnO}_4 \text{ solution} \times 0.02804 \times 100}{0.5}$$

where F = CaO equivalent of the KMnO_4 solution in % CaO/mL based on a 0.5-g sample of cement.

NOTE 37—Because of the instability of the KMnO_4 solution, it is recommended that it be restandardized at least bimonthly.

13.3 Procedure:

13.3.1 Acidify the combined filtrates obtained in the precipitations of the ammonium hydroxide group (7.2.2). Neutralize with HCl to the methyl red end point, make just acid, and add 6 drops of HCl in excess.

13.3.2 *Removal of Manganese*—Evaporate to a volume of about 100 mL. Add 40 mL of saturated bromine water to the hot solution and immediately add NH_4OH until the solution is distinctly alkaline. Addition of 10 mL of NH_4OH is generally sufficient. A piece of filter paper, about 1 cm^2 in area, placed in the heel of the beaker and held down by the end of a stirring rod aids in preventing bumping and initiating precipitation of hydrated manganese oxides (MnO). Boil the solution for 5 min or more, making certain that the solution is distinctly alkaline at all times. Allow the precipitate to settle, filter using medium-textured paper, and wash with hot water. If a precipitate does not appear immediately, allow a settling period of up to 1 h before filtration. Discard any manganese dioxide that may have been precipitated. Acidify the filtrate with HCl using litmus paper as an indicator, and boil until all the bromine is expelled (Note 38).

13.3.3 Add 5 mL of HCl, dilute to 200 mL, and add a few drops of methyl red indicator and 30 mL of warm ammonium oxalate solution (50 g/L) (Note 39). Heat the solution to 70 to 80°C, and add NH_4OH (1+1) dropwise, while stirring until the color changes from red to yellow (Note 40). Allow the solution to stand without further heating for 60 ± 5 min (no longer), with occasional stirring during the first 30 min.

13.3.4 Filter, using retentive paper, and wash the precipitate 8 to 10 times with hot water, the total amount of water used in rinsing the beaker and washing not to exceed 75 mL. During this washing, water from the wash bottle should be directed around the inside of the filter paper to wash the precipitate down, then a jet of water should be gently directed towards the center of the paper in order to agitate and thoroughly wash the precipitate. Acidify the filtrate with HCl and reserve for the determination of MgO.

13.3.5 Place the beaker in which the precipitation was made under the funnel, pierce the apex of the filter paper with the stirring rod, place the rod in the beaker, and wash the precipitate into the beaker by using a jet of hot water. Drop about 10 drops of H_2SO_4 (1+1) around the top edge of the filter paper. Wash the paper five more times with hot water. Dilute to 200 mL, and add 10 mL of H_2SO_4 (1+1). Heat the solution to a temperature just below boiling, and titrate it immediately with the 0.18 N KMnO_4 solution (Note 41). Continue the titration slowly until the pink color persists for at least 10 s.

Add the filter paper that contained the original precipitate and macerate it. If the pink color disappears continue the titration until it again persists for at least 10 s.

NOTE 38—Potassium iodide starch paper may be used to indicate the complete volatilization of the excess bromine. Expose a strip of moistened paper to the fumes from the boiling solution. The paper should remain colorless. If it turns blue bromine is still present.

NOTE 39—If the ammonium oxalate solution is not perfectly clear, it should be filtered before use.

NOTE 40—This neutralization must be made slowly, otherwise precipitated calcium oxalate may have a tendency to run through the filter paper. When a number of these determinations are being made simultaneously, the following technique will assist in ensuring slow neutralization. Add two or three drops of NH_4OH to the first beaker while stirring, then 2 or 3 drops to the second, and so on, returning to the first beaker to add 2 or 3 more drops, etc., until the indicator color has changed in each beaker.

NOTE 41—The temperature of the 0.18 N KMnO_4 solution at time of use should not vary from its standardization temperature by more than 10°F (5.5°C). Larger deviations could cause serious error in the determination of CaO.

13.3.6 *Blank*—Make a blank determination, following the same procedure and using the same amounts of reagents (Note 42), and record the millilitres of KMnO_4 solution required to establish the end point.

NOTE 42—When the amount of calcium oxalate is very small, its oxidation by KMnO_4 is slow to start. Before the titration, add a little MnSO_4 to the solution to catalyze the reaction.

13.4 Calculation:

13.4.1 Calculate the percentage of CaO to the nearest 0.1 as follows:

$$\text{CaO, \%} = E(V - B) \quad (4)$$

where:

E = CaO equivalent of the KMnO_4 solution in % CaO/mL based on a 0.5-g sample,

V = millilitres of KMnO_4 solution required by the sample, and

B = millilitres of KMnO_4 solution required by the blank.

13.4.2 If desired calculate the percentage of CaO corrected for SrO as follows:

$$\text{CaO}_c \% = \text{CaO}_i \% - 0.54 \text{ SrO \%} \quad (5)$$

where:

CaO_c = CaO corrected for SrO, and

CaO_i = initial CaO as determined in 13.4.1

$$0.54 = \frac{56.08}{103.62} = \text{molecular weight ratio } \frac{\text{CaO}}{\text{SrO}}$$

14. Magnesium Oxide (Reference Test Method)

14.1 *Summary of Test Method*—In this test method, magnesium is precipitated as magnesium ammonium phosphate from the filtrate after removal of calcium. The precipitate is ignited and weighed as magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$). The MgO equivalent is then calculated.

14.2 *Reagent*—Ammonium phosphate, dibasic (100 g/L) $(\text{NH}_4)_2\text{HPO}_4$.

14.3 Procedure:

14.3.1 Acidify the filtrate from the determination of CaO (13.3.4) with HCl and evaporate by boiling to about 250 mL.

Cool the solution to room temperature, add 10 mL of ammonium phosphate, dibasic, $(\text{NH}_4)_2\text{HPO}_4$ (100 g/L), and 30 mL of NH_4OH . Stir the solution vigorously during the addition of NH_4OH and then for 10 to 15 min longer. Let the solution stand for at least 8 h in a cool atmosphere and filter. Wash the residue five or six times with NH_4OH (1+20) and ignite in a weighed platinum or porcelain crucible, at first slowly until the filter paper is charred and then burn off (see Note 43), and finally at 1100°C for 30 to 45 min. Weigh the residue as magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

14.3.2 *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.

14.4 Calculation:

14.4.1 Calculate the percentage of MgO to the nearest 0.1 as follows:

$$\text{MgO, \%} = W \times 72.4 \quad (6)$$

where:

W = grams of $\text{Mg}_2\text{P}_2\text{O}_7$, and

72.4 = molecular ratio of 2MgO to $\text{Mg}_2\text{P}_2\text{O}_7$ (0.362) divided by the weight of sample used (0.5 g) and multiplied by 100.

NOTE 43—**Caution:** Extreme caution should be exercised during this ignition. Reduction of the phosphate precipitate can result if carbon is in contact with it at high temperatures. There is also danger of occluding carbon in the precipitate if ignition is too rapid.

15. Sulfur (See Note 44)

15.1 Sulfur Trioxide: (Reference Test Method):

15.1.1 *Summary of Test Method*—In this test method, sulfate is precipitated from an acid solution of the cement with barium chloride (BaCl_2). The precipitate is ignited and weighed as barium sulfate (BaSO_4) and the SO_3 equivalent is calculated.

15.1.2 Procedure:

15.1.2.1 To 1 g of the sample add 25 mL of cold water and, while the mixture is stirred vigorously, add 5 mL of HCl (Note 45). If necessary, heat the solution and grind the material with the flattened end of a glass rod until it is evident that decomposition of the cement is complete (Note 46). Dilute the solution to 50 mL and digest for 15 min at a temperature just below boiling. Filter through a medium-textured paper and wash the residue thoroughly with hot water. Dilute the filtrate to 250 mL and heat to boiling. Add slowly, dropwise, 10 mL of hot BaCl_2 (100 g/L) and continue the boiling until the precipitate is well formed. Digest the solution for 12 to 24 h at a temperature just below boiling (Note 47). Take care to keep the volume of solution between 225 and 260 mL and add water for this purpose if necessary. Filter through a retentive paper, wash the precipitate thoroughly with hot water, place the paper and contents in a weighed platinum crucible, and slowly char and consume the paper without inflaming. Ignite at 800 to 900°C, cool in a desiccator, and weigh.

NOTE 44—When an instrumental test method is used for sulfur or when comparing results of classical wet and instrumental test methods, consult 4.1.2 of these test methods.

NOTE 45—The acid filtrate obtained in the determination of the insoluble residue (5.3.1) may be used for the determination of SO_3 instead

of using a separate sample.

NOTE 46—A brown residue due to compounds of manganese may be disregarded (see Note 11).

NOTE 47—If a rapid determination is desired, immediately after adding the BaCl_2 , place the beaker with the solution in an ultrasonic bath for 5 min, and then continue the determination starting with "Filter through a retentive paper. . .". Qualify the method in accordance with the Performance Requirements for Rapid Test Methods.

15.1.2.2 *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.

15.1.3 *Calculation*—Calculate the percentage of SO_3 to the nearest 0.01 as follows:

$$\text{SO}_3, \% = W \times 34.3 \quad (7)$$

where:

W = grams of BaSO_4 , and

34.3 = molecular ratio of SO_3 to BaSO_4 (0.343) multiplied by 100.

15.2 Sulfide: (Reference Test Method)

15.2.1 *Summary of Test Method*—In this test method sulfide sulfur is determined by evolution as hydrogen sulfide (H_2S) from an acid solution of the cement into a solution of ammoniacal zinc sulfate (ZnSO_4) or cadmium chloride (CdCl_2). The sulfide sulfur is then titrated with a standard solution of potassium iodate (KIO_3). Sulfites, thiosulfates, and other compounds intermediate between sulfides and sulfates are assumed to be absent. If such compounds are present, they may cause an error in the determination.

15.2.2 Apparatus:

15.2.2.1 *Gas-Generating Flask*—Connect a dry 500-mL boiling flask with a long-stem separatory funnel and a small connecting bulb by means of a rubber stopper. Bend the stem of the funnel so that it will not interfere with the connecting bulb, adjust the stem so that the lower end is close to the bottom of the flask, and connect the opening of the funnel with a source of compressed air. Connect the bulb with an L-shaped glass tube and a straight glass tube about 200 mm in length. Insert the straight glass tube in a tall-form, 400-mL beaker. A three-neck distilling flask with a long glass tubing in the middle opening, placed between the source of compressed air and the funnel, is a convenient aid in the regulation of the airflow. Rubber used in the apparatus shall be pure gum grade, low in sulfur, and shall be cleaned with warm HCl.

15.2.3 Reagents:

15.2.3.1 *Ammoniacal Cadmium Chloride Solution*—Dissolve 15 g of cadmium chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$) in 150 mL of water and 350 mL of NH_4OH . Filter the solution after allowing it to stand at least 24 h.

15.2.3.2 *Ammoniacal Zinc Sulfate Solution*—Dissolve 50 g of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) in 150 mL of water and 350 mL of NH_4OH . Filter the solution after allowing it to stand at least 24 h.

15.2.3.3 *Potassium Iodate, Standard Solution (0.03 N)*—Prepare a solution of potassium iodate (KIO_3) and potassium iodide (KI) as follows: Dry KIO_3 at 180°C to constant weight. Weigh 1.0701 g of the KIO_3 and 12 g of KI. Dissolve and dilute to 1 L in a volumetric flask. This is a primary standard and

requires no standardization (Note 48). One millilitre of this solution is equivalent to 0.0004809 g of sulfur.

NOTE 48—The solution is very stable, but may not maintain its titer indefinitely. Whenever such a solution is over 1 year old it should be discarded or its concentration checked by standardization.

15.2.3.4 *Stannous Chloride Solution*—To 10 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in a small flask, add 7 mL of HCl (1+1), warm the mixture gently until the salt is dissolved, cool the solution, and add 95 mL of water. This solution should be prepared as needed, as the salt tends to hydrolyze.

15.2.3.5 *Starch Solution*—To 100 mL of boiling water, add a cool suspension of 1 g of soluble starch in 5 mL of water and cool. Add a cool solution of 1 g of sodium hydroxide (NaOH) in 10 mL of water, then 3 g of potassium iodide (KI), and mix thoroughly.

