Designation: C 25 – 06

Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime[1]

This standard is issued under the fixed designation C 25; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the chemical analysis of high-calcium and dolomitic limestone, quicklime, and hydrated lime. These test methods are classified as either standard (preferred) or alternative (optional).

1.2 The standard test methods are those that employ classical gravimetric or volumetric analytical procedures and are typically those required for referee analyses where chemical specification requirements are an essential part of contractual agreement between buyer and seller.

1.3 Alternative or optional test methods are provided for those who wish to use procedures shorter or more convenient than the standard methods for the routine determinations of certain constituents. Optional test methods may sometimes be preferred to the standard test methods, but frequently the use of modern and expensive instrumentation is indicated which may not be accessible to everyone. Therefore, the use of these test methods must be left to the discretion of each laboratory.

1.4 The analytical procedures appear in the following order:

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1.5 *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.* For specific precautionary statements, see 9.3, 10.2.1, 18.4.3, 31.6.4.2, X2.3.1, and X5.4.1.1.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 50 Practice for Sampling, Sample Preparation, Packaging, and Marking of Lime and Limestone Products

C 51 Terminology Relating to Lime and Limestone (as used by the Industry)

C 911 Specification for Quicklime, Hydrated Lime, and Limestone for Chemical and Industrial Uses

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[1] These test methods are under the jurisdiction of ASTM Committee C07 on Lime and are the direct responsibility of Subcommittee C07.05 on Chemical Tests.

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

D 1193 Specification for Reagent Water
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E 70 Test Method for pH of Aqueous Solutions With the Glass Electrode
E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals [3]
E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E 832 Specification for Laboratory Filter Papers

3. Terminology

3.1 Definitions—Unless otherwise specified, for definitions of terms used in these test methods refer to Terminology C 51.

4. Significance and Use

4.1 These test methods provide accurate and reliable analytical procedures to determine the chemical constituents of limestone, quicklime, and hydrated lime (See Note 1). The percentages of specific constituents which determine a material's quality or fitness for use are of significance depending upon the purpose or end use of the material. Results obtained may be used in relation to specification requirements.

4.2 Because quicklime and hydrated lime quickly absorb water and carbon dioxide from the air, precision and bias are extremely dependent upon precautions taken during sample preparation and analysis to minimize excessive exposure to ambient conditions.

NOTE 1—These test methods can be applied to other calcareous materials if provisions are made to compensate for known interferences.

5. General Apparatus and Materials and Reagents

5.1 *General Apparatus and Materials*:

5.1.1 *Balance*—The balance shall be of an analytical type with a capacity not to exceed 200 g. It may be of conventional design or it may be a constant-load, direct-reading type. It shall be capable of reproducing weighings within 0.0002 g with an accuracy of ± 0.0002 g. Rapid weighing devices that may be provided such as a chain, damper, 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.

5.1.2 *Weights*—Weights used for analysis shall conform to Class S-1 requirements of the National Institute of Standards and Technology as described in NIST Circular 547.[4] They shall be checked at least once a year or when questioned, and adjusted to within allowable tolerances for Class S-1 weights. All new sets of weights purchased shall have the weights of 1 g and larger made of stainless steel or other corrosion-resistant alloy not requiring protective coating and shall meet the density requirements for Class S.

5.1.3 *Glassware and Laboratory Containers*—Standard volumetric flasks, burets, pipets, dispensers, etc., shall be carefully selected precision grade or better and shall be calibrated, if necessary, to meet the requirements of each operation. Standard-type interchangeable ground glass or TFE-fluorocarbon joints are recommended for all volumetric glassware. Polyethylene containers are recommended for all aqueous solutions of alkalies and for standard solutions where the presence of dissolved silica or alkali from the glass would be objectionable.

5.1.4 *Desiccators*—Desiccators shall be provided with a good desiccant such as anhydrous magnesium perchlorate, activated alumina, sulfuric acid, or phosphoric anhydride. Anhydrous calcium sulfate may also be used provided it has been treated with a color-changing indicator to show when the desiccant has lost its effectiveness. Calcium chloride and silica gel are not satisfactory desiccants for this type of analysis.

5.1.5 *Filter Paper*—Filter paper shall conform to the requirements of Specification E 832, Type II (quantitative). Class E shall be used for coarse and gelatinous precipitates. When medium-textured paper is required, Class F filter paper shall be used. When a retentive paper is needed, Class G shall be used.

Recommendations: Class	Filter Pore Size (microns)	Filter Speed
E	20 to 25	fast speed
F	8	medium speed
G	2.5	slow speed

5.1.6 *Crucibles*—Platinum crucibles and tight fitting lids should preferably be made of pure unalloyed platinum and be of 25 to 35-mL capacity. Where alloyed platinum is used for greater stiffness or to obviate sticking of fused material to crucible or lid, the alloyed platinum should not decrease in weight by more than 0.2 mg when heated at 1200 °C for 1 h.

5.1.7 *Muffle Furnace*—The electric muffle furnace should be capable of continuous operation up to 1000 °C and be capable of intermittent operation at higher temperatures if required. It should have an indicating pyrometer accurate to ± 25 °C.

5.2 *Reagents*:

5.2.1 *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[5] where such specifications are available. 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. In addition to this, it is desirable in many cases for the analyst to ensure the accuracy of his results by running blanks or checking against a comparable sample of known composition.

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[3] Withdrawn.

[4] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

[5] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeia Convention, Inc. (USPC), Rockville, MD.

5.2.2 *Purity of Water*—Unless otherwise indicated, references to water are understood to mean distilled water or other water of equivalent purity. Water conforming to Specification D 1193 meets these requirements.

5.2.3 *Concentration of Reagents*:

5.2.3.1 *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 approximating the following specific gravities or concentrations are intended:

Acetic acid ($HC_2H_3O_2$)	99.5 %
Hydrochloric acid (HCl)	sp gr 1.19
Hydrofluoric acid (HF)	48 %
Nitric acid (HNO_3)	sp gr 1.42
Perchloric acid ($HClO_4$)	70 %
Phosphoric acid (H_3PO_4)	85 %
Sulfuric acid (H_2SO_4)	sp gr 1.84
Ammonium hydroxide (NH_4OH)	sp gr 0.90

5.2.3.2 *Dilute Reagents*—The concentration of dilute acids and NH_4OH except when standardized, are specified as a ratio stating the number of measured volumes of the concentrated reagent to be diluted with a given number of measured volumes of water. In conformance with international practice, new and revised methods will use the "plus" designation instead of the ratio (:) symbol as the specified designation of dilution; for example, $H_2SO_4(5 + 95)$ means 5 volumes of concentrated H_2SO_4(sp gr 1.84) diluted with 95 volumes of water.

5.2.3.3 *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 $K_2Cr_2O_7$ solution (1 mL = 0.004 g Fe_2O_3). The average of at least three determinations shall be used for all standardizations. The standardization used to determine the strength of the standard solutions is described in the text under each of the appropriate procedures.

6. General Procedures

6.1 *Sampling*—Samples of lime and limestone for chemical analysis shall be taken and prepared in accordance with the requirements of Practice C 50 applicable to the material to be tested.

6.2 *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.

6.3 *Constancy of Weight of Ignited Residue*—To definitely establish the constancy of weight of the ignited residue, the residue and container shall be ignited at the specified temperature and time, cooled to room temperature in a desiccator, and weighed. The residue and container shall then be reheated for at least 30 min at the same temperature, cooled in a desiccator for the same period of time, and reweighed. Additional ignition periods may be required until two consecutive weights do not differ by more than 0.2 mg, at which time it shall be considered that constant weight has been attained. For ignition loss, each reheating period shall be 5 min.

6.4 *Calculation*:

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

6.4.2 In all mathematical operations on a set of observed values, the equivalent of two more places of figures than in the single observed values shall be retained. 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.

6.5 *Rounding Figures*—Rounding figures to the nearest significant place required in the report should be done after the calculations are completed, in order to keep the final results free from calculation errors. The rounding procedure should follow the principle outlined in Practice E 29.

7. Performance Requirements for Test Methods

7.1 *Referee Analyses*—The reference test methods that appear in Sections 8 through 32, or any other test methods qualified in accordance with 7.3, are required for referee analysis in those cases where conformance to the requirements of a chemical specification are questioned. In these cases a limestone, quicklime, or hydrated lime shall not be rejected for failure to conform to chemical requirements unless all sample preparation and analysis of any one constituent is made entirely by reference test methods prescribed in the appropriate sections of this test method or by other qualified test methods. Exception can be made when specific test methods are prescribed in the standard specification for the limestone, quicklime, or hydrated lime in question. The test methods actually used for the analysis shall be designated.

7.1.1 When there is a question regarding acceptance, referee analyses shall be made in duplicate. If the two results do not agree within the permissible variation given in Table 1, the determination including sample preparation shall be repeated

TABLE 1 Maximum Permissible Variations in Results[A]

(Column 1) Constituent	(Column 2) Maximum Difference Between Duplicates	(Column 3) Maximum Difference of the Average of Duplicates from SRM Certificate Values[B]
Al as Al_2O_3	0.20	± 0.30
Ca as CaO	0.20	± 0.30
Mg as MgO	0.20	± 0.30
C (lime and hydrated lime)	0.20	± 0.30
C (limestone)	0.60	± 0.60
Fe as Fe_2O_3	0.10	± 0.15
Si as SiO_2	0.15	± 0.30
Mn	0.05	± 0.10
P	0.02	± 0.05
Sr as SrO	0.05	[C]
S	0.03	± 0.05

[A] For demonstrating the performance of rapid test methods the SRM closest in overall composition to the limestone shall be used (See Table 2). In the case of quicklime or hydrated lime, the SRM closest in overall composition, after heating at 1000 °C for 1 h, to the product composition shall be used, except for C and S determinations (See Note 3).

[B] Interelement corrections may be used for any standardization provided improved accuracy can be demonstrated.

[C] No SRM currently available.

in duplicate until the results agree within the permissible variation. When the results agree within the permissible variation, their average shall be accepted as the correct value. For the purpose of comparing results, the percentages shall be calculated to one more significant figure than reported 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 constituent.

7.1.2 Test results from Referee methods intended for use as a basis for product acceptance or rejection, or for manufacturer's certification, can be used only after demonstration of precise and accurate analyses by meeting the requirements of 7.1.3, or except when demonstrated under 7.3.2.1. Such demonstrations may be made concurrently with analysis of the limestone, quicklime, or hydrated lime product being tested. The demonstration is required only for those constituents being used as a basis for acceptance, rejection, or certification of a limestone, quicklime, or hydrated lime, but may be made for any constituent of limestone, quicklime, or hydrated lime product for which a standard exists. Such demonstrations must be made annually.

7.1.3 Demonstrations shall be made by analysis of each constituent of concern in a SRM limestone, quicklime, or hydrated lime (See Notes 2 and 3). Duplicate samples shall be run on different days. The same test methods to be used for analysis of the limestone, quicklime, or hydrated lime being tested shall be used for analysis of the SRM. If the duplicate results do not agree within the permissible variation given in Table 1, the determinations shall be repeated, following identification and correction of problems or errors, until a set of duplicate results do agree within the permissible variation.

NOTE 2—The term SRM refers to approved Standard Reference Materials listed in Table 2.

NOTE 3—There are no SRMs that are quicklime or hydrated lime as supplied. When analyzing a quicklime or hydrated lime the SRM in carbonate form needs to be converted to closely resemble the matrix of the product being tested. To accomplish this conversion, heat the chosen SRM for 1 h at 1000 °C, immediately prior to analysis and protect it from hydration or carbonation with sealed containers and desiccation during cooling. Carbon and sulfur may be driven off during heating, rendering the converted SRM unsuitable as a standard for carbon and sulfur determinations. For carbon and sulfur determinations use the appropriate SRM in its normal matrix.

7.1.4 The average of the results of acceptable duplicate determinations for each constituent may differ from the SRM certificate value by no more than the value shown in Column 3 of Table 1. When no SRM certificate value is given, a generally accepted accuracy standard for that constituent has not been identified. In such cases, only the differences between duplicate values as specified in 7.1.3 shall apply and notification of this exception shall be reported.

7.1.5 In questions concerning the acceptance or rejection of a limestone, quicklime, or hydrated lime product, upon request data shall be made available to all parties involved demonstrating that precise and accurate results were obtained with SRM samples by the same analyst making the acceptance determination.

7.2 *Optional Analyses*—The alternative test methods, as opposed to reference methods, provide procedures that are, in some cases, shorter or more convenient to use for routine determination of some constituents (See Note 4). In some instances longer, more complex procedures have been retained as alternative test methods to permit comparison of results by different procedures or for use when unusual materials are being examined, or when unusual preparation for analysis is required. Results from alternative test methods may be used as a basis for acceptance or rejection.

NOTE 4—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.

7.2.1 Duplicate analyses and blank determinations are left to the discretion of the analyst when using the alternative test methods. The final results should include the number of determinations performed and whether or not they were corrected for blank values.

TABLE 2 Approved SRM List

(SRM)	Al as % Al2O3	Ca as % CaO	Mg as % MgO	Fe as % Fe2O3	Si as % SiO2	% Mn	% P	Sr as % SrO	% S	Ti as % TiO2	K as % K2O	Na as % Na_2O	% L.O.I.
ECRM-752-1[A]	0.12	55.4	0.15	0.045	0.70	0.008	NC[B]	0.019	0.007	0.009	0.02	NC	43.4
IPT 35	0.24	53.8	0.70	0.14	1.98	0.009	0.003	0.04	NC	0.013	0.10	0.004	43.0
IPT 44	0.33	50.5	2.93	0.30	2.69	0.012	0.006	0.04	NC	0.019	0.12	0.002	42.9
IRSID DO 1-1[C]	0.55	52.69	0.60	1.04	1.99	0.022	0.022	NC	0.040	0.030	NC	NC	NC
NIST 1C	1.30	50.3	0.42	0.55	6.84	0.019	0.017	0.030	NC	0.07	0.28	0.020	39.9
NIST 88B	0.34	29.95	21.0	0.277	1.13	0.012	0.002	0.0076	NC	(0.016)[D]	0.103	0.029	(46.98)
BCS 368	0.17	30.8	20.9	0.23	0.92	0.05	NC	0.0089	NC	<0.01	NC	(<0.01)	46.7
IRSID 702-1	0.40	30.05	20.51	0.629	2.22	0.098	0.024	NC	0.027	0.022	NC	NC	NC
GBW 07214	0.017	54.95	0.67	0.071	0.38	0.007	0.0011	NC	0.020	NC	NC	NC	43.57
GBW 07215	0.50	51.56	2.67	0.292	1.17	0.014	0.0013	NC	0.196	NC	NC	NC	43.22
GBW 07216	0.027	36.55	16.59	0.226	0.092	0.022	0.0018	NC	0.014	NC	NC	NC	46.23
GBW 07217	0.295	30.60	20.73	0.376	0.96	0.048	0.0012	NC	0.174	NC	NC	NC	46.30
GBW 03106	0.64	50.38	2.28	0.29	4.38	0.0055	0.006	NC	0.006	0.034	0.14	0.070	41.58
GBW 03108	0.88	47.49	3.63	1.97	3.84	0.15	0.017	NC	0.036	0.14	0.23	0.024	41.52
IPT 48	0.17	31.0	21.2	0.17	0.45	0.011	0.0096	0.009	NC	0.006	0.026	0.013	46.9

[A] This SRM is still available, but its name has been changed from BCS 393 to ECRM 752-1.

[B] NC = not certified.

[C] This SRM has been found to be unavailable commercially. The use of private stock, though, is still allowed.

[D] ( ) = not certified, data for information only.

7.3 *Performance Requirements for Alternative Test Methods*:

7.3.1 *Definition and Scope*—When analytical data obtained in accordance with this section is required, any test method may be used that meets the requirements of 7.3.2. 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.

7.3.1.1 If more than one instrument is used for the same analysis, use of each instrument shall constitute a separate test method and each must be qualified separately.

7.3.2 *Qualification of a Test Method*—Prior to use each test method (See 7.3.1) must be qualified for each material that will be tested. Qualification data or, if applicable, requalification data shall be made available.

7.3.2.1 Using the test method chosen, make single determinations for each constituent under consideration on the SRM which in overall composition most closely resembles the limestone, quicklime, or hydrated lime to be tested (See Note 2). Complete two rounds of tests on nonconsecutive days repeating all steps of sample preparations. Calculate the differences between values and the averages of values from the two rounds of tests. Blank determinations are not required, if it has been determined that blank values do not affect the validity of the data. Blank or interference-corrected data must be so designated.

7.3.2.2 The differences between duplicates obtained for any single constituent shall not exceed the limits shown in Column 2 of Table 1.

7.3.2.3 For each constituent the average of the duplicates obtained shall be compared to the SRM Certificate value and shall not differ from the certified value by more than the value in Column 3 of Table 1. The qualification testing shall be conducted with newly prepared specimens.

7.3.2.4 The standardization, if applicable, used for qualification and analysis of each constituent shall be determined by valid curve-fitting procedures (See Note 5). Restandardization shall be performed as frequently as required to ensure that the accuracy and precision in Table 1 are maintained.

NOTE 5—An actual drawing of a curve is not required, if such a 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.

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

7.3.4 *Report of Results*—Chemical analyses obtained by qualified alternative test methods shall be indicated as having been obtained by alternative methods and the type of test method used shall be designated.

7.3.5 *Rejection of Material*—See 7.1 and 7.2.

7.3.6 *Requalification of a Test Method*:

7.3.6.1 Requalification of a test method, as defined in 7.3.2, shall be required annually.

7.3.6.2 Requalification also shall be required upon receipt of substantial evidence that the test method may not be providing data in accordance with Table 1. 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.

7.3.6.3 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 7.1.1, a certified value of an approved SRM, 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 of 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 the analyses on a comparable basis prior to determining the differences (See Note 6). 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 6—Instrumental analyses can usually detect only the element sought. Therefore, to avoid controversy, the actual procedure used for the elemental analysis should be noted when differences with reference procedures exist. For example, Combined Oxides of Iron and Aluminum by Wet Test should be compared to the sum of Fe_2O_3 and Al_2O_3 obtained instrumentally.

7.3.6.4 If an instrument or piece of equipment is replaced even by one of identical make and 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 7.3.2.

7.4 *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 requirements shown in Table 1.

8. Insoluble Matter Including Silicon Dioxide (Standard Method)

8.1 *Scope*—This test method is based on a double evaporation to dryness of the hydrochloric acid solution of the limestone or lime sample to convert silicon dioxide (SiO_2) to the insoluble form. The acid-insoluble residue of a typical limestone consists of free silica and a mixture of minerals such as clay, mica, feldspar, tourmaline, barytes, garnet, zircon, rutile, etc.

8.2 *Summary of Test Method*—After dissolution in hydrochloric acid, the silica is dehydrated by a double evaporation to dryness. After each dehydration, the dry salts are redissolved with dilute hydrochloric acid, the solution is filtered, and the siliceous residue and other insoluble matter separated. The two papers containing the residues are combined, ignited, and weighed.

8.3 *Procedure*:

8.3.1 Weigh 0.5 g of quicklime or hydrated lime, or 1.0 g of limestone ground to pass a No. 50 (250-µm) sieve (See Note 7). If the sample is a limestone or hydrated lime, ignite in a covered platinum crucible in an electric muffle (See Note 8) at 950 °C for 15 min or longer to effect complete decomposition. Transfer to an evaporating dish, preferably of platinum (See Note 9), containing about 10 mL of water, mix to a thin slurry, add 5 to 10 mL of HCl, and digest with the aid of gentle heat and agitation until solution is complete (See Note 10).

NOTE 7—Due to the rapidity with which quicklime and hydrated lime absorb water and carbon dioxide from the air, samples must be protected in tightly stoppered containers at all times. Samples for analysis are to be weighed quickly and the sample container re-stoppered immediately after the sample has been removed.

NOTE 8—Ignition of the sample in an electric muffle is far superior to flame ignition. However, if an electric muffle is not available, flame ignition and the blast lamp may be used.

NOTE 9—If a platinum dish is not available, porcelain may be used. A glass container positively must *not* be used.

NOTE 10—Alternatively, the loss on ignition (LOI) can be determined first, using 0.5 g of sample. The insoluble matter including silicon dioxide can then be assayed using the ignited product that remains in the LOI crucible.

8.3.2 Evaporate the solution to dryness on a steam bath. When dry or nearly so, cover the dish and place it in an air bath or drying oven or on a metal triangle resting on a hot plate. Heat for 1 h at 100 °C, remove the dish from the heat, and allow the dish and contents to cool slightly.

8.3.3 Drench the cooled mass with 20 mL (1 + 1) HCl and place on the water bath for 10 min. Filter the mixture containing the insoluble residue through a retentive filter of suitable size. Wash filter thoroughly with warm, diluted (5 + 95) HCl and then twice with hot water. Reserve the paper and residue.

8.3.4 Evaporate the filtrate to dryness, dehydrate and extract the residue with HCl as before, but this time heat the acidified solution for 1 to 2 min. Filter through a second and smaller piece of retentive filter paper and wash as before. Retain the filtrate for iron, aluminum, calcium, and magnesium determinations; combine the two wet papers containing the separated residues and transfer to a weighed platinum crucible.

8.3.5 Char carefully without allowing the paper to inflame, and then ignite at 1000 °C for 30 min in an electric muffle furnace (See Note 8). Cool in a desiccator and weigh. The increase in weight represents the insoluble matter including SiO_2.