15.2.4 Procedure:

15.2.4.1 Place 15 mL of the ammoniacal ZnSO_4 or CdCl_2 solution (Note 49) and 285 mL of water in a beaker. Put 5 g of the sample (Note 50) and 10 mL of water in the flask and shake the flask gently to wet and disperse the cement completely. This step and the addition of SnCl_2 should be performed rapidly to prevent the setting of the cement. Connect the flask with the funnel and bulb. Add 25 mL of the SnCl_2 solution through the funnel and shake the flask. Add 100 mL of HCl (1+3) through the funnel and shake the flask. During these shakings keep the funnel closed and the delivery tube in the ammoniacal ZnSO_4 or CdCl_2 solution. Connect the funnel with the source of compressed air, open the funnel, start a slow stream of air, and heat the flask and contents slowly to boiling. Continue the boiling gently for 5 or 6 min. Cut off the heat, and continue the passage of air for 3 or 4 min. Disconnect the delivery tube and leave it in the solution for use as a stirrer. Cool the solution to 20 to 30°C (Note 51), add 2 mL of the starch solution and 40 mL of HCl (1+1) and titrate immediately with the 0.03 N KIO_3 solution until a persistent blue color is obtained (Note 52).

NOTE 49—In general, the ZnSO_4 is preferable to the CdCl_2 solution because ZnSO_4 is more soluble in NH_4OH than is CdCl_2 . The CdCl_2 solution may be used when there is doubt as to the presence of a trace of sulfide sulfur, as the yellow cadmium sulfide (CdS) facilitates the detection of a trace.

NOTE 50—If the content of sulfur exceeds 0.20 or 0.25 %, a smaller sample should be used so that the titration with the KIO_3 solution will not exceed 25 mL.

NOTE 51—The cooling is important as the end point is indistinct in a warm solution.

NOTE 52—If the content of sulfur is appreciable but not approximately known in advance, the result may be low due to the loss of H_2S during a slow titration. In such a case the determination should be repeated with the titration carried out more rapidly.

15.2.4.2 Make a blank determination, following the same procedure and using the same amounts of reagents. Record the volume of KIO_3 solution necessary to establish the end point as described in 15.2.4.1.

15.2.5 *Calculation*—Calculate the percentage of sulfide sulfur (see 15.2.1) as follows:

$$\text{Sulfide, \%} = E(V - B) \times 20 \quad (8)$$

where:

- E = sulfide equivalent of the KIO_3 solution, g/mL,
- V = millilitres of KIO_3 solution required by the sample,
- B = millilitres of KIO_3 solution required by the blank, and
- 20 = 100 divided by the weight of sample used (5 g).

16. Loss on Ignition (Reference Test Methods)

16.1 Portland Cement:

16.1.1 *Summary of Test Method*—In this test method, the cement is ignited in a muffle furnace at a controlled temperature. The loss is assumed to represent the total moisture and CO_2 in the cement. This procedure is not suitable for the determination of the loss on ignition of portland blast-furnace slag cement and of slag cement. A test method suitable for such cements is described in 16.2.1 through 16.2.3.

16.1.2 *Procedure*—Weigh 1 g of the sample in a tared platinum crucible. Cover and ignite the crucible and its contents to constant weight in a muffle furnace at a temperature of $950 \pm 50^\circ\text{C}$. Allow a minimum of 15 min for the initial heating period and at least 5 min for all subsequent periods.

16.1.3 *Calculation*—Calculate the percentage of loss on ignition to the nearest 0.1 by multiplying the loss of weight in grams by 100.

16.2 Portland Blast-Furnace Slag Cement and Slag Cement:

16.2.1 *Summary of Test Method*—Since it is desired that the reported loss on ignition represent moisture and CO_2 , this test method provides a correction for the gain in weight due to oxidation of sulfides usually present in portland blast-furnace slag cement and slag cement by determining the increase in SO_3 content during ignition. An optional test method providing for a correction based on the decrease in sulfide sulfur during ignition is given in 23.1.1 through 23.1.3.1.

16.2.2 Procedure:

16.2.2.1 Weigh 1 g of cement into a tared platinum crucible and ignite in a muffle furnace at a temperature of $950 \pm 50^\circ\text{C}$ for 15 min. Cool to room temperature in a desiccator and weigh. Without checking for constant weight, carefully transfer the ignited material to a 400-mL beaker. Break up any lumps in the ignited cement with the flattened end of a glass rod.

16.2.2.2 Determine the SO_3 content by the test method given in 15.1.1.1 through 15.1.3.1 (Note 53). Also determine the SO_3 content of a portion of the same cement that has not been ignited, using the same procedure.

NOTE 53—Some of the acid used for dissolving the sample may first be warmed in the platinum crucible to dissolve any adhering material.

16.2.3 *Calculation*—Calculate the percentage loss of weight occurring during ignition and add 0.8 times the difference between the percentages of SO_3 in the ignited sample and the original cement (Note 54). Report the corrected percentage as loss on ignition.

NOTE 54—If a gain in weight is obtained during ignition, subtract the percentage gain from the correction for SO_3 .

17. Sodium and Potassium Oxides (Reference Test Methods)

17.1 Total Alkalies:

17.1.1 Summary of Test Method—This test method⁷ covers the determination of sodium oxide (Na₂O) and potassium oxide (K₂O) by flame photometry or atomic absorption.

NOTE 55—This test method is suitable for hydraulic cements that are completely decomposed by hydrochloric acid and should not be used for determination of total alkalis in hydraulic cements that contain large amounts of acid-insoluble material, for example, pozzolan cements. It may be used to determine acid-soluble alkalis for such cements. An alternate test method of sample dissolution for such cements is in preparation.

17.1.2 Apparatus:

17.1.2.1 Instrument—Any type flame photometer or atomic absorption unit may be used provided it can be demonstrated that the required degree of accuracy and precision is as indicated in 17.1.3.

NOTE 56—After such accuracy is established, for a specific instrument, further tests of instrument accuracy are not required except when it must be demonstrated that the instrument gives results within the prescribed degree of accuracy by a single series of tests using the designated standard samples.

NOTE 57—For normal laboratory testing, it is recommended that the accuracy of the instrument be routinely checked by the use of either a National Institute of Standards and Technology cement or cement of known alkali content.

17.1.2.2 The instrument shall consist at least of an atomizer and burner; suitable pressure-regulating devices and gages for fuel and oxidant gas; an optical system, capable of preventing excessive interference from wavelengths of light other than that being measured; and a photosensitive indicating device.

17.1.3 Initial Qualification of Instrument—Qualify the instrument in accordance with 3.3.2 to establish that an instrument provides the desired degree of precision and accuracy.

17.1.4 Reagents and Materials:

17.1.4.1 Laboratory Containers—All glassware shall be made of borosilicate glass and all polyethylene shall comply with the requirements of 4.2.3.

17.1.4.2 Calcium Carbonate—The calcium carbonate (CaCO₃) used in the preparation of the calcium chloride stock solution (17.1.5.1) shall contain not more than 0.020 % total alkalis as sulfate.

NOTE 58—Materials sold as a primary standard or ACS “low alkali” grade normally meet this requirement. However, the purchaser should assure himself that the actual material used conforms with this requirement.

17.1.4.3 Potassium Chloride (KCl).

17.1.4.4 Sodium Chloride (NaCl).

17.1.4.5 Commercially available solutions may be used in place of those specified in 17.1.5.

17.1.5 Preparation of Solutions:

17.1.5.1 Calcium Chloride Stock Solution—Add 300 mL of water to 112.5 g of CaCO₃ in a 1500-mL beaker. While stirring, slowly add 500 mL of HCl. Cool the solution to room

temperature, filter into a 1-L volumetric flask, dilute to 1 L, and mix thoroughly. This solution contains the equivalent of 63 000 ppm (6.30 %) CaO.

17.1.5.2 Sodium-Potassium Chloride Stock Solution—Dissolve 1.8858 g of sodium chloride (NaCl) and 1.583 g of potassium chloride (KCl) (both dried at 105 to 110°C for several hours prior to weighing) in water. Dilute to 1 L in a volumetric flask and mix thoroughly. This solution contains the equivalent of 1000 ppm (0.10 %) each of Na₂O and K₂O. Separate solutions of Na₂O and of K₂O may be used provided that the same concentration solutions are used for calibration for cement analysis as were used for the calibration when qualifying the instrument in accordance with 17.1.3.

17.1.5.3 Standard Solutions—Prepare the standard solutions prescribed for the instrument and method used. Measure the required volume of NaCl-KCl stock solutions in calibrated pipets or burets. The calcium chloride stock solutions, if needed, may be measured in appropriate graduated cylinders. If the instrument being used requires an internal standard, measure the internal standard solution with a pipet or buret. Place each solution in a volumetric flask, dilute to the indicated volume, and mix thoroughly.

17.1.5.4 If more dilute solutions are required by the method in use, pipet the required aliquot to the proper sized volumetric flask, add any necessary internal standard, dilute to the mark, and mix thoroughly.

17.1.6 Calibration of Apparatus:

NOTE 59—No attempt is made in this section to describe in detail the steps for putting the instrument into operation since this will vary considerably with different instruments. The manufacturer’s instructions should be consulted for special techniques or precautions to be employed in the operation, maintenance, or cleaning of the apparatus.

17.1.6.1 Turn on the instrument and allow it to warm up in accordance with the manufacturer’s instructions. (A minimum of 30 min is required for most instruments.) Adjust the fuel and oxidant gas pressures as required by the instrument being used. Light and adjust the burner for optimum operation. Make any other adjustments that may be necessary to establish the proper operating conditions for the instrument.

17.1.7 Procedure:

17.1.7.1 Solution of the Cement—Prepare the solution of the cement in accordance with the procedure specified by the instrument manufacturer. If no procedure is specified, or if desired, proceed as specified in 17.1.7.1.1 or 17.1.7.1.2 (Note 59).

NOTE 60—The presence of SiO₂ in solution affects the accuracy of some flame photometers. In cases where an instrument fails to provide results within the prescribed degree of accuracy outlined in 3.3.2.1-3.3.3 tests should be made on solutions from which the SiO₂ has been removed. For this removal proceed as in .

17.1.7.1.1 Place 1.000 ± 0.001 g of the cement in a 150-mL beaker and disperse with 20 mL of water using a swirling motion of the beaker. While still swirling add 5.0 mL of HCl all at once. Dilute immediately to 50 mL with water. Break up any lumps of cement remaining undispersed with a flat-end stirring rod. Digest on a steam bath or hot plate for 15 min, then filter through a medium-textured filter paper into a 100-mL volumetric flask. Wash beaker and paper thoroughly with hot-water,

⁷ The 1963 revision of these test methods deleted the classical (J. L. Smith) gravimetric method for the determination of Na₂O and K₂O in cements. Those interested in this method should refer to the 1961 Book of ASTM Standards, Part 4.

The 1983 revision of these test methods deleted the details of the flame photometric procedure for the determination of Na₂O and K₂O. Those interested in this method should refer to the 1982 Annual Book of ASTM Standards, Part 13.

cool contents of the flask to room temperature, dilute to 100 mL, and mix the solution thoroughly. Continue as given in 17.1.7.2.

17.1.7.1.2 Place 1.000 ± 0.001 g of cement into a platinum evaporating dish and disperse with 10 mL of water using a swirling motion. While still swirling, add 5.0 mL of HCl all at once. Break up any lumps with a flat-end stirring rod and evaporate to dryness on a steam bath. Make certain that the gelatinous appearance is no longer evident. Treat the residue with 2.5 mL of HCl and about 20 mL of water. Digest on a steam bath for 5 to 10 min and filter immediately through a 9-cm medium-textured filter paper into a 100-mL volumetric flask. Wash thoroughly with repeated small amounts of hot water until the total volume of solution is 80 to 95 mL. Cool to room temperature, dilute to the mark, and mix thoroughly.

When it has been demonstrated that the removal of SiO_2 is necessary to obtain the required accuracy described in 3.3.2.1-3.3.3 for a specific flame photometer, SiO_2 must always be removed when making analyses that are used as the basis for rejection of a cement for failure to comply with specifications or where specification compliance may be in question. Where there is no question as to specification compliance, analyses may be made by such instruments without SiO_2 removal provided the deviations from certificate values obtained by the tests prescribed in 3.3.2.1-3.3.3 are not more than twice the indicated limits.

17.1.7.2 If the test method in use requires more dilute solutions, an internal standard, or both, carry out the same dilutions as in 17.1.5.4 as needed. The standard and the sample solutions to be analyzed must be prepared in the same way and to the same dilution as the solutions of standard cements analyzed for the qualification of the instrument.

17.1.7.3 *Procedure for Na_2O* (Note 62)—Warm up and adjust the instrument for the determination of Na_2O as described in 17.1.6.1. Immediately following the adjustment and without changing any instrumental settings, atomize the cement solution and note the scale reading (Note 61). Select the standard solutions which immediately bracket the cement solution in Na_2O content and observe their readings. Their values should agree with the values previously established during calibration of the apparatus. If not, recalibrate the apparatus for that constituent. Finally, alternate the use of the unknown solution and the bracketing standard solutions until readings of the unknown agree within one division on the transmission or meter scale, or within 0.01 weight percent for instruments with digital readout, and readings for the standards similarly agree with the calibration values. Record the average of the last two readings obtained for the unknown solution.