8.4 *Calculation*—Calculate the percentage of insoluble matter including silicon dioxide to the nearest 0.01 % as follows:

$$\text{Insoluble matter including } SiO_2 = (A/B) \times 100 \quad (1)$$

where:

A = mass of ignited residue, g, and
B = original mass of sample, g.

8.5 *Precision and Bias*—This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

9. Insoluble Matter Including Silicon Dioxide (Optional Perchloric Acid Method)

9.1 *Scope*—In this test method the insoluble matter including silicon dioxide is determined gravimetrically as in the standard method except that perchloric acid is used to dehydrate the silica. The procedure is more rapid than in the standard method because only a single dehydration is necessary. Fuming perchloric acid is a very powerful dehydrating agent, and silicic acid can usually be completely converted to the insoluble silicon dioxide in less than 20 min. This test method has been determined by other agencies such as the Association of Official Agricultural Chemists (AOAC) to be comparable to the standard hydrochloric acid method.

9.2 *Summary of Test Method*—The sample is decomposed without prior ignition by a mixture of nitric (HNO_3) and perchloric ($HClO_4$) acids and evaporated to fumes of $HClO_4$. The fuming perchloric acid is refluxed at this temperature for a short period of time to completely dehydrate the silica. The residue of silica and insoluble matter is filtered and washed free of acids and salts. The filter paper containing the residue is burned off, the resultant ash is ignited at high temperature until the ash is white, and then is weighed.

9.3 *Procedure*:

Warning—Perchloric acid ($HClO_4$) is an extremely reactive liquid. When using $HClO_4$, there are precautions to be followed which, if unheeded, may lead to serious explosions. Contact of the hot concentrated acid with organic matter must be absolutely avoided. Any organic matter in the sample must first be destroyed by the addition of nitric acid (HNO_3) to the sample prior to fuming with $HClO_4$. All evaporations involving $HClO_4$ must be done in a well-ventilated hood made of nonporous and inorganic material, preferably Type 316L stainless steel. Facilities should be provided for washdown procedures that should be performed regularly and thoroughly. These precautions on perchloric acid use are fully discussed in Practices E 50.

9.3.1 Weigh 0.5 g of quicklime or hydrated lime, or 1 g of limestone ground to pass a No. 50 (250-μm) sieve. Transfer the sample to a 250-mL beaker, wet carefully with a few millilitres of water, and dissolve cautiously with 10 mL of concentrated nitric acid. Add 20 mL of perchloric acid and boil until dense white fumes appear. If the solution darkens at this point, add several millilitres of HNO_3 until the solution clears. Heat again to fumes.

9.3.2 With the beaker covered, boil gently for 15 min to completely dehydrate the silica. Never allow contents to become solid or go to dryness, otherwise the separation of silica will be incomplete. If this happens, add more $HClO_4$ and repeat the dehydration.

9.3.3 Cool, add 50 mL of water, heat to boiling, and filter immediately using medium textured paper. Wash paper and residue thoroughly (at least 15 times) with hot water. Test with pH paper until washings are free of acid (See Note 11). Reserve the filtrate for iron, aluminum, calcium, and magnesium determinations.

NOTE 11—The filter paper and silica residue must be washed free of perchlorate salts to prevent small explosions from occurring in the crucible when the filter paper is charred and ignited.

9.3.4 Place the filter paper and contents in a weighed platinum or porcelain crucible and heat gently with a low flame until paper chars without inflaming, or alternatively char in an electric muffle at 300 to 400 °C. Slowly raise the temperature until the carbon has been burned and the ash is white. Finally, ignite at 1000 °C for 30 min. Cool in a desiccator and weigh as insoluble matter including SiO_2.

9.4 *Calculation*—Calculate the percentage of insoluble matter including silicon dioxide to the nearest 0.01 % as follows:

$$\text{Insoluble matter including SiO}_2\text{, \%} = (A/B) \times 100 \quad (2)$$

where:

A = mass of ignited residue, g, and
B = original mass of sample, g.

9.5 *Precision and Bias*:

9.5.1 Four laboratories cooperated in testing on four limestone samples and three laboratories cooperated in testing on an additional eight limestone samples thereby obtaining the precision data summarized in Table 3.

9.5.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

10. Silicon Dioxide

10.1 *Scope*—For control purposes or routine determinations, a separate analysis of SiO_2 may not be necessary. However, for certain applications in process industries, the amount of silica derived from the lime or limestone could be important. To satisfy situations such as this, silicon dioxide may be determined by volatilizing the SiO_2 from the insoluble residue with hydrofluoric acid and the percent SiO_2 determined by the difference in mass obtained.

10.2 *Procedure*:

10.2.1 To the ignited residue in the platinum crucible (See 8.3.5 or 9.3.4), add 5 mL of water, 5 mL of hydrofluoric acid (HF), and 1 or 2 drops of H_2SO_4.

Warning—All acids should be handled with care, but extra precaution is required with hydrofluoric acid. This is a very dangerous acid, harmful to eyes and skin; rubber gloves and goggles should be worn when using this acid. It does its work silently and leaves a festering sore that is slow to heal. Any acid that touches the skin should be immediately washed off with copious quantities of water. A physician should be notified immediately if any acid is sprayed into the eyes or if prolonged contact with the skin occurs.

10.2.2 Evaporate to dryness on a hot plate and heat in an electric muffle at 1000 °C (See Note 8) for 2 or 3 min. Cool in a desiccator and weigh. The difference between this mass and the mass of insoluble matter including silicon dioxide is the mass of SiO_2.

10.3 *Calculation*—Calculate the percent of silicon dioxide to the nearest 0.01 % as follows:

$$\text{SiO}_2\text{, \%} = ([A - B]/C) \times 100 \quad (3)$$

where:

A = mass of ignited residue, g (insoluble matter including SiO_2),
B = mass of ignited residue less SiO_2, g, and
C = original mass of sample, g.

10.4 *Precision and Bias*:

10.4.1 Three laboratories cooperated in testing on four limestone samples and two laboratories cooperated in testing on an additional eight limestone samples thereby obtaining the precision data summarized in Table 3.

10.4.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

11. Insoluble Matter

11.1 *Scope*—The difference between the mass of insoluble matter (including silicon dioxide) and silicon dioxide represents the mass of insoluble matter other than silicon dioxide. The insoluble matter contains the remnants of any clay, siliceous minerals, or other refractory material present in limestone. The elemental components are mainly iron and aluminum which should be removed and added to the main filtrate from the SiO_2 separation. If the insoluble matter including silica is reported as such and no hydrofluoric acid treatment is indicated, then there is no need to make a recovery of the metals and the insoluble residue may be discarded.

11.2 *Procedure*—The insoluble matter left in the crucible after the silica is volatilized with HF may be dissolved by fusing the residue with 2 to 3 g of sodium carbonate (Na_2CO_3) (See Note 12). Cool the melt and dissolve it in diluted HCl. Add the solution to the filtrate from the dehydration and separation of insoluble matter including silicon dioxide (See 8.3.4 or 9.3.3).

NOTE 12—Fusion with pyrosulfate is to be avoided because this will introduce undesirable sulfates into the solution.

11.3 An alternative fusion can also be made using either lithium metaborate or lithium tetraborate as opposed to using sodium carbonate.

TABLE 3 Precision Summary of Classical Test Methods

Section	Test Method	Average,[A] % Found	Range,[A] % Found	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
8	Insol + SiO_2 (Standard)	. . .	. . .	. . .	. . .
9	Insol + SiO_2 (Optional)	1.405	0.09–6.40	0.184	0.351
10	SiO_2	1.177	0.03–5.36	0.128	0.146
11	Insoluble Matter	0.242	0.02–0.93	0.169	0.204
12	Combined Oxides	0.459	0.22–1.21	0.181	0.282
13	Fe_2O_3	0.180	0.05–0.36	0.064	0.183
15	Al_2O_3	0.268	0.10–0.88	0.165	0.223
16	CaO (Gravimetric)	54.46	53.4–55.1	0.558	1.020
17	CaO (Volumetric)	30.57	30.4–30.7	0.371	1.132
17	CaO (Volumetric)	53.82	49.6–55.3	0.187	0.298
18	MgO (Gravimetric)	0.817	0.19–2.28	0.158	0.210
18	MgO (Gravimetric)	21.34	21.1–21.5	0.652	1.716
19	Loss on Ignition	43.73	43.6–43.9	0.158	0.463

[A] Average and range of the limestones tested.

11.4 *Calculation*—Calculate the percentage of insoluble matter other than silicon dioxide to the nearest 0.01 % as follows:

$$\text{Insoluble matter other than SiO}_2\text{, \%} = A - B \tag{4}$$

where:

A = insoluble matter including SiO_2, %, and
B = SiO_2, %.

11.5 *Precision and Bias*:

11.5.1 Three laboratories cooperated in testing on four limestone samples and two laboratories cooperated in testing on an additional eight limestone samples thereby obtaining the precision data summarized in Table 3.

11.5.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

12. Combined Oxides (Iron, Aluminum, Phosphorus, Titanium, Manganese)

12.1 *Scope*—The combined oxides describe a group of metals that form precipitates with ammonium hydroxide which may then be ignited to their respective oxides. Historically, it has been the practice to report the combined oxides present in limestone samples as a group because it was not always easy or desirable to determine each metal oxide separately. The group of metal oxides consists primarily of the oxides of iron and aluminum, with minor amounts of titanium dioxide (TiO_2), phosphorus pentoxide (P_2O_5), and manganese oxide (Mn_3O_4) also present. Where separate determinations are preferred, the combined oxides are usually weighed first, iron oxide is then assayed separately, and aluminum oxide is finally determined by calculating the difference between the percent combined oxides and the percent Fe_2O_3. The other metal oxides are generally assumed to be present in trace amounts and are often disregarded. When necessary, these metals may be analyzed separately and appropriate corrections made in the Al_2O_3 analysis.

12.2 *Summary of Test Method*—In this test method, aluminum, iron, titanium, and phosphorus are precipitated from the filtrate after SiO_2 removal, by means of ammonium hydroxide. With care, little if any manganese will be precipitated. The precipitate is ignited and weighed as the combined metal oxides.

12.3 *Special Solution*:

12.3.1 *Methyl Red Solution (0.2 %)*—Dissolve 2 g of methyl red indicator with 1 L of 95 % ethyl alcohol.

12.4 *Procedure*:

12.4.1 To the acid solution from the determination of SiO_2(See 8.3.4 or 9.3.3), add hydrochloric acid (HCl) if necessary to ensure a total of 10 to 15 mL of HCl.

NOTE 13—Sufficient hydrochloric acid must be present before the solution is rendered ammoniacal to prevent the precipitation of magnesium.