NOTE 61—The order in determining Na_2O or K_2O is optional. In all cases, however, the determination should immediately follow the adjustment of the instrument for that particular constituent.

17.1.7.4 If the reading exceeds the scale maximum, either transfer a 50-mL aliquot of the solution prepared in 17.1.7.1 to a 100-mL volumetric flask or, if desired, prepare a new solution by using 0.500 g of cement and 2.5 mL of HCl (instead of 5.0 mL) in the initial addition of acid. In the event silica has to be removed from the 0.5-g sample of cement, treat the dehydrated material with 1.25 mL of HCl and about 20 mL of water, then

digest, filter, and wash. In either case, add 5.0 mL of calcium chloride stock solution (17.1.5.1) before diluting to mark with water. Dilute to the mark. Proceed as in 17.1.5.4 if more dilute solutions are required by the test method in use. Determine the alkali content of this solution as described in (17.1.7.3) and multiply by a factor of 2 the percentage of alkali oxide.

17.1.7.5 *Procedure for K_2O* —Repeat the procedure described in 17.1.7.3 except that the instrument shall be adjusted for the determination of K_2O . For instruments that read both Na_2O and K_2O simultaneously, determine K_2O at the same time as determining Na_2O .

17.1.8 *Calculation and Report*—From the recorded averages for Na_2O and K_2O in the unknown sample, report each oxide to the nearest 0.01 %.

17.2 Water-Soluble Alkalies:

NOTE 62—The determination of water-soluble alkali should not be considered as a substitute for the determination of total alkali according to 17.1.2.1 to 17.1.8. Moreover, it is not to be assumed that in this method all water-soluble alkali in the cement will be dissolved. Strict adherence to the procedure described is essential where there is a specified limit on the content of water-soluble alkali or where several lots of cement are compared on the basis of water-soluble alkali.

17.2.1 Procedure:

17.2.1.1 Weigh 25.0 g of sample into a 500-mL Erlenmeyer flask and add 250 mL of water. Stopper the flask with a rubber stopper and shake continuously for 10 min at room temperature. Filter through a Büchner funnel which contains a well-seated retentive, dry filter paper, into a 500-mL filtering flask, using a weak vacuum. Do not wash.

17.2.1.2 Transfer a 50-mL aliquot (Note 63) of the filtrate to a 100-mL volumetric flask and acidify with 0.5 mL of concentrated HCl (sp gr 1.19). Add 9.0 mL of stock CaCl_2 solution (63 000 ppm CaO), described in 17.1.5.1, to the 100-mL flask, and dilute the solution to 100 mL. If the test method in use requires more dilute solutions, an internal standard, or both, carry out the same dilutions as in 17.1.5.4, as needed. Determine the Na_2O and K_2O contents of this solution as described in 17.1.7.3 and 17.1.7.5. Record the parts per million of each alkali in the solution in the 100-mL flask.

NOTE 63—The aliquot of the filtrate taken for the analysis should be based on the expected water-soluble alkali content. If the expected level of either K_2O or Na_2O is more than 0.08 weight % of cement, or if the water soluble alkali level is unknown, a 50-mL aliquot as given in 17.2.1.2 should be used to make up the initial test solution. If either the Na_2O or K_2O exceeds 0.16 %, place a 50-mL aliquot of the solution from 17.2.1.2 in a 100-mL volumetric flask, add 5 mL of CaCl_2 stock solution, and dilute to 100 mL. When the level of either K_2O or Na_2O is less than 0.08 %, take a 100-mL aliquot from the original filtrate (obtained by 17.2.1.1), add 1 mL of HCl, and evaporate on a hot plate in a 250-mL beaker to about 70 mL. Add 8 mL of stock CaCl_2 solution and transfer the sample to a 100-mL volumetric flask, rinsing the beaker with a small portion of distilled water. Cool the solution to room temperature and dilute to 100 mL.

17.2.2 *Calculations*—Calculate the percentage of the water-soluble alkali, expressed as Na_2O , to the nearest 0.01 as follows:

$$\text{Total water-soluble alkali, as } \text{Na}_2\text{O} = A + E \quad (9)$$

$$A = B/(V \times 10)$$

$$C = D/(V \times 10)$$



$$E = C \times 0.658$$

where:

- A** = percentage of water-soluble sodium oxide (Na_2O),
V = millilitres of original filtrate in the 100-mL flask,
B = parts per million of Na_2O in the solution in the 100-mL flask,
C = percent of water-soluble potassium oxide (K_2O),
D = parts per million of K_2O in the 100-mL flask,
E = percentage Na_2O equivalent to K_2O determined, and
 0.658 = molecular ratio of Na_2O to K_2O .

18. Manganic Oxide (Reference Method)

18.1 Summary of Method—In this procedure, manganic oxide is determined volumetrically by titration with sodium arsenite solution after oxidizing the manganese in the cement with sodium metabisulfate (NaBiO_3).

18.2 Reagents:

18.2.1 Sodium Arsenite, Standard Solution (1 mL = 0.0003 g Mn_2O_3)—Dissolve in 100 mL of water 3.0 g of sodium carbonate (Na_2CO_3) and then 0.90 g of arsenic trioxide (As_2O_3), heating the mixture until the solution is as complete as possible. If the solution is not clear or contains a residue, filter the solution. Cool it to room temperature, transfer to a volumetric flask, and dilute to 1 L.

18.2.1.1 Dissolve 0.58 g of potassium permanganate (KMnO_4) in 1 L of water and standardize it against about 0.03 g of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) oxidimetric standard furnished by NIST (Standard Sample No. 40 or its replacement) according to the directions furnished with the sodium oxalate. Put 30.0 mL of the KMnO_4 solution in a 250-mL Erlenmeyer flask. Add 60 mL of HNO_3 (1+4) and 10 mL of sodium nitrite (NaNO_2 , 50 g/L) to the flask. Boil the solution until the HNO_3 is completely expelled. Cool the solution, add NaBiO_3 , and finish by titrating with the standard sodium arsenite (NaAsO_2) solution as described in 18.3.2. Calculate the manganic oxide (Mn_2O_3) equivalent of the NaAsO_2 solution, g/mL, as follows:

$$E = (A \times 7.08)/BC \quad (10)$$

where:

- E** = Mn_2O_3 equivalent of the NaAsO_2 solution, g/mL,
A = grams of $\text{Na}_2\text{C}_2\text{O}_4$ used,
B = millilitres of KMnO_4 solution required by the $\text{Na}_2\text{C}_2\text{O}_4$,
C = millilitres of NaAsO_2 solution required by 30.0 mL of KMnO_4 solution, and
 7.08 = molecular ratio of Mn_2O_3 to 5 $\text{Na}_2\text{C}_2\text{O}_4$ (0.236) multiplied by 30.0 (millilitres of KMnO_4 solution).

18.2.2 Sodium Metabisulfate (NaBiO_3).

18.2.3 Sodium Nitrite Solution (50 g NaNO_2 /L).

18.3 Procedure:

18.3.1 Weigh 1.0 to 3.0 g of the sample (Note 64) into a 250-mL beaker and treat it with 5 to 10 mL of water and then with 60 to 75 mL of HNO_3 (1+4). Boil the mixture until the solution is as complete as possible. Add 10 mL of NaNO_2 solution (50 g/L) to the solution and boil it until the nitrous acid is completely expelled (Note 65), taking care not to allow the volume of the solution to become so small as to cause the precipitation of gelatinous SiO_2 . There may be some separated

SiO_2 , which may be ignored, but if there is still a red or brown residue, use more NaNO_2 solution (50 g/L) to effect a complete decomposition, and then boil again to expel the nitrous acid. Filter the solution through a medium-textured paper into a 250-mL Erlenmeyer flask and wash the filter paper with water.

NOTE 64—The amount of cement taken for analysis depends on the content of manganese, varying from 1 g for about 1 % of Mn_2O_3 to 3 g for 0.25 % or less of Mn_2O_3 .

NOTE 65—When NaNO_2 is added, the expulsion of HNO_2 by boiling must be complete. If any HNO_2 remains in the solution, it will react with the added NaBiO_3 and decrease its oxidizing value. If there is any manganese in the cement, the first small quantity of NaBiO_3 should bring out a purple color.

18.3.2 The solution should have a volume of 100 to 125 mL. Cool it to room temperature. To the solution add a total of 0.5 g of NaBiO_3 in small quantities, while shaking intermittently. After the addition is completed, shake the solution occasionally for 5 min and then add to it 50 mL of cool HNO_3 (1+33) which has been previously boiled to expel nitrous acid. Filter the solution through a pad of ignited asbestos in a Gooch crucible or a carbon or fritted-glass filter with the aid of suction. Wash the residue four times with the cool HNO_3 (1+33). Titrate the filtrate immediately with the standard solution of NaAsO_2 . The end point is reached when a yellow color is obtained free of brown or purple tints and does not change upon further addition of NaAsO_2 solution.

18.3.3 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.

18.4 Calculate the percentage of Mn_2O_3 to the nearest 0.01 as follows:

$$\text{Mn}_2\text{O}_3, \% = (EV/S) \times 100 \quad (11)$$

where:

- E** = Mn_2O_3 equivalent of the NaAsO_2 solution, g/mL,
V = millilitres of NaAsO_2 solution required by the sample, and
S = grams of sample used.

19. Chloride (Reference Test Method)

19.1 Summary of Test Method—In this test method total chloride content of portland cement is determined by the potentiometric titration of chloride with silver nitrate. The procedure is also applicable to hardened concrete, clinker, and portland cement raw mix. Under the conditions of the test, no constituent normally present in these materials will interfere.

NOTE 66—Species that form insoluble silver salts or stable silver complexes in acid solution interfere with potentiometric measurements. Thus, iodides and bromides interfere while fluorides will not. Sulfide salts in concentrations typical of these materials should not interfere because they are decomposed by acid treatment.

19.2 Apparatus:

19.2.1 Chloride, Silver/Sulfide Ion Selective Electrode, or a silver billet electrode coated with silver chloride (Note 67), with an appropriate reference electrode.

19.2.2 Potentiometer, with millivolt scale readable to 1 mV or better. A digital read-out is preferred but not required.

19.2.3 *Buret*, Class A, 10-mL capacity with 0.05-mL divisions. A buret of the potentiometric type, having a displaced delivery tip, is convenient, but not required.

NOTE 67—Suitable electrodes are available from Orion, Beckman Instruments, and Leeds and Northrup. Carefully following the manufacturer's instructions, add filling solution to the electrodes. The silver billet electrodes must be coated electrolytically with a thin, even layer of silver chloride. To coat the electrode, dip the clean silver billet of the electrode into a saturated solution of potassium chloride (about 40 g/L) in water and pass an electric current through the electrode from a 1½ to 6-V dry cell with the silver billet electrode connected to the positive terminal of the battery. A carbon rod from an all-dry cell or other suitable electrode is connected to the negative terminal and immersed in the solution to complete the electrical circuit. When the silver chloride coating wears off, it is necessary to rejuvenate the electrode by repeating the above procedure. All of the old silver chloride should first be removed from the silver billet by rubbing it gently with fine emery paper followed by water rinsing of the billet.

19.3 Reagents:

19.3.1 *Sodium Chloride* (NaCl), primary standard grade.

19.3.2 *Silver Nitrate* (AgNO₃), reagent grade.

19.3.3 *Potassium Chloride* (KCl), reagent grade (required for silver billet electrode only).

19.3.4 *Reagent Water* conforming to the requirements of Specification D 1193 for Type III reagent water.

19.4 Preparation of Solutions:

19.4.1 *Sodium Chloride, Standard Solution* (0.05 N NaCl)—Dry sodium chloride (NaCl) at 105 to 110°C to a constant weight. Weigh 2.9222 g of dried reagent. Dissolve in water and dilute to exactly 1 L in a volumetric flask and mix thoroughly. This solution is the standard and requires no further standardization.

19.4.2 *Silver Nitrate, Standard Solution* (0.05 N AgNO₃)—Dissolve 8.4938 g of silver nitrate (AgNO₃) in water. Dilute to 1 L in a volumetric flask and mix thoroughly. Standardize against 5.00 mL of standard 0.05 N sodium chloride solution diluted to 150 mL with water following the titration test method given in 19.5.4 beginning with the second sentence. The exact normality shall be calculated from the average of three determinations as follows:

$$N = 0.25/V \quad (12)$$

where:

N = normality of AgNO₃ solution,

0.25 = milliequivalents NaCl (5.0 mL $\times$ 0.05 N), and

V = volume of AgNO₃ solution, mL.

Commercially available standard solutions may be used provided the normality is checked according to the standardization procedure.

19.4.3 *Methyl Orange Indicator*—Prepare a solution containing 2 g of methyl orange per litre of 95 % ethyl alcohol.

19.5 Procedure:

19.5.1 Weigh a 5.0-g sample of the cement or a 10.0-g sample of concrete into a 250-mL beaker (Note 68). Disperse the sample with 75-mL of water. Without delay slowly add 25 mL of dilute (1+1) nitric acid, breaking up any lumps with a glass rod. If the smell of hydrogen sulfide is strongly evident at this point, add 3 mL of hydrogen peroxide (30 % solution) (Note 69). Add 3 drops of methyl orange indicator and stir.

Cover the beaker with a watch glass and allow to stand for 1 to 2 min. If a yellow to yellow-orange color appears on top of the settled solids, the solution is not sufficiently acidic. Add additional dilute nitric acid (1+1) dropwise while stirring until a faint pink or red color persists. Then add 10 drops in excess. Heat the covered beaker rapidly to boiling. Do not allow to boil for more than a few seconds. Remove from the hot plate (Note 70).

NOTE 68—Use a 5-g sample for cement, and 10 g for concrete and other materials having an expected chloride content of less than about 0.15 % Cl. Use proportionally smaller samples for materials with higher chloride concentrations. Use cement and other powdered materials as is without grinding. Coarse samples require grinding to pass a 20-mesh sieve. If a sample is too fine, excessive silica gel may form during digestion with nitric acid, thereby slowing subsequent filtration.

NOTE 69—Slags and slag cements contain sulfide sulfur in concentrations that can interfere with the determination.

NOTE 70—It is important to keep the beaker covered during heating and digestion to prevent the loss of chloride by volatilization. Excessive amounts of acid should not be used since this results in early removal of the silver chloride coating from the silver billet electrode. A slurry that is only slightly acidic is sufficient.

19.5.2 Wash a 9-cm coarse-textured filter paper with four 25-mL increments of water using suction filtering provided by a 250-mL or 500-mL Büchner funnel and filtration flask. Discard the washings and rinse the flask once with a small portion of water. Reassemble the suction apparatus and filter the sample solution. Rinse the beaker and the filter paper twice with small portions of water. Transfer the filtrate from the flask to a 250-mL beaker and rinse the flask once with water. The original beaker may be used (Note 71). Cool the filtrate to room temperature. The volume should not exceed 175 mL.

NOTE 71—It is not necessary to clean all the slurry residue from the sides of the beaker nor is it necessary that the filter remove all of the fine material. The titration may take place in a solution containing a small amount of solid matter.

19.5.3 For instruments equipped with dial readout it is necessary to establish an approximate "equivalence point" by immersing the electrodes in a beaker of water and adjusting the instrument to read about 20 mV lower than mid-scale. Record the approximate millivoltmeter reading. Remove the beaker and wipe the electrodes with absorbent paper.

19.5.4 To the cooled sample (Note 72) beaker from 19.5.2, carefully pipet 2.00 mL of standard 0.05 N NaCl solution. Place the beaker on a magnetic stirrer and add a TFE-fluorocarbon-coated magnetic stirring bar. Immerse the electrodes into the solution taking care that the stirring bar does not strike the electrodes; begin stirring gently. Place the delivery tip of the 10-mL buret, filled to the mark with standard 0.05 N silver nitrate solution, in (preferably) or above the solution (Note 73).

NOTE 72—It is advisable to maintain constant temperature during measurement, for the solubility relationship of silver chloride varies markedly with temperature at low concentrations.

NOTE 73—If the tip of the buret is out of the solution, any adhering droplet should be rinsed onto the beaker with a few millilitres of water following each titration increment.

19.5.5 Gradually titrate, record the amount of standard 0.05 *N* silver nitrate solution required to bring the millivoltmeter reading to -60.0 mV of the equivalence point determined in the water.

19.5.6 Continue the titration with 0.20-mL increments. Record the buret reading and the corresponding millivoltmeter reading in columns 1 and 2 of a four-column recording form like that shown in Appendix X1. Allow sufficient time between each addition for the electrodes to reach equilibrium with the sample solution. Experience has shown that acceptable readings are obtained when the minimum scale reading does not change within a 5-s period (usually within 2 min).

19.5.7 As the equivalence point is approached, the equal additions of AgNO₃ solution will cause larger and larger changes in the millivoltmeter readings. Past the equivalence point the change per increment will again decrease. Continue to titrate until three readings past the approximate equivalence point have been recorded.

19.5.8 Calculate the difference in millivolt readings between successive additions of titrant and enter the values in Column 3 of the recording form. Calculate the difference between consecutive values in Column 3 and enter the results in Column 4. The equivalence point of the titration will be within the maximum Δ mV interval recorded in Column 3. The precise equivalence point can be interpolated from the data listed in Column 4 as shown in the Appendix X1.

19.5.9 *Blank*—Make a blank determination using 75 mL of water in place of the sample, following the same procedure starting with the third sentence of 19.5.1 without delay. Correct the results obtained in the analysis accordingly (Note 74) by subtracting the blank.

19.6 *Calculation*— Calculate the percent chloride to the nearest 0.001 % as follows:

$$\text{Cl, \%} = \frac{3.545 [(V_1 - V_2)N]}{W} \quad (13)$$

where:

- V_1 = millilitres of 0.05 *N* AgNO₃ solution used for sample titration (equivalence point),
- V_2 = millilitres of 0.05 *N* AgNO₃ solution used for blank titration (equivalence point),
- N = exact normality of 0.05 *N* AgNO₃ solution,
- 0.10 = milliequivalents of NaCl added (2.0 mL $\times$ 0.05 *N*), and
- W = weight of sample, g.

NOTE 74—For nonreferee analysis the blank may be omitted.

20. Chloroform-Soluble Organic Substances (Reference Test Method)

20.1 *Summary of Test Method*—This test method⁸ was specially designed for the determination of Vinsol resin and tallow in portland cement, although mineral oil, common rosin, calcium stearate, and other fatty acid compounds, and probably some other substances, if present, will be included in the

determination. Extreme care is necessary in the entire procedure. The test method may be applied to types of cement other than portland cement, although if the cement contains a large amount of acid-insoluble matter, the emulsions may separate slowly, and less vigorous shaking, more chloroform, and more washing may be necessary.

20.2 Reagents:

20.2.1 *Chloroform*—If the blank determination as described in 20.3.5 exceeds 0.0015 g, the chloroform should be distilled before use. Chloroform recovered in the procedure may be slightly acid but can be reused for the portions to be shaken with the aqueous acid solution of the sample in the 1-L funnel. Chloroform used for washing the filter and transferring the extract should be fresh or distilled from fresh chloroform.

20.2.2 Stannous Chloride (SnCl₂).

20.3 Procedure:

20.3.1 Place 40 g of cement in a 1-L Squibb separatory funnel (Note 75) and mix it with 520 mL of water added in two approximately equal portions. Shake vigorously immediately after the addition of the first portion to effect complete dispersion. Then add the second portion and shake again. At once add rapidly 185 mL of HCl in which 10 g of SnCl₂ (Note 76) have been dissolved, rapidly insert the stopper in the funnel, invert, and shake with a swirling motion for a few seconds to loosen and disperse all the cement, taking care to avoid the development of great internal pressure due to unnecessarily violent shaking. Release internal pressure immediately by opening and closing the stopcock. Repeat the shaking and release the pressure until the decomposition of the cement is complete. If necessary, break up persistent lumps with a long glass rod. Cool to room temperature rapidly by allowing tap water to run on the flask.

NOTE 75—The use of grease to lubricate the stopcocks and glass stoppers of the separatory funnels should be avoided. Wetting the stopcocks with water before using will assist in their easy operation.

NOTE 76—The purpose of the SnCl₂ is to prevent the oxidation of sulfide sulfur to elemental sulfur, which is soluble in chloroform.

20.3.2 Add 75 mL of chloroform to the solution, stopper the funnel, shake it vigorously for 5 min, and allow the water and chloroform to stand 15 min to separate. Draw off the lower chloroform layer into a 125-mL Squibb separatory funnel, including the scum (Note 77) and a few millilitres of the aqueous layer, making certain that all the scum is transferred. Keep the amount of the aqueous layer transferred to an absolute minimum, since excessive water in the 125-mL funnel may result in incomplete extraction of the scum and may cause an emulsion which does not separate readily. Shake the funnel vigorously to ensure the complete extraction of the scum. Allow the chloroform to separate, and draw it into a 250-mL Squibb separatory funnel which contains 50 mL of water and a few drops of HCl, making sure to keep the scum behind in the 125-mL funnel. Shake the 250-mL funnel, and draw the chloroform into another 250-mL funnel that contains 50 mL of water and a few drops of HCl. Shake this funnel as in the case of the first 250-mL funnel. When the chloroform separates, draw it into a standard-taper flat-bottom boiling flask (Note 78), taking care not to allow any water to enter the flask.

NOTE 77—There is usually a dark colored scum at the liquid interface.

⁸ The 1965 revision of these test methods deleted the methoxyl test method for determining Vinsol resin. Those interested in this test method should refer to the 1966 Book of ASTM Standards, Part 9.

It may contain chloroform-soluble organic substance after shaking in the funnel, where the proportion of water to chloroform is great. It may be concentrated and confined to a small volume by gently twirling the funnel after the scum has been drawn into the narrower part of the funnel.

NOTE 78—The liquid is later distilled. No cork or rubber stoppers should be used. A 250 or 300-mL soil analysis flask, fitted with a condenser tube by means of a ground joint, is satisfactory. The tube may be bent near the neck and the remaining part fitted with a water-cooling jacket. Chloroform thus recovered may be reused as described in 20.2.1.

20.3.3 Add 25 mL of chloroform to the solution in the original 1-L separatory funnel, and carry out the operations as described in 20.3.2, retaining the original wash water in the 250-mL funnels. Repeat, using another 25-mL portion of chloroform.

20.3.4 Distill the combined chloroform extracts in the boiling flask until their volume is reduced to 10 to 15 mL. Filter the remaining liquid into a weighed 100-mL glass beaker or platinum dish (Note 79) through a small medium-textured filter paper that has been washed with fresh chloroform. Rinse the flask and wash the paper with several small portions of fresh chloroform. Evaporate the extracts at a low temperature (not over 63°C) to dryness (Note 80) and heat it in an oven at 57 to 63°C for 3 min. Pass dry air into the vessel for 15 s, cool, and weigh. Repeat the heating and weighing until two successive weighings do not differ by more than 0.0010 g. The higher of the last two weights shall be taken as the true weight.

NOTE 79—A platinum dish is preferable, as it quickly attains the temperature of the balance. If a glass beaker is used, it should be allowed to stand in the case of the balance for at least 20 min before weighing.

NOTE 80—Care should be taken in drying the extract, as many of the chloroform-soluble organic substances are somewhat volatile when heated for a long time at even moderate temperatures. With protection from the accumulation of dust, the solution may be evaporated at room temperature overnight.

When a quick evaporation is desired, the solution may be evaporated on a hot plate at low heat under a stream of dry air through a glass tube (about 10 mm in inside diameter) until it is about 3 mm in depth. Then remove the vessel from the hot plate and continue a slow stream of dry air until the residue appears dry. Then continue with a more rapid stream of dry air for 5 min at room temperature before placing the vessel in the oven at 57 to 63°C. After each 3-min heating period in the oven, pass dry air into the vessel for about 15 s before weighing. The air may be dried by passing it through a cheap desiccant, such as calcium chloride or sulfuric acid, followed by a desiccant of high efficiency, such as magnesium perchlorate or anhydrous calcium sulfate, with care taken to avoid the carrying of dust from the desiccant by the air. Instead of using compressed air, which is often contaminated with oil, dirt, and moisture, one can place the chloroform solution under a bell glass and induce a stream of air through the desiccants by means of an aspirator or vacuum pump.

When Vinsol resin is known to be the only substance present, the residue is more stable and may be heated at 100 to 105°C, instead of 57 to 63°C, in order to expel all possible traces of chloroform.

20.3.5 *Blank*—Make a blank determination. Ignite a 40-g sample of the cement at 950 to 1000°C for 1 h (Note 81) and regrind. Treat this ignited sample by the same procedure and using the same reagents as in the analysis and correct the results accordingly.

NOTE 81—Care should be taken to completely burn off the organic substance. A 100-mL flat platinum dish, in which the sample is well spread out, and a muffle furnace are advised for this purpose. If such a furnace is not available, a large high-temperature burner of the Meker type may be used. Thorough stirring of the sample should be done frequently—every

5 min when a burner is used.

20.4 *Calculation*—Calculate the percentage of chloroform-soluble organic substances to the nearest 0.001 by multiplying the weight in grams of residue (Note 82) by 2.5 (100 divided by the weight of the sample used (40 g)).