12.4.2 If a platinum evaporating dish has been used for the dehydration of SiO_2, or a fusion made in the platinum crucible containing the HF-insoluble residue, iron may have been partially reduced. The iron must then be oxidized by adding 1 mL of saturated bromine water to the filtrate. Boil the filtrate to eliminate the excess bromine completely before adding methyl red indicator.

12.4.3 Dilute with water to a volume of 200 to 250 mL, add a few drops of methyl red solution, and heat just to boiling. Add NH_4OH (1 + 1) (See Note 14) until the color of the solution becomes distinctly yellow, then add 1 drop in excess (See Note 15). Heat the solution containing the precipitate to boiling and boil for 50 to 60 s. Remove from heat and allow the precipitate to settle (not more than 5 min). Filter using medium-textured paper and wash the precipitate two or three times without delay with a hot, 2 % solution of ammonium chloride (NH_4Cl) (See Note 16).

NOTE 14—The NH_4OH used to precipitate the hydroxides must be free of any dissolved carbon dioxide (CO_2).

NOTE 15—At the neutral point, 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 the color fades during the precipitation or while heating, add more of the indicator. The boiling should not be prolonged as the precipitate may peptize and 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).

NOTE 16—Two drops of methyl red indicator solution should be added to the NH_4Cl 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).

12.4.4 Set aside the filtrate and dissolve any precipitate from the paper with 40 mL hot (1 + 3) HCl, pouring the hot acid through the paper into the beaker in which the precipitation was made. Wash the filter paper thoroughly with hot HCl (1 + 19) followed by hot water and reserve the paper. Boil the solution and precipitate the hydroxides with NH_4OH as before. The precipitate is filtered through a fresh piece of medium textured filter paper and washed four or five times (See Note 17) with a hot 2 % solution of NH_4Cl. Combine filtrates for Ca and calcium magnesium analysis.

NOTE 17—If perchloric acid has been used, the final precipitate should be washed at least eight times to remove all traces of perchlorate salts (See 9.3).

12.4.5 Place the moist precipitate and the two filter papers in a weighed platinum crucible (See Note 9), heat slowly until the papers are charred, and finally ignite to constant weight at 1050 to 1100 °C. Cool in a desiccator and weigh.

12.5 *Calculation*—Calculate the percentage of ammonium hydroxide group (combined oxides) to the nearest 0.01 % as follows:

$$\text{Combined oxides, \%} = (A/C) \times 100 \tag{5}$$

where:

A = mass of the combined oxides, g, and
C = original mass of sample, g.

12.6 *Precision and Bias*:

12.6.1 Four laboratories cooperated in testing on four limestone samples and three laboratories cooperated in testing on an additional seven limestone samples thereby obtaining the precision data summarized in Table 3.

12.6.2 The user is cautioned to verify by the use of test reference materials, if available, that the bias of this test method is adequate for the contemplated use.

13. Total Iron, Standard Method

13.1 *Scope*—Iron in limestone is usually present as pyrite (FeS_2) with occasional occurrences of other discrete iron minerals. The amount present varies according to the location and geological history of the deposit. During lime calcination, most if not all of the iron minerals present in the limestone ore will be converted to iron oxide or sulfate.

13.2 *Summary of Test Method*—In this test method, the total Fe_2O_3 content of the sample is determined from the ignited combined oxides by fusing the oxides with potassium pyrosulfate and leaching the melt with sulfuric acid. The iron is reduced to the ferrous state with stannous chloride and titrated with a standard solution of potassium dichromate ($K_2Cr_2O_7$).

13.3 *Special Solutions*:

13.3.1 *Stannous Chloride Solution* (50 g/L)—Dissolve 5 g of $SnCl_2 \cdot 2H_2O$ in 10 mL of HCl and dilute to 100 mL with water. Add several pieces of mossy tin metal to the bottle to preserve the $SnCl_2$ solution.

13.3.2 *Sodium Diphenylamine Sulfonic Acid Indicator* (2 g/L)—Dissolve 0.20 g sodium diphenylamine sulfonate in 100 mL of water. Store in a dark-colored bottle.

13.3.3 *Mercuric Chloride Solution* (5 %)—Dissolve 5 g of $HgCl_2$ in 100 mL of water.

13.3.4 *Potassium Dichromate, Standard Solution* (0.05 *N*)—Dry pure crystals of $K_2Cr_2O_7$ at 110 °C, then pulverize and dry at 180 °C to constant weight. Dissolve 2.4518 g of pulverized $K_2Cr_2O_7$ in water and dilute to 1 L. This is a primary standard, 1 mL = 0.0040 g Fe_2O_3.

13.4 *Procedure*:

13.4.1 To the combined oxides of iron and aluminum (See Note 18) in the platinum crucible, add 3 to 4 g of potassium pyrosulfate ($K_2S_2O_7$). Fuse at low heat until the oxides form a clear melt in the crucible. Cool, break up the button by gently tapping the crucible on the bench, and wash fragments into a small beaker with hot H_2SO_4(5 + 95). Add 5 mL of H_2SO_4(sp gr 1.82) to the contents in the beaker, and heat to dissolve the fused mass. Evaporate the solution to fumes of sulfuric acid and fume strongly for about 10 min. Cool, add 20 mL of water, and warm to dissolve the salts. There may be traces of silica appearing at this point, which for most routine work can be ignored. If the analyst prefers to determine it, however, the precipitate can be filtered, washed, and ignited. The recovered SiO_2 can then be added to the mass of SiO_2 previously found and its mass deducted from the gross mass of iron and aluminum reported (See Note 18).

NOTE 18—When the iron is present in small quantities, it is not always desirable to determine it in the ignited oxides from the 0.5-g sample. Under these conditions, the alternative procedure should be used with a larger sample weight.

NOTE 19—The recovered SiO_2 is usually small, but could be as much as 1 to 2 mg, even after two evaporations.

13.4.2 To the sulfuric acid solution, add 10 mL HCl (1 + 1) and heat to near boiling. Add dropwise stannous chloride solution (See Note 20) until the yellow color of the ferric iron just disappears. Add 2 or 3 drops of $SnCl_2$ in excess.

NOTE 20—If the stannous chloride has little effect and more than 5 to 10 mL are required, it has probably become oxidized to stannic chloride and a fresh supply should be obtained.

13.4.3 Cool the mixture and add approximately 100 mL of cold water. Add 10 mL of mercuric chloride solution, stir, and allow to stand for 3 to 5 min.

NOTE 21—A slight, white, silky precipitate should form. If the precipitate appears gray or black, it indicates too much $SnCl_2$ was added and the analysis must be repeated.

13.4.4 Add 5 mL of H_3PO_4 and 3 drops of sodium diphenylamine sulfonate indicator.

13.4.5 Titrate with standard 0.05 *N* $K_2Cr_2O_7$ solution adding the solution slowly while stirring constantly. The end point is indicated by a change in color from green to deep blue-violet.

13.5 *Calculation*:

$$Fe_2O_3, \% = (A/C) \times B \times 100 \tag{6}$$

where:

A = $K_2Cr_2O_7$ used in titration, mL,
B = 0.004 (Fe_2O_3 equivalent of $K_2Cr_2O_7$), and
C = sample, g.

13.6 *Precision and Bias*:

13.6.1 Four laboratories cooperated in testing on four limestone samples and three laboratories cooperated in testing on an additional seven limestone samples thereby obtaining the precision data summarized in Table 3.

13.6.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

14. Total Iron by Ortho-Phenanthroline Photometric Method

14.1 *Scope*—When the iron oxide content is very low, less than 0.1 %, and an accurate analysis at this low level is required, it is preferable to determine iron using procedures that have better sensitivity than the titrimetric methods. For an accurate determination of minute amounts of iron, the ortho phenanthroline method has proved invaluable.[6] In general, the method consists of reducing the iron to the ferrous state and then adding a slight excess of 1, 10 phenanthroline, which forms a complex with ferrous iron, giving an orange-pink color. The color intensity is proportional to the iron content of the solution.

14.2 *Summary of Test Method*—The bulk of the iron in the sample is dissolved with HCl, the silica dehydrated and separated by filtration, and the insoluble matter including SiO_2, ignited in a platinum crucible and treated with HF and H_2SO_4 to expel the SiO_2 and recover the small amount of iron that may not have dissolved with HCl. The acidified solution is transferred to a volumetric flask and diluted to volume. The iron is reduced with hydroxylamine hydrochloride and the

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[6] Sandel, E. B., *Colorimetric Determination of Traces of Metals,* 3rd Ed., Interscience Publications, 1959.

color of the ferrous complex is developed with 1,10 phenanthroline and compared against a set of iron standards similarly treated.

14.3 *Special Solutions*:

14.3.1 *Hydroxylamine Hydrochloride* (10 g/100)—Dissolve 10 g of hydroxylamine hydrochloride in 100 mL of water. Prepare fresh every week.

14.3.2 *Ammonium Acetate* (20 g/100)—Dissolve 200 g in 1 L of water.

14.3.3 *1,10 (Ortho) Phenanthroline* (0.1 g/100)—Dissolve 1.0 g in 1 L of hot water.

14.3.4 *Iron Standard Solution* (1 mL = 1.0 mg Fe_2O_3)—Dissolve 0.7000 g of pure iron wire by heating gently in 20 mL of HCl (1 + 1) and dilute to 1 L in a volumetric flask.

14.3.4.1 *Iron Work Standard Solution* (1 mL = 0.01 mg Fe_2O_3)—Transfer 10 mL of the iron standard solution to a 1 L volumetric flask and dilute to volume with water.

14.3.5 *Preparation of Calibration Curve*—To each of six 50 mL volumetric flasks, add, respectively, 1, 2, 4, 6, 8, and 10 mL of working iron standard solution. When diluted to volume, each mL of the prepared standard solutions will contain, respectively 0.2, 0.4, 0.8, 1.2, 1.6, and 2.0 micrograms Fe_2O_3.

14.3.5.1 Add to each flask in the following sequence, mixing after each addition, 1 mL of hydroxylamine hydrochloride solution, 5 mL of ammonium acetate, and 5 mL of 1,10 phenanthroline. Roll a small piece of congo red paper into a ball and insert it into the volumetric flask. Add NH_4OH (1 + 1) until the congo red indicator turns bright red, then add 1 drop of NH_4OH (1 + 1) in excess. Dilute to 50 mL, mix, and let stand for 15 to 20 min. Determine the absorbance of the solution in a spectrophotometer at a wavelength setting of 510 nm using water in the reference cell. Prepare a calibration curve by plotting the absorbance versus the concentration of Fe_2O_3 in µg/mL of solution.

14.4 *Procedure*:

14.4.1 Weigh 1 g of the properly prepared sample in 10 mL HCl (1 + 1) and evaporate rapidly to dryness. Add 50 mL of HCl (1 + 4) and heat to dissolve the salts. Filter the insoluble matter including SiO_2 through a retentive paper and wash several times with hot water. Reserve the residue. Heat the filtrate to boiling.

14.4.2 Place the paper containing the insoluble matter from the evaporated HCl solution in a platinum crucible. Char the paper at low heat without inflaming, then ignite at higher heat until the carbon has been completely burned off. Cool, add 1 mL H_2SO_4 and 10 to 15 mL HF and evaporate to fumes of sulfuric acid. Cool, dilute the contents of the crucible with water, and warm to dissolve salts. Transfer the acidified solution to the main solution containing the bulk of the iron.

14.4.3 Transfer the combined solutions to a 100 mL volumetric flask and dilute to volume. Pipet the aliquot containing 0.02 to 0.10 mg Fe_2O_3 into a 50 mL volumetric flask. Dilute to about 25 mL and add in the following sequence, mixing well after each addition: 1 mL hydroxylamine hydrochloride, 5 mL ammonium acetate, and 5 mL of 1,10 phenanthroline. Roll a small piece of congo red paper into a ball and insert into the volumetric flask. Add NH_4OH (1 + 1) until the congo red indicator turns a bright red, then add one drop of NH_4OH (1 + 1) in excess. Dilute to 50 mL, mix and let stand for 15 to 20 min. Determine the absorbance of the solution in a spectrophotometer at a wavelength setting of 510 nm using water in the reference cell. Compare against a set of standards similarly treated.

14.5 *Calculation*:

14.5.1 Calculate the % Fe_2O_3 as follows:

$$\%\ Fe_2O_3 = \frac{C \times D}{W \times 10^4} \qquad (7)$$

where:

C = concentration of Fe_2O_3 in sample solution, µg/mL (determined from calibration curve),

D = dilution factor, and

W = sample mass, g.

14.6 *Precision and Bias*:

14.6.1 The number of laboratories, materials, and determinations in this study does not meet the minimum requirements for determining precision prescribed in Practice E 691:

	Test Methods C 25	Practice E 691 Minimum
Laboratories	2	6
Materials	5	4
Determinations	4	2

14.6.2 The following precision statements are provisional. Within five years, additional data will be obtained and processed which does meet the requirements of Practice E 691.

14.6.2.1 Precision, characterized by repeatability, *Sr* and *r,* and reproducibility, *SR* and *R,* has been determined for the following test method and materials to be:

Precision Statement for Test Method:		% Fe_2O_3		Color	
Material	Average	*Sr*	*SR*	*r*	*R*
S-1143	0.0358	0.0058	0.0201	0.0163	0.0564
S-1145	0.0480	0.0053	0.0214	0.0148	0.0599
S-1141	0.1688	0.0466	0.0640	0.1306	0.1792
S-1142	0.2025	0.0141	0.0631	0.0396	0.1767
S-1144	0.9252	0.0562	0.2096	0.1574	0.5870

15. Aluminum Oxide

15.1 *Scope*—Aluminum oxide, for the purpose of this test method, is considered to be the difference between the combined oxides and Fe_2O_3. When phosphorus or titanium are determined, their oxides must also be deducted.

15.2 *Procedure*—Subtract the percent Fe_2O_3 obtained in accordance with Sections 5.1.1 and 5.1.2 from the percent combined oxides (See Section 5.1). Report the remainder as percent Al_2O_3. In special cases where P_2O_5 and TiO_2 need to be reported, a correction for these oxides must be made.

15.3 *Calculation*—Calculate the percent Al_2O_3 as follows:

$$Al_2O_3,\ \% = A - B \qquad (8)$$

where:

A = combined oxides ($Al_2O_3 + Fe_2O_3$), %, and

B = Fe_2O_3, %.

15.4 *Precision and Bias*:

15.4.1 Four laboratories cooperated in testing on four limestone samples and three laboratories cooperated in testing on an additional seven limestone samples thereby obtaining the precision data summarized in Table 3.

15.4.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

16. Calcium Oxide by Gravimetric Method

16.1 *Scope*—Calcium is separated from magnesium by means of a double precipitation as the oxalate after the determination of the ammonium hydroxide group. The precipitate is converted to CaO by ignition and weighed. The gravimetric method should be used when a recovery of aluminum is indicated or when a determination of strontium by gravimetric analysis is required.

16.2 *Summary of Test Method*—Calcium is precipitated with ammonium oxalate $(NH_4)_2C_2O_4$, filtered, ignited to the oxide, and redissolved with HCl. Any of the NH_4OH group of metals that escaped precipitation before may be recovered at this point by the addition of a small amount of NH_4OH and boiling. Any precipitate that separates out is assumed to be $Al(OH)_3$ and after ignition to Al_2O_3 this amount is added to the mass of Al_2O_3 calculated in 16.2. Calcium is precipitated a second time as the oxalate, filtered, washed, ignited, and weighed as CaO.

16.3 *Special Solutions*:

16.3.1 *Ammonium Oxalate Solution* (saturated)—Dissolve 45 g of ammonium oxalate $(NH_4C_2O_4)$ in 1 L of hot water. When cooled to room temperature the supersaturated solution will partially crystallize out and the supernatant solution will then be saturated with ammonium oxalate.

16.3.2 *Ammonium Oxalate Wash Solution* (1 g/L)—Dissolve 1 g of $(NH_4)_2C_2O_4$ in 1 L of water.

16.4 *Procedure*:

16.4.1 Add 30 mL of HCl (1 + 1) and 20 mL of 10 % oxalic acid to the combined filtrates from the iron and aluminum hydroxide precipitation and heat the solution to boiling. To the boiling solution, add ammonium hydroxide (1 + 3) slowly until a precipitate begins to form. At this point, add the ammonium hydroxide still more slowly (dropwise, with a pipet) while stirring continuously until the methyl red just turns yellow. Add 25 mL of hot saturated ammonium oxalate solution while stirring. Remove from the heat and let stand until the precipitate has settled and the supernatant liquid is clear. Allow to cool for a minimum of 1 h, and filter using a retentive paper. Wash the paper and precipitate with five 10-mL portions of cold, neutral 0.1 % solution of $(NH_4)_2C_2O_4$(See Note 22). Reserve filtrate for the magnesium determination.

NOTE 22—Hot solutions should be avoided when washing the CaC_2O_4 precipitate. One litre of hot water will dissolve 5 mg of CaO. One litre of cold 0.1 % $(NH_4)_2C_2O_4$ solution will dissolve only 0.1 mg of CaO.

16.4.2 Place the wet filter and precipitate in a platinum crucible, and char the paper without inflaming at low heat. Increase the heat to burn off all the carbon and ignite at 1000 °C for about 10 min. Cool, dissolve the ignited oxide in 50 mL of dilute HCl (1 + 4), and dilute to about 100 mL with water. Add a few drops of methyl red indicator and neutralize with NH_4OH till the color of indicator changes to yellow. Heat just to boiling. If a small amount of $Al(OH)_3$ separates, filter it, wash with a hot 2 % solution of NH_4Cl, ignite, weigh, and add this to the mass of Al_2O_3 determined in 15.2.

16.4.3 Heat the filtrate to boiling and add slowly, while stirring, 35 mL of saturated $(NH_4)_2C_2O_4$ solution. Digest, filter, and wash as in 16.4.1. Combine the filtrate and washing with the ones reserved from the first precipitation, and retain for the determination of MgO. Place the filter in a tared platinum crucible with cover and carefully char the paper without inflaming. Increase the heat to burn off the carbon and ignite the calcium oxide in the covered platinum crucible at 1000 °C. Cool in a desiccator and weigh as CaO. Repeat the ignition to constant weight avoiding any hydration or carbonation of the lime.

16.5 *Calculation*—Calculate the percent calcium oxide (CaO) as follows:

$$\text{CaO, \%} = (M/W) \times 100 \tag{9}$$

where:

M = mass of CaO, g, and
W = mass of sample, g.

16.6 *Precision and Bias*:

16.6.1 Two laboratories cooperated in testing on four limestone samples and obtained the precision data summarized in Table 3.

16.6.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

17. Calcium Oxide by Volumetric Method

17.1 *Scope*—This volumetric test method is used mostly for ordinary control work in the plant laboratory, but it is capable of giving exact results, especially with those products that are free of interfering elements. Traces of strontium, barium, magnesium, or oxalate that may be present will also be titrated and calculated as calcium on an equivalence, not weight, basis.

17.2 *Summary of Test Method*—In this test method, the calcium oxalate precipitate is dissolved with dilute sulfuric acid and the liberated oxalic acid is titrated with standard potassium permanganate. The calcium equivalent of the oxalic acid is determined and the grams of CaO calculated.

17.3 *Special Solutions*:

17.3.1 *Potassium Permanganate, Standard Solution* (0.175 *N*):

17.3.1.1 Dissolve 5.64 g of potassium permanganate $(KMnO_4)$ in 1 L of water and boil gently for 20 to 30 min. Dilute again to 1 L, cover and allow to age for several days. Filter through purified asbestos or a wad of glass wool, and standardize against the National Institute of Standards and Technology's standard sample 40C of sodium oxalate $(Na_2C_2O_4)$ or equivalent as follows:

17.3.1.2 Transfer 0.5 g of the standard sodium oxalate dried at 105 °C to a 400-mL beaker. Add 250 mL of diluted H_2SO_4(5 + 95) freshly boiled for 10 to 15 min and cooled to 27 ± 3 °C. Stir until the oxalate has dissolved. Add 40 to 42 mL of the standard $KMnO_4$ solution at the rate of 25 to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 60 s) (See Note X1.2).

17.3.1.3 Heat the contents of the beaker to 60 °C and complete the titration at this temperature by adding $KMnO_4$ solution until a slight pink color persists for 30 s. Add the last

0.5 to 1 mL dropwise, allowing each drop to become decolorized before the next one is added.

17.3.1.4 Determine the exact normality of the $KMnO_4$ solution from the following:

$$N = W/V \times 0.06701 \quad (10)$$

where:
N = normality of $KMnO_4$ solution,
W = mass of standard sodium oxalate,
V = $KMnO_4$ used to titrate sodium oxalate, mL, and
0.06701 = sodium oxalate equivalent to 1 mL of 1 *N* $KMnO_4$ solution, g.

17.3.1.5 Determine the CaO equivalent of the $KMnO_4$ solution as follows:

$$F = N \times 0.02804 \quad (11)$$

where:
F = CaO equivalent of the $KMnO_4$ solution in grams CaO/mL,
N = normality of $KMnO_4$ solution, and
0.02804 = CaO equivalent to 1 mL of 1 *N* $KMnO_4$ solution, g.