NOTE 82—If the organic substance in the cement is tallow, the residue is the fatty acids resulting from the hydrolysis of the tallow in the hot acid solution, and its weight should be multiplied by 1.05 to give the weight of the original glycerides in the tallow. If the original substance is calcium stearate, the residue is stearic acid, and its weight multiplied by 1.07 gives the weight of calcium stearate.

ALTERNATIVE TEST METHODS

21. Calcium Oxide (*Alternative Test Method*)

21.1 *Summary of Test Method:*

21.1.1 This test method covers the gravimetric determination of CaO after removal of SiO₂ and the ammonium hydroxide groups and double precipitation of calcium as the oxalate. The precipitate is converted to CaO by ignition and is weighed.

21.1.2 Strontium, usually present in portland cement as a minor constituent, is precipitated with calcium as the oxalate and is subsequently calculated as CaO. If the SrO content is known and correction of CaO for SrO is desired as, for example, for research purposes or to compare results with CRM certificate values, the CaO obtained by this test method may be corrected by subtracting percent SrO. In determining conformance of a cement to specifications the correction of CaO for SrO should not be made.

21.2 *Procedure* (Note 83):

21.2.1 Acidify the combined filtrates obtained in the determination of the ammonium hydroxide group (7.1-7.3) and, if necessary, evaporate to a volume of about 200 mL. Add 5 mL of HCl, a few drops of methyl red indicator solution, and 30 mL of warm ammonium oxalate solution (50 g/L) (Note 39). Heat the solution to 70 to 80°C and add NH₄OH (1+1) dropwise with stirring until the color changes from red to yellow (see Note 40). Allow the solution to stand without further heating for 1 h (not longer), with occasional stirring during the first 30 min. Filter using a retentive paper and wash moderately with cold ammonium oxalate solution (1 g/L). Reserve the filtrate and washings.

NOTE 83—When analyses are being made for determining conformity to specifications and there is a possibility that sufficient manganese will be present to cause the percentage of magnesium determined by alternate test methods to exceed the specification limit, manganese may be removed as directed in 13.3.2 before CaO is determined by this alternative test method.

21.2.2 Transfer the precipitate and filter paper to the beaker in which the precipitation was made. Dissolve the oxalate in 50 mL of hot HCl (1+4) and macerate the filter paper. Dilute to 200 mL with water, add a few drops of methyl red indicator and 20 mL of ammonium oxalate solution, heat the solution nearly to boiling, and precipitate calcium oxalate again by neutralizing the acid solution with NH₄OH as described in 13.3.1. Allow the solution to stand 1 to 2 h (standing for 2 h at this point does no harm), filter, and wash as before. Combine the

filtrate with that already obtained and reserve for the determination of MgO (14.3.1).

21.2.3 Dry the precipitate in a weighed covered platinum crucible. Char the paper without inflaming, burn the carbon at as low a temperature as possible, and, finally, heat with the crucible tightly covered in an electric furnace or over a blast lamp at a temperature of 1100 to 1200°C. Cool in a desiccator and weigh as CaO. Repeat the ignition to constant weight.

21.2.4 *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.

21.3 Calculation:

21.3.1 Calculate the percentage of CaO to the nearest 0.1 by multiplying the weight in grams of CaO by 200 (100 divided by the weight of sample used (0.5 g)).

21.3.2 Correct the percent CaO for SrO, if desired, by subtracting the percent SrO.

22. Magnesium Oxide (Alternative Test Method)

22.1 *Summary of Test Method*—This alternative test method is a volumetric procedure suitable for use when the determinations of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), and calcium oxide (CaO) are omitted.

22.2 *Rapid Volumetric Test Method (Titration of Magnesium Oxyquinolate)*:

22.3 Reagents:

22.3.1 *Ammonium Nitrate Solution* (20 g $\text{NH}_4\text{NO}_3/\text{L}$).

22.3.2 *Ammonium Oxalate Solution* (50 g/L).

22.3.3 *Hydroxyquinoline Solution*—Dissolve 25 g of 8-hydroxyquinoline in 60 mL of acetic acid. When the solution is complete, dilute to 2 L with cold water. One millilitre of this solution is equivalent to 0.0016 g of MgO.

22.3.4 *Potassium Bromate-Potassium Bromide, Standard Solution* (0.2 N)—Dissolve 20 g of potassium bromide (KBr) and 5.57 g of potassium bromate (KBrO_3) in 200 mL of water and dilute to 1 L. Obtain the ratio of the strength of this solution to that of the 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution (22.2.6) as follows: To 200 mL of water in a 500-mL Erlenmeyer flask add 25.0 mL of the 0.2 N KBrO_3 -KBr solution, measured from a pipet or buret. Add 20 mL of HCl, stir, and add immediately 10 mL of potassium iodide (KI) (250 g/L). Mix well and titrate at once with the $\text{Na}_2\text{S}_2\text{O}_3$ solution until nearly colorless. Add 2 mL of starch solution and titrate to the disappearance of the blue color. Calculate the ratio in strength of the KBrO_3 -KBr solution to the $\text{Na}_2\text{S}_2\text{O}_3$ solution by dividing the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution by the volume of KBrO_3 -KBr solution used in the titration.

22.3.5 *Potassium Iodide Solution* (250 g KI/L).

22.3.6 *Sodium Thiosulfate, Standard Solution* (0.1 N)—Dissolve 25 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 200 mL of water, add 0.1 g of sodium carbonate (Na_2CO_3), and dilute to 1 L. Let stand at least 1 week. Standardize this solution directly against primary standard potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). One millilitre of 0.10 N $\text{Na}_2\text{S}_2\text{O}_3$ solution is equivalent to 0.000504 g of MgO.

22.3.7 *Starch Solution*—To 500 mL of boiling water add a cold suspension of 5 g of soluble starch in 25 mL of water, cool

to room temperature, add a cool solution of 5 g of sodium hydroxide (NaOH) in 50 mL of water, add 15 g of KI, and mix thoroughly.

22.4 Procedure:

22.4.1 Disperse 0.5 g (Note 84) of the sample of cement in a 400-mL beaker with 10 mL of water, using a swirling motion. While still swirling, add 10 mL of HCl all at once. Dilute immediately to 100 mL. Heat gently and grind any coarse particles with the flattened end of a glass rod until decomposition is complete, add 2 or 3 drops of HNO_3 and heat to boiling (Note 85).

NOTE 84—If SiO_2 , ammonium hydroxide group, and CaO are separated and determined in accordance with the appropriate sections for either the reference or alternative test methods, the remaining filtrate may be used for the determination of MgO as described in 22.4.1, starting with the third from the last sentence of 22.4.2, “Add 5 mL of HCl. . .”.

NOTE 85—In the case of cements containing blast-furnace slag or a significant quantity of sulfide sulfur, add 12 drops of HNO_3 and boil for 20 min to oxidize iron and remove sulfide.

22.4.2 Add 3 drops of methyl red indicator to the solution and then add NH_4OH until the solution is distinctly yellow. Heat this solution 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 a hot plate having the approximate temperature of a steam bath, may be substituted for the 50 to 60-s boiling period. Remove from the burner, steam bath, or hot plate and allow to stand until the precipitate has settled. Using medium-textured paper, filter the solution without delay, wash the precipitate twice with hot NH_4NO_3 (20 g/L), and reserve the filtrate. Transfer the precipitate with the filter paper to the beaker and dissolve in 10 mL of HCl (1+1). Macerate the filter paper. Dilute to about 100 mL and heat to boiling. Reprecipitate, filter, and wash the hydroxides as above. Combine this filtrate and washings with those from the first precipitation taking care that the volume does not exceed 300 mL (Note 86). Add 5 mL of HCl, a few drops of methyl red indicator solution and 30 mL of warm ammonium oxalate solution (50 g/L). Heat the solution to 70 to 80°C and add NH_4OH (1+1) dropwise, while stirring, until the color changes from red to yellow (see Note 40). Allow the solution to stand without further heating for 15 min on a steam bath.

NOTE 86—In the case of cements containing blast-furnace slag, or which are believed to contain a significant quantity of manganese, acidify with HCl, evaporate to about 100 mL, and remove the manganese, using the procedure described in 13.3.1.

22.4.3 Add 10 to 25 mL of the 8-hydroxyquinoline reagent (Note 87) and then 4 mL of $\text{NH}_4\text{OH}/100$ mL of solution. Stir the solution on a mechanical stirring machine for 15 min and set aside until the precipitate has settled (Note 88). Filter the solution using medium-textured paper and wash the precipitate with hot NH_4OH (1+40). Dissolve the precipitate in 50 to 75 mL of hot HCl (1+9) in a 500-mL Erlenmeyer flask. Dilute the resulting solution to 200 mL and add 15 mL of HCl. Cool the solution to 25°C and add 10 to 35 mL of the 0.2 N KBrO_3 -KBr solution (Note 89) from a pipet or buret. Stir the solution and allow to stand for about 30 s to ensure complete bromination. Add 10 mL of KI (250 g/L). Stir the resulting solution well and

then titrate with the 0.1 N Na₂S₂O₃ solution until the color of the iodine becomes faintly yellow. At this point add 2 mL of the starch solution and titrate the solution to the disappearance of the blue color.

NOTE 87—An excess of the 8-hydroxyquinoline reagent is needed to avoid a low result for MgO, but too great an excess will yield high results. The following guide should be used to determine the amount of reagent added:

Approximate Content of MgO, %	Approximate Amount of Reagent Required, mL
0 to 1.5	10
1.5 to 3.0	15
3.0 to 4.5	20
4.5 to 6.0	25

NOTE 88—The precipitate should be filtered within an hour. Prolonged standing may cause high results.

NOTE 89—The amount of the standard KBrO₃–KBr solution used should be as follows:

Approximate Content of MgO, %	Amounts of Standard KBrO ₃ – KBr Solution, mL
0 to 1	10
1 to 2	15
2 to 3	20
3 to 4	25
4 to 5	30
5 to 6	35

22.4.4 *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.

22.5 *Calculation*— Calculate the percentage of MgO to the nearest 0.1 as follows: (Note 90)

$$\text{MgO, \%} = E(V_{1R} - V_2) \times 200 \quad (14)$$

where:

- E = MgO equivalent of the Na₂S₂O₃ solution, g/mL,
- V_1 = millilitres of KBrO₃–KBr solution used,
- R = ratio in strength of the KBrO₃–KBr solution to the Na₂S₂O₃ solution,
- V_2 = millilitres of Na₂S₂O₃ solution used, and
- 200 = 100 divided by the weight of sample used (0.5 g).

NOTE 90— V_{1R} represents the volume of Na₂S₂O₃ solution equivalent to the volume of KBrO₃–KBr solution used. V_2 represents the amount of Na₂S₂O₃ required by the excess KBrO₃–KBr which is not reduced by magnesium oxyquinolate.

23. Loss on Ignition

23.1 *Portland Blast-Furnace Slag Cement and Slag Cement (Alternative Test Method)*:

23.1.1 *Summary of Test Method*—This test method covers a correction for the gain in weight due to oxidation of sulfides usually present in such cement by determining the decrease in the sulfide sulfur content during ignition. It gives essentially the same result as the reference test method (16.2.1 through 16.2.3) which provides for applying a correction based on the increase in SO₃ content.

23.1.2 *Procedure*:

23.1.2.1 Weigh 1 g of cement in a tared platinum crucible, cover, and ignite in a muffle furnace at a temperature of 950 ± 50°C for 15 min. Cool to room temperature in a

desiccator and weigh. After weighing carefully transfer the ignited material to a 500-mL boiling flask. Break up any lumps in the ignited cement with the flattened end of a glass rod.

23.1.2.2 Determine the sulfide sulfur content of the ignited sample using the procedure described in 15.2.1 through 15.2.5. Using the same procedure, also determine the sulfide sulfur content of a portion of the cement that has not been ignited.

23.1.3 *Calculation*—Calculate the percentage loss of weight occurring during ignition (23.1.2.1) and add twice the difference between the percentages of sulfide sulfur in the original sample and ignited sample as determined in 23.1.2.2. Report this value as the loss on ignition.

NOTE 91—If a gain of weight is obtained during the ignition, subtract the percentage of gain from the correction for sulfide oxidation.

24. Titanium Dioxide (Alternative Test Method)

24.1 *Summary of Test Method*—In this test method, titanium dioxide (TiO₂) is determined colorimetrically by comparing the color intensity of the peroxidized solution of the titanium in the sample with the color intensity of a peroxidized standard solution of titanate sulfate.

24.2 *Interferences*— Interfering elements in the peroxide method for TiO₂ are vanadium, molybdenum, and chromium. In very small quantities the interference of the last two is negligible. However, vanadium in very small quantities causes interference and, as some cements contain this element, the Na₂CO₃ fusion (24.5.4) and extraction with water are necessary.