17.4 *Procedure*:

17.4.1 Add 30 mL of HCl (1 + 1) and 20 mL of 10 % oxalic acid to the combined filtrates from the iron and aluminum hydroxide precipitation and heat the solution to boiling. To the boiling solution, add ammonium hydroxide (1 + 3) slowly until a precipitate begins to form. At this point, add the ammonium hydroxide still more slowly (dropwise, with a pipet) while stirring continuously until the methyl red just turns yellow. Add 25 mL of hot saturated ammonium oxalate while stirring. Remove from the heat and let stand until the precipitate has settled and the supernatant liquid is clear. Allow to cool and filter at the end of 1 h. Wash the paper with cold water, limiting the total washings to 125 mL (See Note 23). Retain the filtrate for magnesium.

NOTE 23—A Gooch crucible may be used instead of filter paper to filter the CaC_2O_4 precipitate.

17.4.2 With a jet of hot water, wash the precipitate from the paper into the beaker in which the precipitation was made. Fold the paper and leave it adhering to the upper portion of the beaker. Add to the contents of the beaker 250 mL of hot, diluted H_2SO_4(1 + 19) and heat to 80 to 90 °C.

17.4.3 Titrate with 0.175 *N* $KMnO_4$ solution until the pink end point is obtained. Drop the folded filter paper that contained the original precipitate into the liquid and macerate it with a stirring rod; the pink color of the solution will be discharged (See Note 24). Finish the titration by adding the $KMnO_4$ standard solution dropwise until the end point is again obtained.

NOTE 24—There will always be some fine particles of precipitate imbedded in the pores of the filter paper which are dissolved by the acid in solution. The filter paper is not introduced at the beginning of the titration to avoid introduction of traces of organic matter due to the action of the hot sulfuric acid on the paper; these would consume $KMnO_4$ and give high results for CaO.

17.5 *Calculation*—Calculate the percentage of CaO in the sample using the CaO equivalent from 17.3.1.5 as follows:

$$\text{CaO, \%} = (V \times F)/W \times 100 \quad (12)$$

where:
V = $KMnO_4$ solution used in titration, mL,
F = CaO equivalent of $KMnO_4$, and
W = original mass of sample, g.

17.6 *Precision and Bias*:

17.6.1 Two laboratories cooperated in testing on twelve limestone samples and obtained the precision data summarized in Table 3.

17.6.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

18. Magnesium Oxide

18.1 *Scope*—Magnesium oxide in lime and limestone may vary from a few tenths to 2 % for high-calcium limestone to as much as 22 % for dolomitic limestone. The pyrophosphate gravimetric method has been used successfully throughout the industry to determine magnesium within this wide range.

18.2 *Summary of Test Method*—In this test method, magnesium is doubly precipitated as magnesium ammonium phosphate from the filtrate after removal of calcium. The precipitate is ignited and weighed as magnesium pyrophosphate ($Mg_2P_2O_7$). The MgO equivalent is then calculated.

18.3 *Special Solutions*:

18.3.1 *Ammonium Phosphate, Dibasic Solution* (250 g/L)—Dissolve 250 g of dibasic ammonium phosphate ($(NH_4)_2HPO_4$) in 1 L of water.

18.3.2 *Ammonium Hydroxide Wash Solution* (5 + 95)—Dilute 50 mL of NH_4OH with 950 mL of water and add 1 or 2 mL of HNO_3.

18.4 *Procedure*:

18.4.1 Add 2 drops of methyl red indicator to the combined filtrates from the determination of calcium, acidify with HCl, and concentrate to about 250 mL. Add to this solution about 10 mL of the $(NH_4)_2HPO_4$ solution, 250 g/L, and cool the solution to room temperature. Add NH_4OH slowly while stirring constantly until the solution is alkaline or the crystalline magnesium ammonium phosphate begins to form; then add about 15 to 20 mL of NH_4OH in excess and continue stirring for several more minutes. Allow the beaker and precipitate to stand in a cool place overnight. Filter and wash with cold dilute ammonium hydroxide wash solution (5 + 95).

18.4.2 Dissolve the precipitate with hot diluted HCl (1 + 9) and wash the filter paper well with hot diluted HCl (1 + 99). Dilute the solution to 100 mL, cool to room temperature, and add 1 mL of the 20 % solution of $(NH_4)_2HPO_4$. Precipitate the magnesium ammonium phosphate as before and allow to stand for about 2 h in a cool place.

18.4.3 Filter the precipitate on paper or in a tared Gooch crucible, washing with diluted NH_4OH (5 + 95). If filtered through a Gooch, place directly in a muffle at 400 °C and raise heat to 1100 °C. If filtration was through paper, place paper and precipitate in a weighed platinum or porcelain crucible. Slowly char the paper without inflaming and carefully burn off the resulting carbon (**Warning**—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 a danger of occluding carbon in the precipitate if ignition is too rapid.). Ignite at 1100 °C for ½ h, cool in desiccator, and weigh as $Mg_2P_2O_7$ (See Note 25).

NOTE 25—For research purposes or in the most exacting types of work, the manganese content of the pyrophosphate residue should be determined and deducted as $Mn_2P_2O_7$.

18.5 *Calculation*—Calculate the percentage of MgO to the nearest 0.01 % as follows:

$$\text{MgO, } \% = A \times 36.2 / B \qquad (13)$$

where:

A = $Mg_2P_2O_7$, g,
B = sample, g, and
36.2 = molecular ratio of 2MgO to $Mg_2P_2O_7 \times 100$.

18.6 *Precision and Bias*:

18.6.1 Four laboratories cooperated in testing on three limestone samples and three laboratories cooperated in testing on an additional nine limestone samples thereby obtaining the precision data summarized in Table 3.

18.6.2 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

19. Loss on Ignition

19.1 *Scope*—Loss on ignition (LOI) is the loss in weight expressed as percent of the initial "as received" sample weight obtained after ignition of the sample at 1000 °C to constant weight. The loss in weight is due to a release of free moisture, chemically combined "lattice" or "hydroxy" water, CO_2, SO_2, and volatile pyrolytic products of any organic material that may be present.

19.2 *Summary of Test Method*—The tared crucible containing the weighed sample is ignited to constant weight. The loss in weight is the LOI of the sample.

19.3 *Procedure*—Transfer approximately 1 g of the sample prepared to pass a 100-mesh (149-µm) U.S. standard sieve to a tare-weighed porcelain or platinum crucible. Cover with a lid and weigh accurately to within 0.1 mg. When testing quicklime, the crucible cover is not required. Also, quicklime may be placed directly into a muffle at 1000 °C avoiding preignition. Pre-ignite in a muffle furnace at approximately 400 °C for 30 min. Then increase muffle temperature to 1000 °C ± 20 °C, and maintain at this temperature for a minimum of 20 min or until constant mass is obtained. The difference between the original mass of the sample and the final mass represents the loss on ignition.

19.4 *Calculation*—Calculate LOI as follows:

$$\text{LOI, } \% = (A - B)/C \times 100 \qquad (14)$$

where:

A = mass of crucible + sample, g,
B = mass of crucible plus sample after ignition, g, and
C = mass of sample, g.

19.5 *Precision and Bias*:

19.5.1 Fifteen laboratories cooperated in testing on three samples of high calcium limestone to obtain the precision data for percent LOI given in 19.5.2 and 19.5.3.

19.5.2 The repeatability (Practice E 691 [r]) was found to be 0.158 % LOI.

19.5.3 The reproducibility (Practice E 691 [R]) was found to be 0.463 % LOI.

19.5.4 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

20. Free Moisture in Limestone

20.1 *Scope*—For the purpose of this test method, the conventional definition of "hygroscopic moisture" or "free water" (also known as "free-moisture") is accepted; that is, the amount of water and any other volatile matter than can be expelled from a sample of the material by drying to constant weight at a temperature slightly above the boiling point of water.

20.2 *Summary of Test Method*—The sample in a container is heated in a drying oven at 115 to 120 °C constant weight. The loss in weight represents the free moisture.

20.3 *Special Apparatus*:

20.3.1 *Bottle,* weighing, low-form, glass-stoppered, or wide-form, large porcelain crucible.

20.4 *Procedure*—Weigh 1 g of the prepared sample in the stoppered weighing bottle. Remove the stopper and heat in a drying oven at 115 to 120 °C for 2 h. Quickly stopper, cool in a desiccator, and weigh, lifting the stopper momentarily just before weighing. The use of a similar weighing bottle as a counterpoise carried through all the operations is a desirable procedure unless a single pan balance is used. The loss in weight represents "free moisture" loss at 120 °C.

20.5 *Calculation*—Calculate the percent "free moisture" as follows:

$$\text{Free-moisture, } \% = (A - B)/C \times 100 \qquad (15)$$

where:

A = mass of crucible and sample before heating, g,
B = mass of crucible and sample after heating at 120 °C, g, and
C = original mass of sample, g.

20.6 *Precision and Bias*—The precision and bias of this test method have not been determined.

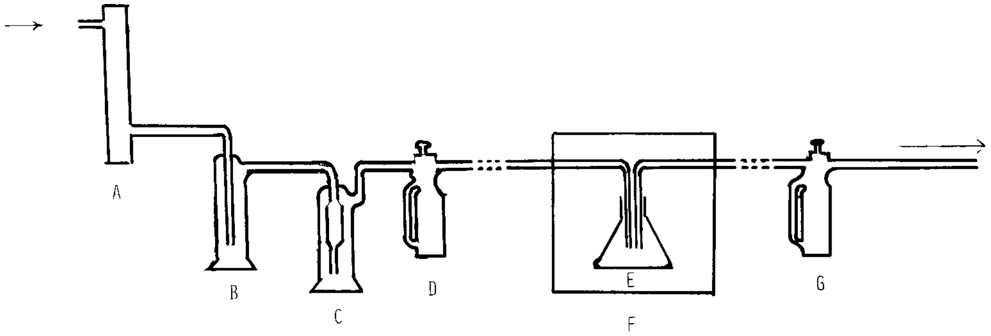
21. Free Moisture in Hydrated Lime

21.1 *Scope*—The free moisture in hydrated lime is that water that is released from the sample at a temperature of 115 to 120 °C. This distinguishes it from the hydroxyl water that is chemically bound to the lime and which cannot be liberated except at higher temperatures.

21.2 *Summary of Test Method*—Free moisture in hydrated lime is determined by aspirating a slow stream of CO_2-free air over the sample in a container placed inside a 115 to 120 °C oven. The loss in weight of the sample is equal to the free moisture of the hydrated lime.

21.3 *Special Apparatus*:

21.3.1 *Sample Flask E,* illustrated in Fig. 1, consists of a 50-mL flat-bottom, glass-stoppered flask, supplied with a ground glass joint and solid ground glass stopper.



A Soda-Lime Tower at inlet to remove CO_2.
B Bottle containing lime water to show when soda lime tower is exhausted.
C Fleming jar containing sulfuric acid to remove water from air.
D Absorption bulb filled with Anhydrone (Magnesium Perchlorate) to complete drying of air.
E 50-mL sample flask.
F Drying oven operating at 110 °C.
G Absorption bulb filled with Anhydrone to prevent moisture backup into sample.

FIG. 1 Apparatus for Free Moisture in Hydrated Lime

21.3.1.1 The flask shall be fitted with an interchangeable hollow ground-glass stopper, equipped with two glass entry tubes for conducting the dry air over the sample.

21.3.2 *Purifying Train* (See Fig. 1), located outside the oven *F* for conducting the dry air over the samples, shall consist of a series of scrubbers and absorption bulbs to remove CO_2 and moisture from the air. The apparatus are arranged in the following order starting from the air source:

21.3.2.1 *Soda-Lime Tower A,* at the air inlet to remove CO_2 from the air.

21.3.2.2 *Bottle B,* containing lime water to show when the soda lime is exhausted.

21.3.2.3 *Fleming Jar C,* containing sulfuric acid to remove water from the air.

21.3.2.4 *Absorption Bulb D,* filled with Anhydrone (magnesium perchlorate) to complete the drying of the air.

21.3.2.5 *Sample Flask E.*

21.3.2.6 *Drying Oven F.*

21.3.2.7 *Absorption Bulb G,* also filled with Anhydrone and located on the exit side of the sample bulb as a protective barrier against atmospheric moisture.

21.4 *Procedure*—Weigh 2.5 to 3 g of the prepared sample, and using glazed paper folded in the shape of a funnel, transfer it rapidly into the previously weighed bottle and immediately restopper it. Insert the bottle into the 120 °C oven and quickly exchange stoppers. Connect the sample bottle to the purifying train by means of flexible tubing and pass a slow current of dry CO_2-free air through the apparatus for 2 h. Disconnect the sample bottle from the train, remove it from the oven with another quick exchange of stoppers, and place it in a desiccator to cool. When cool, remove it to the balance case for several minutes before weighing it, and just before weighing, lift the stopper slightly for an instant to relieve any vacuum that may exist in the bottle. The loss in weight of the sample represents "free moisture" loss as 120 °C. Use a bottle similar to the one containing the sample as a counterpoise in all weighings unless a single-pan balance is used.

21.5 *Calculation*—Calculate the percent "free moisture" in the sample as follows:

$$\text{Free moisture, }\% = (A - B)/C \times 100 \tag{16}$$

where:
A = mass of sample flask + sample, g,
B = mass of sample flask after drying, g, and
C = mass of sample, g.

21.6 *Precision and Bias*—The precision and bias of this test method have not been determined.

22. Carbon Dioxide by Standard Method

22.1 *Scope*—Carbon dioxide in limestone is sometimes determined to verify the presence of carbonates other than calcium or magnesium. These may include carbonates of iron, manganese, and occasionally traces of other substances. Samples of lime and hydrated lime are analyzed for CO_2 to check for the presence of carbonates, most of which are there as uncalcined limestone.

22.2 *Summary of Test Method*—The sample is decomposed with HCl and the liberated CO_2 is passed through a series of scrubbers to remove water and sulfides. The CO_2 is absorbed with Ascarite, a special sodium hydroxide absorbent, and the gain in weight of the absorbtion tube is determined and calculated as percent CO_2.

22.3 *Special Apparatus*:

22.3.1 The apparatus illustrated in Fig. 2 consists of the following:

22.3.1.1 *Purifying Jar A,* Fleming, containing sulfuric acid.

22.3.1.2 *Drying Tube B,* U-shaped with side arms and glass stoppers. Side arms are shaped to hold rubber tubing. Contains Anhydrone on left side and Ascarite on right side.

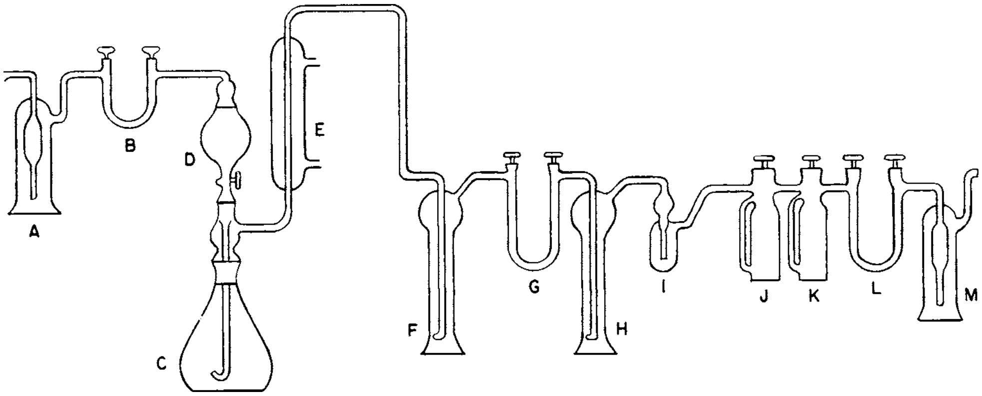
22.3.1.3 *Erlenmeyer Flask C,* 250-mL, 24/40 ground-glass joint.

22.3.1.4 *Separatory Funnel D,* with ground-glass stopper and interchangeable hollow ground-glass joint. A delivery tube bent at the end extends into the sample flask about ½ in. from the bottom. Used to introduce acid into flask.

22.3.1.5 *Condenser E.*

22.3.1.6 *Gas-Washing Bottle F,* 250-mL, with fritted disk containing distilled water to retain most of the acid volatilized from the alkalimeter.

22.3.1.7 *U-Tube G,* containing mossy zinc to remove the last traces of HCl.



A Purifying jar, Fleming, containing concentrated H_2SO_4.
B Drying tube, U-shaped, Ascarite in right side, Anhydrone in left side.
C Erlenmeyer flask, 250-mL, 24/40 glass joint.
D Separatory funnel.
E Condenser.
F Gas-washing bottle, 250-mL with fritted disk, containing water to retain most of the acid volatilized from the alkalimeter.
G U-tube containing mossy zinc to remove the last traces of HCl.
H Gas-washing bottle, 250-mL with fritted disk, containing concentrated H_2SO_4.
I Trap.
J Absorption bulb containing Anydrone.
K CO_2 absorption bulb containing Ascarite.
L U-guard tube with Anhydrone in left side and Ascarite in right side.
M Purifying jar, Fleming, containing concentrated H_2SO_4.

FIG. 2 Apparatus for Carbon Dioxide by Standard Method

22.3.1.8 *Gas-Washing Bottle H,* 250-mL, with fritted disk, containing concentrated H_2SO_4 and trap *I,* to remove any SO_3 mist that may have been carried over.

22.3.1.9 *Absorption Bulb J,* containing Anhydrone to remove last traces of water vapor.

22.3.1.10 *CO_2 Absorption Bulb,* containing Ascarite filled as follows: On the bottom of the bulb, place a layer of glass wool extending above the bottom outlet and on top of this a layer of Anhydrone about ⅜ in. thick; immediately above this is placed another layer of glass wool, and Ascarite is then added to almost fill the bulb. A top layer of Anhydrone about ⅜ in. thick is placed on top of the Ascarite and topped off with a covering of glass wool.

22.3.1.11 *U-Guard Tube L,* filled with Anhydrone in left side and Ascarite in right side.

22.3.1.12 *Purifying Jar M,* Fleming, containing H_2SO_4.

22.4 *Procedure*:

22.4.1 Weigh an indicated amount of prepared sample, 0.5 g for limestone and 5 g for lime or hydrated lime, and transfer to the 250-mL Erlenmeyer flask. Connect the sample flask to apparatus as shown in the diagram (See Fig. 2). Purge the system free of carbon dioxide by passing a current of CO_2-free air through the apparatus for 10 to 15 min.

22.4.2 Weigh the absorption bulb and attach it to the train. Remove the glass stopper from separatory funnel, place 50 mL of dilute HCl (1 + 1) in the separatory funnel (*D*) and replace the stopper with the interchangeable hollow ground-glass joint through which passes a tube for admitting purified air. Open the stopcock of the separatory funnel and admit air through the top of the funnel to force the hydrochloric acid into the Erlenmeyer flask (*C*).

22.4.3 Start cold water circulating through the condenser (*E*) and, with CO_2-free air passing at a moderate rate through the absorption train, place a small hot plate or gas burner under the sample flask and boil for about 2 min. Remove the hot plate and continue the flow of purified air at about three bubbles per second for 30 min to sweep the apparatus free of CO_2. Close the absorption bulb, disconnect it from the train and weigh, opening the stopper momentarily to equalize the pressure. Use a second absorption bulb as counterpoise in all weighings unless a single pan balance is used.

22.5 *Calculation*—Calculate the percent CO_2 as follows:

$$CO_2, \% = (A - B)/C \times 100 \tag{17}$$

where:

A = mass of absorption bulb + CO_2, g,
B = mass of absorption bulb before the run, g, and
C = mass of sample, g.

22.6 *Precision and Bias*—The precision and bias of this test method have not been determined.

23. Sulfur Trioxide

23.1 *Scope*—This test method will determine sulfur compounds, mostly present as sulfates in lime and limestone, that are soluble in dilute HCl. Iron pyrites and other sulfides will not be included because they will either be volatilized as H_2S or not react at all with the acid.

23.2 *Summary of Test Method*—In this test method, sulfate is precipitated from an acid solution of the lime or limestone with barium chloride ($BaCl_2$) and the SO_3 equivalent is calculated.

23.3 *Special Solution*:

23.3.1 *Barium Chloride Solution* (100 g/L)—Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in 1 L of water.

23.4 *Procedure*—Select and weigh the prepared sample into a 250-mL beaker containing 50 mL of cold water in accordance with the following:

Expected SO_3 Range, %	Sample Weight, g
0.001 to 0.500	10.00
0.500 to 2.50	5.00
2.50 to 12.5	2.00

Stir until all lumps are broken and the lighter particles are in suspension. Add 50 mL of diluted HCl (1 + 1) and heat until the reaction has stopped and decomposition is complete. Digest for several minutes at a temperature just below boiling. Add a few drops of methyl red indicator and render the solution alkaline (yellow color) with NH_4OH (1 + 1). Heat the solution to boiling. Filter through a medium-textured paper and wash the residue thoroughly with hot water. Dilute the filtrate to 250 mL, add 5 mL of HCl (1 + 1), heat to boiling, and add slowly 10 mL of hot $BaCl_2$ solution. Continue the boiling until the precipitate is well formed, stir well, and allow to stand overnight at room temperature. Take care to keep the volume of solution between 225 and 250 mL, and add water for this purpose if necessary. Filter through a retentive paper and wash the precipitate with hot water. Place the paper and contents in a weighed platinum crucible, and slowly char the paper without flaming. Burn off all the carbon, ignite in a muffle at 1000 °C, cool in a desiccator, and weigh.