24.3 *Apparatus*:

24.3.1 *Colorimeter*— The apparatus shall consist of a colorimeter of the Kennicott or Duboscq type, or other colorimeter or spectrophotometer designed to measure light transmittancy, and suitable for measurements at wavelengths between 400 and 450 nm.

24.4 *Reagents*:

24.4.1 *Ammonium Chloride* (NH₄Cl).

24.4.2 *Ammonium Nitrate* (20 g NH₄NO₃/L).

24.4.3 *Ferrous Sulfate Solution* (1 mL = 0.005 g Fe₂O₃)— Dissolve 17.4 g of ferrous sulfate (FeSO₄ · 7H₂O) in water containing 50 mL of H₂SO₄ and dilute to 1 L. One millilitre is equivalent to 1 % of Fe₂O₃ in 0.5 g of sample.

24.4.4 *Hydrogen Peroxide* (30 %)—Concentrated hydrogen peroxide (H₂O₂).

24.4.5 *Sodium Carbonate* (20 g Na₂CO₃/L).

24.4.6 *Sodium or Potassium Pyrosulfate* (Na₂S₂O₇ or K₂S₂O₇).

24.4.7 *Titanic Sulfate, Standard Solution* (1 mL = 0.0002 g TiO₂)—Use standard TiO₂ furnished by NIST (Standard Sample 154 or its replacements). Dry for 2 h at 105 to 110°C. Transfer a weighed amount, from 0.20 to 0.21 g of the TiO₂ to a 125-mL Phillips beaker. Add 5 g of ammonium sulfate ((NH₄)₂SO₄) and 10 mL of H₂SO₄ to the beaker and insert a short-stem glass funnel in the mouth of the beaker. Heat the mixture cautiously to incipient boiling while rotating the flask over a free flame. Continue the heating until complete solution has been effected and no unattacked material remains on the wall of the flask (Note 92). Cool and rapidly pour the solution into 200 mL of cold water while stirring vigorously. Rinse the

flask and funnel with $\text{H}_2\text{SO}_4(1+19)$, stir, and let the solution and washings stand for at least 24 h. Filter into a 1-L volumetric flask, wash the filter thoroughly with $\text{H}_2\text{SO}_4(1+19)$, dilute to the mark with $\text{H}_2\text{SO}_4(1+19)$, and mix.

NOTE 92—There may be a small residue, but it should not contain more than a trace of TiO_2 if the operations have been properly performed.

24.4.8 Calculate the TiO_2 equivalent of the titanic sulfate solution, g/mL, as follows:

$$E = AB/1000 \quad (15)$$

where:

- E = TiO_2 equivalent of the $\text{Ti}(\text{SO}_4)_2$ solution, g/mL,
- A = grams of standard TiO_2 used (corrected for loss on drying),
- B = percentage of TiO_2 in the standard TiO_2 as certified by the National Institute of Standards and Technology, divided by 100, and
- 1000 = Number of millilitres in the volumetric flask.

24.5 Procedure:

24.5.1 Mix thoroughly 0.5 g of the sample of cement 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, stir the mixture with a glass rod, replace the cover, and set the beaker on a steam bath for 30 min (Note 93). 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 and transfer the precipitate to the filter. Scrub the beaker with a rubber policeman and rinse the beaker and policeman. Wash the filter two or three times with hot $\text{HCl}(1+99)$ and then with ten or twelve small portions of hot water, allowing each portion to drain through completely.

NOTE 93—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.

24.5.2 Transfer the filter and residue to a platinum crucible (Note 94), dry, and ignite slowly until the carbon of the paper is completely consumed without inflaming. Treat the SiO_2 thus obtained with 0.5 to 1 mL of water, about 10 mL of HF , and 1 drop of H_2SO_4 , and evaporate cautiously to dryness (Note 95).

NOTE 94—When it is desired to shorten the procedure for purposes other than referee analysis, usually with little sacrifice of accuracy, the procedure given in 24.5.2 may be omitted.

NOTE 95—When a determination of SiO_2 is desired in addition to one of TiO_2 , the SiO_2 may be obtained and treated with HF as directed in 6.2.3.1 through 6.2.4.

24.5.3 Heat the filtrate to boiling and add NH_4OH until the solution becomes distinctly alkaline, as indicated by an ammoniacal odor. Add a small amount of filter paper pulp to the solution and boil for 50 to 60 s. Allow the precipitate to settle, filter through a medium-textured paper, and wash twice with hot NH_4NO_3 solution (20 g/L). Place the precipitate in the platinum crucible in which the SiO_2 has been treated with HF and ignite slowly until the carbon of the paper is consumed.

NOTE 96—When a determination of ammonium hydroxide group is desired in addition to one of TiO_2 , the precipitation and ignition may be

made as described in 7.2.1-7.2.4. However, the crucible must contain the residue from the treatment of the SiO_2 with HF unless circumstances permit its omission as indicated in Note 95.

24.5.4 Add 5 g of Na_2CO_3 to the crucible and fuse for 10 to 15 min (see 24.2.1). Cool, separate the melt from the crucible, and transfer to a small beaker. Wash the crucible with hot water, using a policeman. Digest the melt and washings until the melt is completely disintegrated, then filter through a 9-cm medium-textured filter paper and wash a few times with Na_2CO_3 (20 g/L). Discard the filtrate. Place the precipitate in the platinum crucible and ignite slowly until the carbon of the paper is consumed.

24.5.5 Add 3 g of $\text{Na}_2\text{S}_2\text{O}_7$ or $\text{K}_2\text{S}_2\text{O}_7$ to the crucible and heat below red heat until the residue is dissolved in the melt (Note 97). Cool and dissolve the fused mass in water containing 2.5 mL of H_2SO_4 . If necessary, reduce the volume of the solution (Note 98), filter into a 100-mL volumetric flask through a 7-cm medium-textured filter paper, and wash with hot water. Add 5 mL of H_3PO_4 , and cool the solution to room temperature. Add H_2O_2 (1.0 mL of 30 % strength or its equivalent) (Note 99), dilute to the mark with water, and mix thoroughly.

NOTE 97—Start the heating with caution because pyrosulfates (also known as fused bisulfates) as received often foam and spatter in the beginning due to an excess of H_2SO_4 . Avoid an unnecessarily high temperature or unnecessarily prolonged heating, as fused pyrosulfates may attack platinum. A supply of nonspattering pyrosulfates may be prepared by heating some pyrosulfate in a platinum vessel to eliminate the excess H_2SO_4 and crushing the cool fused mass.

NOTE 98—If the solution is evaporated to too small a volume and allowed to cool, there may be a precipitate of sulfates difficult to redissolve. In case of over-evaporation, do not permit the contents to cool, but add hot water and digest on a steam bath or hot plate until the precipitate is redissolved, with the possible exception of a small amount of SiO_2 .

NOTE 99—Hydrogen peroxide deteriorates on standing. Its strength may be determined by adding a measured volume of the solution to 200 mL of cold water and 10 mL of $\text{H}_2\text{SO}_4(1+1)$ and titrating with a standard solution of potassium permanganate (KMnO_4) prepared in accordance with 13.2.2. If the standard solution contains 0.0056357 g of KMnO_4 /mL, 49.5 mL of it will be required by 0.50 mL of H_2O_2 (30 %).

24.5.6 Prepare from the standard $\text{Ti}(\text{SO}_4)_2$ solution a suitable reference standard solution or a series of reference standard solutions in 100-mL volumetric flasks, depending upon the type of colorimeter to be used. To each solution add 3 g of $\text{Na}_2\text{S}_2\text{O}_7$ or $\text{K}_2\text{S}_2\text{O}_7$ dissolved in water, an amount of FeSO_4 solution equivalent to the Fe_2O_3 content in 0.5 g of the cement under test, 2.5 mL of H_2SO_4 , and 5 mL of H_3PO_4 (Note 100). When the solution is at room temperature, add H_2O_2 (1.0 mL of 30 % strength or its equivalent), dilute to the mark with water, and mix thoroughly (Note 101).

NOTE 100—The color imparted to the solution by $\text{Fe}_2(\text{SO}_4)_3$ is partly offset by the bleaching effect of H_2SO_4 , H_3PO_4 , and alkali salts on ferric and peritanic ions. The directions should be followed closely for the highest degree of precision. However, when it is desired to shorten this procedure for purposes other than referee analysis, the addition of pyrosulfate, FeSO_4 solution and H_3PO_4 to the color comparison solutions may be omitted provided the Fe_2O_3 of the sample cement is less than 5 %. This usually leads to little sacrifice to accuracy.

NOTE 101—The color develops rapidly and is stable for a sufficient period of time, but if the peroxidized solution is allowed to stand a long

time, bubbles of oxygen may appear and interfere with color comparison. When the contents of a tube are first mixed, there may be fine bubbles which should be allowed to clear up before the comparison is made. Comparison between the standard and unknown solution should be made not less than 30 min after addition of H_2O_2 .

24.5.7 Compare the color, light transmittancy, or absorbance of the unknown solution with the reference standard solution. The technique of comparing colored solutions or measuring transmittancy or absorbance depends on the type of apparatus (see 24.5.8-24.5.10) and should be in accordance with standard practice appropriate to the particular type used or with instructions supplied by the manufacturer of the equipment. If the peroxidized solution of cement is compared with a single standard peroxidized solution, bear in mind that a single peroxidized solution cannot be used for the whole range in TiO_2 content that may be encountered. The difference in volume or depth for the two liquids should not exceed 50 % of the smaller value. All solutions should contain the prescribed concentrations of H_2SO_4 , H_3PO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and persulfate except under the circumstances indicated in Note 101.

24.5.8 *Colorimeter of the Kennicott Type*—By means of a plunger in a reservoir of standard peroxidized solution, adjust the amount of solution through which light passes until it gives the same color intensity as the peroxidized solution of the sample.

24.5.9 *Colorimeter of the Duboscq Type*—Lower or raise the plungers in the cups until the two solutions give the same color intensity when viewed vertically. The color matching may be done either visually or photoelectrically.

24.5.10 *Colorimeter Designed to Measure Light Transmittancy*—The measurement should be made between 400 to 450 nm and may be made either visually or photoelectrically. In most colorimeters of this type, the instrument is calibrated with standard solutions and a calibration curve showing the relation of light transmittancy or absorbance to TiO_2 content is prepared in advance of the analysis of the sample for TiO_2 .

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

24.6 *Calculation*—Calculate the percentage of TiO_2 to the nearest 0.01. When a colorimeter designed to measure light transmittancy is used, read the percentage of TiO_2 from a calibration curve showing the relation of light intensity to TiO_2 content. When the peroxidized solution of the sample is compared with a single reference standard solution, calculate the percentage of TiO_2 as follows (Note 102):

24.6.1 *For Colorimeters of the Kennicott Type*:

$$\text{TiO}_2, \% = (100 \text{ VE/S}) \times (D/C) \quad (16)$$

24.6.2 *For Colorimeters of the Duboscq Type*:

$$\text{TiO}_2, \% = (100 \text{ VE/S}) \times (F/G) \quad (17)$$

where:

V = millilitres of standard $\text{Ti}(\text{SO}_4)_2$ solution in the peroxidized standard solution,

E = TiO_2 equivalent of the standard $\text{Ti}(\text{SO}_4)_2$ solution, g/mL,

S = Grams of sample used,

C = total volume of the peroxidized reference standard solution, mL,

D = Volume of peroxidized reference standard solution that matches the peroxidized solution of the sample, mL,

F = Depth of peroxidized reference standard solution through which light passes, and

G = Depth of peroxidized solution of the sample through which light passes.

NOTE 102—The difference between D and C or between F and G should not exceed 50 % of the smaller value.

25. Phosphorus Pentoxide (Alternative Test Method)

25.1 *Summary of Test Method*—In this test method, phosphorus is determined volumetrically by precipitation of the phosphorus as ammonium phosphomolybdate and titration with NaOH and H_2SO_4 .

25.2 *Reagents*:

25.2.1 *Ammonium Molybdate Solution*—Prepare the solution in accordance with 9.3.1.

25.2.2 *Ammonium Nitrate* (NH_4NO_3).

25.2.3 *Potassium Nitrate Solution* (10 g/L)—Dissolve 10 g of potassium nitrate (KNO_3) in water freshly boiled to expel CO_2 and cooled, and dilute to 1 L.

25.2.4 *Sodium Hydroxide, Standard Solution* (0.3 N)—Dissolve 12 g of sodium hydroxide (NaOH) in 1 L of water that has been freshly boiled to expel CO_2 , and cooled. Add 10 mL of a freshly filtered, saturated solution of barium hydroxide ($\text{Ba}(\text{OH})_2$). Shake the solution frequently for several hours, and filter it. Protect it from contamination by CO_2 in the air. Standardize the solution against standard acid potassium phthalate (Standard Sample No. 84) or benzoic acid (Standard Sample No. 39) furnished by the National Institute of Standards and Technology, according to the directions furnished with the standard. Calculate the phosphorus pentoxide (P_2O_5) equivalent (Note 103) of the solution, g/mL, as follows:

$$E = N \times 0.003086 \quad (18)$$

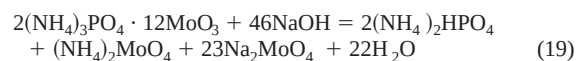
where:

E = P_2O_5 equivalent of the NaOH solution, g/mL,

N = normality of the NaOH solution, and

0.003086 = P_2O_5 equivalent of 1 N NaOH solution, g/mL.

NOTE 103—The value of the solution is based on the assumption that the phosphorus in cement is precipitated as ammonium phosphomolybdate ($2(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$) and that the precipitate reacts with the NaOH solution thus:



The number of 0.003086 is obtained by dividing the molecular weight of P_2O_5 (141.96) by 46 (for 46 NaOH in the equation) and by 1000 (number of millilitres in 1 L).

As the actual composition of the precipitate is influenced by the conditions under which the precipitation is made, it is essential that all the details of the procedure are followed closely as prescribed.

25.2.5 *Sodium Nitrite* (50 g NaNO_2/L).

25.2.6 *Sulfuric Acid, Standard Solution* (0.15 N)—Dilute 4.0 mL of H_2SO_4 to 1 L with water that has been freshly boiled and cooled. Standardize against the standard NaOH solution. Determine the ratio in strength of the standard H_2SO_4 solution

to the standard NaOH solution by dividing the volume of NaOH solution by the volume of H₂SO₄ solution used in the titration.

25.3 Procedure:

25.3.1 Weigh 1 to 3 g of the sample (Note 104) and 10 g of NH₄NO₃ into a 150-mL beaker. Mix the contents, add 10 mL of HNO₃, and stir quickly, using the flattened end of a glass rod to crush lumps of cement, until the cement is completely decomposed and the thick gel of silica (SiO₂) is broken up. Cover the beaker with a watch glass, place it on a water bath or a hot plate at approximately 100°C for 15 to 20 min, and stir the contents occasionally during the heating. Add 20 mL of hot water to the beaker and stir the contents. If the cement contains an appreciable amount of manganese, as shown by the presence of a red or brown residue, add a few millilitres of NaNO₂ (50 g/L) to dissolve this residue. Boil the contents of the beaker until all nitrous fumes are completely expelled. This procedure should not take more than 5 min, and water should be added to replace any lost by evaporation. Filter, using medium-textured paper, into a 400-mL beaker under suction and with a platinum cone to support the filter paper. Wash the residue of SiO₂ with hot water until the volume of filtrate and washings is about 150 mL.

NOTE 104—The amounts of sample and reagents used depend on the content of phosphorus in the cement. The minimum requirements are sufficient if the cement contains 0.5 % P₂O₅ or more. The maximum amounts are required if the content of P₂O₅ is 0.1 % or less.

25.3.2 Heat the solution to 69 to 71°C, remove it from the heat source, and immediately add 50 to 100 mL of the ammonium molybdate solution. Stir the solution vigorously for 5 min, wash down the sides of the beaker with cool KNO₃ solution (10 g/L), cover the beaker with a watch glass, and allow to stand 2 h. Using suction, filter the precipitate (Note 105), decanting the solution with as little disturbance to the precipitate as possible. Stir the precipitate in the beaker with a stream of the cool KNO₃ solution, decant the liquid, then wash the precipitate onto the filter. Scrub the stirring rod and beaker with a policeman and wash the contents onto the filter. Wash and precipitate until it is acid-free (Note 106), allowing each portion of wash solution to be sucked completely through before adding the next.

NOTE 105—The filter may be a small medium-textured filter paper supported by a platinum cone, or a small Hirsch funnel may be used with filter paper cut to fit and a thin mat of paper pulp or acid-washed asbestos pulp. The filtration should be carried out with care to avoid any loss of the precipitate. The filter should fit well, and the suction should be started before filtration and maintained until the end of the washing.

NOTE 106—About ten washings are usually required. Test the tenth washing with one drop of neutral phenolphthalein indicator and half a drop of the standard NaOH solution. If a definite pink color lasts at least 5 min, the precipitate is considered to be acid-free; otherwise, continue the washing.

25.3.3 Transfer the filter and precipitate to the beaker in which the precipitation took place, using small damp pieces of paper to wipe out the funnel and to pick up portions of the precipitate that may remain on it. Add 20 mL of cool CO₂-free water to the beaker, and break up the filter by stirring rapidly with the policeman that was used to scrub the beaker. Add an excess of the 0.3 N NaOH solution, stir the contents until all

trace of yellow has disappeared, wash down the policeman and sides of the beaker with 50 mL of cool, CO₂-free water, and add 2 drops of neutral phenolphthalein indicator solution. Treat the solution with a measured quantity of the 0.15 N H₂SO₄ solution, sufficient to destroy completely the pink color. Complete the titration with the NaOH solution until there is a definite faint pink color that lasts at least 5 min.

25.3.4 *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.

25.4 *Calculation*—Calculate the percentage of P₂O₅ to the nearest 0.01 as follows:

$$P_2O_5, \% = [E(V_1 - V_2R)/S] \times 100 \quad (20)$$

where:

- E = P₂O₅ equivalent of the NaOH solution, g/mL,
- V_1 = millilitres of NaOH solution used,
- V_2 = millilitres of H₂SO₄ solution used,
- R = ratio in strength of the H₂SO₄ solution to the NaOH solution, and
- S = grams of sample used.

26. Manganic Oxide (Alternative Test Method)

26.1 *Summary of Test Method*—In this test method manganic oxide is determined volumetrically by titration with potassium permanganate solution.

26.2 Reagents:

26.2.1 *Potassium Permanganate, Standard Solution* (0.18 N)—Prepare a solution of potassium permanganate (KMnO₄) and standardize as described in 13.2.2, except that the manganic oxide (Mn₂O₃) equivalent of the solution is calculated instead of the calcium oxide (CaO) equivalent. Calculate the Mn₂O₃ equivalent of the solution as follows:

$$E = (B \times 0.3534)/A \quad (21)$$

where:

- E = Mn₂O₃ equivalent of the KMnO₄ solution, g/mL,
- B = grams of Na₂C₂O₄ used,
- A = millilitres of KMnO₄ solution required by the Na₂C₂O₄, and
- 0.3534 = mole ratio of 3 Mn₂O₃ to 10 Na₂C₂O₄.

26.2.2 Zinc Oxide (ZnO), powder.

26.3 Procedure:

26.3.1 Place 2 g of the sample in a 250-mL beaker and add about 50 mL of water to the cement. Stir the mixture until it is in suspension and then add about 15 mL of HCl. Heat the mixture gently until the solution is as complete as possible. Add 5 mL of HNO₃ and 50 mL of water to the solution and boil it until most of the chlorine has been expelled. If necessary, add hot water to maintain the solution at a volume of about 100 mL. Stop the boiling and add ZnO powder to the solution until the acid is neutralized. Add an excess of 3 to 5 g of ZnO powder to the solution and boil it for a few minutes.

26.3.2 Without filtering, and while keeping the solution hot (90 to 100°C) by intermittent or continuous heating, titrate the solution with the 0.18 N KMnO₄ solution until a drop of it gives a permanent pink color (Note 107). When the end point is approached, add the standard solution dropwise. After each drop, stir the solution, allow the precipitate to settle a little, and

observe the color of the stratum of the solution by looking through the side of the beaker.

NOTE 107—In the case of a cement in which the approximate content of Mn_2O_3 is unknown, a preliminary determination may be made with rapid titration, 0.5 to 1 mL of the standard solution being added at a time, and without an attempt to keep the solution close to the boiling point.

26.3.3 *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.

26.4 *Calculation*—Calculate the percentage of Mn_2O_3 to the nearest 0.01 as follows:

$$\text{Mn}_2\text{O}_3, \% = EV \times 50 \quad (22)$$

where:

E = Mn_2O_3 equivalent of the KMnO_4 solution, g/mL,

V = millilitres of KMnO_4 solution used, and

50 = 100 divided by the weight of sample used (2 g).

27. Free Calcium Oxide (Alternative Test Methods)

27.1 *Summary of Test Methods*—These are rapid test methods for the determination of free calcium oxide in fresh clinker. When applied to cement or aged clinker, the possibility of the presence of calcium hydroxide should be kept in mind since these methods do not distinguish before free CaO and free $\text{Ca}(\text{OH})_2$. Two test methods are provided. Alternate Test Method A is a modified Franke procedure in which uncombined lime is titrated with dilute perchloric acid after solution in an ethylacetoacetate-isobutylalcohol solvent. Alternate Test Method B is an ammonium acetate titration of the alcohol-glycerin solution of uncombined lime with $\text{Sr}(\text{NO}_3)_2$ as an accelerator.

27.2 *Modified Franke Test Method (Alternative Test Method A)*:

27.2.1 *Apparatus*:

27.2.1.1 *Refluxing Assembly*, consisting of a flask with flat-bottom short neck Erlenmeyer flask with 250-mL capacity. The water-cooled refluxing condenser should have a minimum length of 300 mm. The flask and reflux condenser shall be connected with standard tapered ground glass joints. The reflux condenser shall be fitted with an absorption tube containing a desiccant, such as indicating silica gel, and a material for the removal of CO_2 , such as Ascarite. The absorption tube shall be inserted with a rubber stopper in the upper end of the reflux column.

27.2.1.2 *Buret*, having a 10-mL capacity and graduated in units not more than 0.05 mL.

27.2.1.3 *Vacuum Filtration Assembly*, consisting of a Gooch crucible size No. 3, 25-mL capacity in which is placed a suitable filter paper, 21-mm size, a Walter crucible holder, a 500-mL vacuum flask, and vacuum source. The crucible is half filled with compressed filter pulp.

27.2.1.4 *Glass Boiling Beads*:

27.2.2 *Solutions Required*:

27.2.2.1 *Ethyl Acetoacetate-Isobutyl Alcohol Solvent*—3 parts of volume of ethyl acetoacetate and 20 parts by volume of isobutyl alcohol.

27.2.2.2 *Thymol Blue Indicator*—Dissolve 0.1 g of thymol blue indicator powder in 100 mL of isobutyl alcohol.

27.2.2.3 *Perchloric Acid, Standard Solution (0.2 N)*—Dilute 22 mL of 70 to 72 % perchloric acid to 1 L with isobutyl alcohol. Standardize this solution as follows: Ignite 0.1000 g of primary standard calcium carbonate in a platinum crucible at 900 to 1000°C. Cool the crucible and contents in a desiccator and weigh to the nearest 0.0001 g to constant weight. Perform the weighings quickly to prevent absorption of water and CO_2 . Immediately transfer the CaO without grinding to a clean, dry Erlenmeyer flask and reweigh the empty crucible to the nearest 0.0001 g to determine the amount of CaO added. Then follow procedure beginning with “Add 70 mL of the ethyl acetoacetate-isobutyl alcohol. . .” in 27.2.3.1. Calculate the CaO equivalents of the standard perchloric acid solution in grams per millilitre by dividing the weight of CaO used by the volume of perchloric acid required for the titration.

27.2.3 *Procedure*:

27.2.3.1 Weigh 1.0000 g of ground sample (Note 108) and transfer it into a clean, dry 250-mL Erlenmeyer flask. Add four to five glass boiling beads. Add 70 mL of prepared ethyl acetoacetate-isobutyl alcohol solvent. Agitate the flask to disperse the sample.

NOTE 108—Thorough grinding of the sample is essential for proper exposure of the free lime grains that often are occluded in crystals of tricalcium silicate in the cement. However, exposure of the sample to the air must be kept at a minimum to prevent carbonation of the free lime. In particular, direct breathing into the sample must be avoided. The sample should be sufficiently fine to easily pass a No. 200 (75- μm) sieve but actual sieving is not recommended. If the sample is not to be immediately tested, it must be kept in an airtight container to avoid unnecessary exposure to the atmosphere.

27.2.3.2 Attach the flask to a reflux condenser and bring the material to a boil. Reflux for 15 min.

27.2.3.3 Remove flask from condenser, stopper, and cool rapidly to room temperature.

27.2.3.4 Filter the sample and solution using the vacuum assembly. Wash the flask and residue with small increments (10 to 15 mL) of isobutyl alcohol until a total of 50 mL has been used for wash solution.

27.2.3.5 Add 12 drops of the thymol blue indicator to the filtrate and immediately titrate with 0.2 N perchloride acid to the first distinct color change.

27.2.4 *Calculation*—Calculate the percent free calcium oxide to the nearest 0.1 % as follows:

$$\text{free CaO}, \% = \frac{EV \times 100}{W} \quad (23)$$

where:

E = CaO equivalent of the perchloric acid, g/mL,

V = millilitres of perchloric acid solution required by sample, and

W = weight of the sample, g.

27.3 *Rapid $\text{Sr}(\text{NO}_3)_2$ Method (Alternative Test Method B)*:

27.3.1 *Reagents*:

27.3.1.1 *Ammonium Acetate, Standard Solution* (1 mL = 0.005 g CaO)—Prepare a standard solution of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) by dissolving 16 g of desiccated ammonium acetate in 1 L of ethanol in a dry, clean, stoppered bottle. Standardize this solution by the same procedure as described in 27.3.2.1, except use the following in place of the sample: ignite



to constant weight approximately 0.1 g of calcium carbonate (CaCO_3) in a platinum crucible at 900 to 1000°C, cool the contents in a desiccator, and weigh to the nearest 0.0001 g. Perform the weighings quickly to prevent absorption of water and CO_2 . Immediately transfer the CaO without grinding to a 250-mL boiling flask (containing glycerin–ethanol solvent and $\text{Sr}(\text{NO}_3)_2$), and reweigh the empty crucible to determine the weight of CaO to the nearest 0.0001 g. Continue as described in 27.3.2.1 and 27.3.2.2. Calculate the CaO equivalent of the ammonium acetate in grams per millilitre by dividing the weight of CaO used by the volume of solution required.

27.3.1.2 *Phenolphthalein Indicator*—Dissolve 1.0 g of phenolphthalein in 100 mL of ethanol (Formula 2B) (Note 109).

27.3.1.3 *Glycerin-Ethanol Solvent (1+2)*—Mix 1 volume of glycerin with 2 volumes of ethanol (Formula 2B). To each litre of this solution, add 2.0 mL of phenolphthalein indicator solution.

NOTE 109—Ethanol denatured in accordance with Formula 2B (99.5 % ethanol and 0.5 % benzol) is preferred but may be replaced by isopropyl alcohol, A.R.

27.3.1.4 *Strontium Nitrate* ($\text{Sr}(\text{NO}_3)_2$), reagent grade.

27.3.2 *Procedure*:

27.3.2.1 Transfer 60 mL of the glycerin–ethanol solvent into a clean, dry, 250-mL standard-taper flat-bottom boiling flask. Add 2 g of anhydrous strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), and adjust

the solvent to slightly alkaline with a dropwise addition of a freshly prepared dilute solution of NaOH in ethanol until a faint pink color is formed. Weigh 1.000 g of the finely ground sample (Note 109) into the flask, add encapsulated stirring bar, and immediately attach a water-cooled condenser (with a standard 24/40 glass joint). Boil the solution in the flask on a magnetic stirrer hot plate for 20 min with mild stirring.

27.3.2.2 Remove the condenser and filter the contents of the flask on a small polypropylene Büchner funnel under vacuum, using a 250-mL filtering flask with side tube. Bring the filtrate to a boil and immediately titrate with standard ammonium acetate solution to a colorless end point.

27.3.3 *Calculation*— Calculate the percent free CaO to the nearest 0.1 % as follows:

$$\text{free CaO, \%} = EV \times 100 \quad (24)$$

where:

E = CaO equivalent of the ammonium acetate solution, g/mL, and

V = millilitres of ammonium acetate solution required by the sample.

28. Keywords

28.1 chemical analysis; compositional analysis; hydraulic cements

APPENDIXES

(Nonmandatory Information)

X1. EXAMPLE OF DETERMINATION OF EQUIVALENCE POINT FOR THE CHLORIDE DETERMINATION

(Column 1) AgNO ₃ , mL	(Column 2) Potential, mV	(Column 3) Δ mV ^A	(Column 4) Δ^2 mV ^B
1.60	125.3		
1.80	119.5	5.8	1.4
2.00	112.3	7.2	1.3
2.20	103.8	8.5	1.3
2.40	94.0	9.8	0.6
2.60	84.8	9.2	2.3
2.80	77.9	6.9	0.8
3.00	71.8	6.1	1.3
3.20	67.0	4.8	

The equivalence point is in the maximum Δ mV interval (Column 3) and thus between 2.20 and 2.40 mL. The exact equivalence point in this 0.20 increment is calculated from the Δ^2 mV (Column 4) data as follows:

$$E = 2.20 + 1.3/1.3 + 0.6 \times 0.20 = 2.337 \text{ mL. Round to 2.34.}$$

^A Differences between successive readings in Column 2.

^B Differences between successive Δ readings in Column 3 "second differentials".

X2. CO₂ DETERMINATIONS IN HYDRAULIC CEMENTS

X2.1 Scope

X2.1.1 This appendix contains information about methods for determination of carbon dioxide (CO₂) in hydraulic cement. The methods listed received a favorable evaluation by Task Group C01.23.04.

X2.1.2 Section X2.2 lists the analytical methods that received a favorable evaluation, briefly describes each method, suggests analytical techniques or cautions that may be useful, and indicates limitations to some of the methods.

X2.1.3 The methods listed as X2.2.1, X2.2.4, X2.2.5, and X2.2.6 determine total carbon calculated as CO₂. For that reason, they are not appropriate for determination of carbon dioxide in fly ash, limestones containing carbon in the form of graphite or kerogen, in other carbon bearing materials, or in blended cements produced from these materials.

X2.1.4 The methods listed in X2.2.2 and X2.2.3 can determine actual CO₂ directly rather than by calculation from total carbon. They are suggested for analysis of blended cements and blended cement ingredients which are likely to contain non-carbonate carbon.

X2.1.5 The split loss on ignition method in X2.2.1 can give misleading results when used with materials containing CaOH₂ (calcium hydroxide). This can occur with aged cement, cement made from aged clinker, or high free lime clinker, in addition to cements with a lime or hydrated lime ingredient.

X2.2 Analytical Methods

X2.2.1 *Split Loss on Ignition*—This procedure is comparable to the analytical method described in Test Methods C 114, Section 3.3.1.1, with the following modifications:

1. A crucible of known mass and containing a sample of known mass is initially heated at 500°C for 2 h.
2. After being cooled to room temperature in a desiccator, and its mass determined, the crucible with sample is then heated at 950°C for 2 h.
3. Finally, the crucible with sample is cooled and its mass is determined as per Step No. 2.
4. The difference in residue masses after the respective heat treatments is assumed to be carbon dioxide.

TGA results indicated that CaOH_2 can lose a significant portion of its mass above 500°C . Thus, the Split Loss on Ignition procedure should not be used when situations described in X2.1.5 exist.

X2.2.2 Thermogravimetric Analysis (TGA)—This method involves the determination of sample mass loss at various temperatures. The heating of a sample through a temperature range allows for mass loss differentiation based on mineral form (for example, CaCO_3 , MgCO_3 , CaOH_2 , etc.). Specific operational information is provided by the equipment manufacturers. If free carbon is present, an inert atmosphere (for example, nitrogen) should be used for sample analysis.

X2.2.3 Test Methods C 25, Section 22—“Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime.” This method involves decomposition of the sample with HCl. The liberated CO_2 is then passed through a series of scrubbers to remove water and sulfides. The CO_2 is absorbed with special Sodium Hydroxide Absorbent (Ascarite). The gain in mass of the absorption tube is determined and calculated as percent CO_2 . Calcium carbonate, for instance, can be calculated by multiplying the determined CO_2 content by a conversion factor (for example, $\text{CO}_2 \times 2.2742 = \text{CaCO}_3$).

X2.2.4 X-ray Fluorescence Spectroscopy—In this method the sample is ground to a fine particle size, pressed into a flat pellet and irradiated with the chosen instrument. Carbon content is determined by comparing the collected carbon emissions to calibration standards.

X2.2.5 Combustion by Induction Furnace/IR—This method involves volatilization by induction furnace and detection by infrared absorption. Suitable calibration standards (for example, calcium carbonate and synthetic carbon) are available from some instrument manufacturers. NIST cement SRMs with known additions of NIST argillaceous limestone (or other suitable standards) should also be considered to check instrument calibration.

X2.2.6 “Test Methods E 350—This method, Total Carbon by the Combustion Gravimetric Method from Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron,” is suitable for the determination of carbon in concentrations from 0.05 to 1.80 % (as carbon dioxide 0.18 to 6.60 %). The test method involves burning the sample in a stream of oxygen; the carbon dioxide in the evolved gases is then collected in a suitable absorbent and its mass determined. Time of analysis is less than 10 min.

X2.3 Cooperative Test Results

X2.3.1 Tables X2.1 and X2.2 list results from two series of cooperative tests using several of the analytical methods evaluated by the Task Group. In all, five of the six methods receiving favorable ratings were included. The sixth method, Test Methods C 25, was specifically not tested in these cooperative series, but was rated favorably because of long history of use with related materials.

X2.3.2 Table X2.1 includes results of single determinations using three of the different analytical methods. The methods used were Split Loss on Ignition, Test Methods E 350, and Combustion by Induction Furnace with Infra-Red Detection.

TABLE X2.1 Cooperative Test Series No. 1

	Single Determinations			
	Carbon Dioxide Unknown ^A	Determinations Base Cement ^B	Added CO_2 , % Determined ^C	Added CO_2 , % Known ^D
Split LOI	2.40	0.45	1.97	2.00
	2.52	0.56	1.99	
	2.41	0.36	2.07	
	2.39	0.32	2.09	
	2.41	0.36	2.07	
	2.28	0.27	2.02	
Test Methods E 350	2.00	0.02	1.98	1.98
	2.00	0.02	1.98	
Induction Furnace/IR	2.46	0.40	2.07	2.08
	2.53	0.48	2.08	
	2.38	0.40	2.00	
	2.42	0.48	1.97	
Average Standard Deviation			2.02	0.05

^A The Unknown was prepared by blending/grinding a mixture of 5.00 % NIST SRM 1C Argillaceous Limestone and 95.00 % CCRL Portland Cement Reference Sample No. 85. According to the Certificate of Analysis, the SRM 1C had a loss on ignition of 39.9 %. For the purpose of the cooperative test series, the loss on ignition was assumed to be CO_2 only.

^B The Base Cement was CCRL Portland Cement Reference Sample No. 85.

^C The Determined % Added CO_2 was obtained by subtracting the Base Cement % CO_2 from the Unknown % CO_2 .

^D The addition of 5.00 % NIST SRM 1C (with a loss on ignition value of 39.9 %) would provide 2.00 % Added CO_2 . (Again, it was assumed that the SRM 1C loss on ignition was only carbon dioxide.)

TABLE X2.2 Cooperative Test Series No. 2

	Averages from Three Determinations			
	Carbon Dioxide Unknown ^A	Determinations Base Cement ^B	Added CO_2 , % Determined ^C	Added CO_2 , % Known ^D
Split LOI	2.00	0.41	1.59	1.60
	1.65	0.32	1.33	
	2.02	0.46	1.56	
	1.91	0.35	1.56	
	2.10	0.43	1.67	
	1.91	0.41	1.50	
	1.98	0.46	1.52	
	1.68 ^E	0.00 ^E	1.68 ^E	
	2.23	0.28	1.95	
XRFA	1.96	0.28	1.68	1.55
	1.95	0.40	1.55	
	1.77	0.20	1.57	
Induction Furnace/IR	1.87	0.25	1.62	1.60
			1.60	
Average Standard Deviation			0.14	

^A The Unknown was prepared by blending/grinding a mixture of 4.00 % NIST SRM 1C Argillaceous Limestone and 96.00 % CCRL Portland Cement Reference Sample No. 85. According to the Certificate of Analysis, the SRM 1C had a loss on ignition of 39.9 %. For the purpose of the cooperative test series, the loss on ignition was assumed to be CO_2 only.

^B The Base Cement was CCRL Portland Cement Reference Sample No. 85.

^C The Determined % Added CO_2 was obtained by subtracting the Base Cement % CO_2 from the Unknown % CO_2 .

^D The addition of 4.00 % NIST SRM 1C (with a loss on ignition value of 39.9 %) would provide 1.60 % Added CO_2 . (Again, it was assumed that the SRM 1C loss on ignition was only carbon dioxide.)

^E The XRF instrument was calibrated using standards composed of the Base Cement (that is, CCRL No. 85) and NIST SRM 1C. It was assumed that the Base Cement contained 0 % CO_2 .

X2.3.3 Table X2.2 includes results based on average of three determinations. Results from four of the different analytical methods are included. Methods used were Split Loss on Ignition, X-Ray Fluorescence Analysis, Induction furnace with

Infra-Red Detection, and Thermo-Gravimetric Analysis. Test Methods E 350 was not used in this series of tests.

For additional useful information on details of cement test methods, reference may be made to the “Manual of Cement Testing,” which appears in Vol 04.01 of the Annual Book of ASTM Standards.

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