23.5 *Calculation*—Calculate the percentage of SO_3 to the nearest 0.001 as follows:

$$SO_3, \% = A \times 0.343/W \times 100 \quad (18)$$

where:

A = mass of $BaSO_4$, g,
W = mass of sample, g, and
0.343 = molecular ratio of SO_3 to $BaSO_4$.

23.6 *Precision and Bias*:

23.6.1 Six laboratories cooperated in testing on four samples of limestone and lime materials covering the range from 0.04 to 5.15 % SO_3 to obtain the precision data given in 23.6.2 and 23.6.3.

23.6.2 The repeatability (Practice E 173 R_1) was found to be (0.135 % SO_3 per weight in grams of sample analyzed).

23.6.3 The reproducibility (Practice E 173 R_2) was found to be (0.271 % SO_3 per weight in grams of sample analyzed).

23.6.4 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

24. Total Sulfur by Sodium Carbonate Fusion

24.1 *Scope*—Sulfur in limestone is chiefly, if not wholly, present as sulfide, usually as pyrite. If the total sulfur obtained in the following test method is in excess of that present as soluble sulfate, the difference can be assumed to be present as iron disulfide.

24.2 *Summary of Test Method*—The sample is fused with sodium carbonate and the ignited mass is leached in water and dissolved with HCl. The solution is made ammoniacal and the hydroxide precipitate is filtered. The sulfur in the filtrate is precipitated with a 10 % solution of barium chloride. The precipitate is ignited and weighed as barium sulfate ($BaSO_4$) and the SO_3 equivalent is calculated.

24.3 *Procedure*:

24.3.1 Select and weigh the prepared sample into a porcelain crucible in accordance with the following:

Expected S Range, %	Sample Weight, g	Na_2CO_3 Weight, g
0.001 to 0.20	10.00	5.00
0.200 to 1.00	5.00	2.50
1.00 to 5.00	2.00	1.00

Add the indicated amount of Na_2CO_3 and mix well. Heat in a muffle at 600 °C for 15 min. Increase the heat 50 °C every 15 min until 1000 °C is reached and maintain at this temperature for 15 min. (See Note 26). Cool, place the crucible and cover in a 400-mL beaker, and cover with hot water. Add 10 mL bromine water (See Note 27) and then add sufficient HCl (1 + 1) to make the solution slightly acid to methyl red. Boil until solution is complete and all bromine has been expelled. Remove the crucible and wash with hot water.

NOTE 26—Since not enough flux is used to produce more than a sintering, the air entering the crucible after the bulk of the carbon dioxide has been released effects very speedy oxidation in the porous mass.

NOTE 27—It has been found that 10 mL of 30 % hydrogen peroxide (H_2O_2) may be substituted for the bromine water to accomplish oxidation without affecting the analytical result.

24.3.2 Add a few drops of methyl red indicator and render the solution alkaline with NH_4OH (1 + 1). Heat the solution to boiling, filter using a retentive paper and wash with hot water. To the filtrate add 5 mL of HCl (1 + 1), adjust the volume to about 250 mL, and bring the solution to boiling. To the boiling solution, add 10 mL of hot $BaCl_2$ solution, slowly and with stirring. Allow to stand overnight. Filter through a retentive paper and wash the precipitate with hot water. Place paper and contents in a weighed platinum crucible and slowly char the paper without flaming. Burn off the carbon and ignite in a muffle at 1000 °C for 1 h. Cool in a desiccator and weigh as $BaSO_4$.

24.4 *Calculation*—Calculate the percentage of sulfur to the nearest 0.001 as follows:

$$S, \% = A \times 13.73/W \quad (19)$$

where:

A = mass of $BaSO_4$, g,
W = sample, g, and
13.73 = mass of molecular ratio of S to $BaSO_4$ × 100.

24.5 *Precision and Bias*:

24.5.1 Six laboratories cooperated in testing on four samples of limestone and lime materials covering the range from 0.021 to 2.15 % sulfur to obtain the precision data given in 24.5.2 and 24.5.3.

24.5.2 The repeatability (Practice E 173 R_1) was found to be (0.065 % S per weight in grams of sample analyzed).

24.5.3 The reproducibility (Practice E 173 R_2) was found to be (0.094 % S per weight in grams of sample analyzed).

24.5.4 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

25. Total Sulfur by the Combustion-Iodate Titration Method

25.1 *Scope*—This test method covers the determination of sulfur in concentration from 0.005 to 1 %. At the combustion temperature of approximately 1650 °C, complete combustion of the sulfur in the sample will take place regardless of sulfur form or sample matrix.

25.2 *Summary of Test Method*—A major portion of the sulfur in various types of lime and limestone samples is converted to oxides of sulfur, primarily sulfur dioxide (SO_2), by combustion in a stream of oxygen at the elevated temperature of a high-frequency induction furnace. During the combustion, the SO_2 is absorbed in an acidified starch-iodine solution and titrated with potassium iodate. The latter is standardized against limestone standard samples of known sulfur content to compensate for characteristics of a given apparatus and for day-to-day variation in the percentage of sulfur recovered as SO_2. Compensation is also made for the blank due to accelerators and crucibles.

25.3 *Apparatus:*

25.3.1 *Induction Furnace*—The induction furnace shall be supplied with a rheostat used to control the power input to the reduction coil that will avoid heating some types of samples too rapidly during the early stages of combustion. The train of the induction furnace shall include an oxygen purifier, described in 25.3.3.

25.3.2 *Automatic Titrator*—This apparatus shall consist of an absorption and titration vessel of appropriate volume and contain an inlet bubbler tube for the sulfur gases with a float valve to prevent backflow of liquid when the sample is starting to consume oxygen. The vessel must be shaped to effect complete absorption of SO_2 in a small volume of solution. The titrator comes equipped with a buret that should be approximately 10 mL in capacity marked with 200 divisions. The automatic titrator utilizes a photoelectric cell to activate a titrator inlet valve that allows the titration to proceed without the presence of an operator.

25.3.3 *Oxygen Purifiers*—Reagent-grade oxygen from a commercial tank is passed through a suitable two-stage reduction valve to provide an even and adequate flow of oxygen through a purifying train consisting of a sulfuric acid tower, an absorption bulb containing 20 to 30-mesh inert base impregnated with NaOH, and another absorption bulb containing anhydrous magnesium perchlorate Mg (ClO_4). A flowmeter precedes the induction furnace assembly.

25.3.4 *Combustion Crucibles*—The crucibles for use with the induction furnace must be of adequate thickness to retain the molten slag and have a sulfur blank as low and consistent as possible. The crucibles for use in the induction furnace must have adequate capacity and may be provided with suitable covers.

25.3.5 *Glass Accelerator Scoop.*

25.3.6 *Starch Dispenser*—A plastic bottle with a device for dispensing a few millilitres of starch solution at a time.

25.3.7 *Timer,* having a 0 to 15-min range in ¼-min intervals. Turns off the furnace at end of preset time and automatically resets.

25.3.8 *Loading Funnel*—Three-legged funnel that fits over the crucible and simplifies addition of sample.

25.4 *Reagents:*

25.4.1 *Copper (Low-Sulfur) Ring Accelerator.*

25.4.2 *Iron (Low-Sulfur) Accelerator*—Iron chips. (For samples containing very low percentages of sulfur, the use of iron powder is recommended because of its low blank.)

25.4.3 *Tin Metal (Low-Sulfur) Accelerator,* granular.

25.4.4 *Potassium Iodate* (KIO_3) *Crystal.*

25.4.5 *Potassium Iodide* (KI) *Crystal.*

25.4.6 *Starch,* soluble.

25.5 *Special Solutions*:

25.5.1 *Potassium Iodate,* standard solutions.

25.5.1.1 KIO_3*Standard Solution A*—Dissolve 0.2227 g KIO_3 in 900 mL of water containing 1 g sodium hydroxide (NaOH) and dilute to 1 L. For a 0.500-g sample, the buret reads directly in percent sulfur.

25.5.1.2 *Starch-Iodide Solution*—Transfer 2 g of soluble starch (for example, Arrowroot) to a 50-mL beaker, add a few millilitres of water, and stir into a smooth paste. Slowly add starch to 500 mL of distilled water while stirring. Add 4 g of NaOH and continue stirring the solution until the appearance changes from cloudy to translucent. Add 6 g of potassium iodide (KI), stir until the KI is dissolved, and dilute to 1 L.

NOTE 28—Discard any starch solution that imparts a red tinge to the blue color when titrating.

25.6 *Calibration*—This test method and instrument should be standardized by using a limestone sample of known sulfur content as determined by the Total Sulfur Method by Sodium Carbonate Fusion, Section 24. The Leco instrument, in addition, may be standardized daily by running limestone reference materials whose sulfur content, as determined by the Total Sulfur Method, ranges from 0.02 to 0.05 %. The limestone standards are run to determine the day-to-day variations in the test method and to verify that the electronics in the Leco are working properly.

25.6.1 It has been found through round robin studies that the practice of pre-igniting samples at 1000 °C causes erratic recovery of sulfur. This practice should not be used.

25.7 *Procedure*:

25.7.1 Allow 15 min for the electronics in the furnace assembly and titrator to warm up.

25.7.2 Set the grid-current tap switch to low, medium, or high position. Determine the position on a test run, with the sample and accelerators that will give a complete combustion at approximately 400 mA as indicated on the plate current ammeter.

25.7.3 Set the automatic timer to the estimated time required to evolve the sulfur in the sample completely, as follows:

Sample	Time, Min
Quicklime	8
Hydrated Lime	10
Limestone	12

25.7.4 Weigh the sample and brush carefully into the combustion crucible using the loading funnel. The correct sample weight is determined by the estimated sulfur content of the sample as follows:

Sulfur %	Sample Weight (g)
0.001	0.500

25.7.5 The choice of accelerators is left to the discretion of the user, as each furnace will burn differently in accordance with type and amount used. Generally, the more accelerator used, the greater the furnace temperature. Tin metal, iron chip, iron powder, and copper ring have been found to be suitable materials. Porous covers should be used to prevent splattering of the hot flux and damage to the combustion tube. Do not re-use crucibles or covers.

25.7.6 Run a blank determination before each series (of sulfur determinations) using a crucible that contains all the accelerators but no sample.

25.7.7 Place the crucible and sample on the pedestal and lift into position in the combustion tube.

25.7.8 With the oxygen flow at 1 L/min, close stopcock on bottom of titration vessel, and add the HCl to the middle of the bell-shaped portion of the titration vessel. Always fill to the same level.

25.7.8.1 Add one measure of starch solution to the titration vessel. Fill the iodate buret.

25.7.9 Turn the double throw switch on the titrator to the end-point position (down). Slowly rotate the end-point control in a clockwise direction until it has added KIO_3 in the amount to give a solid medium blue color. After the indicator light (for solenoid valve) has stopped blinking, place the switch in the neutral position and fill the KIO_3 buret again. Turn the switch to the titrate position.

25.7.10 Turn on the power of the high-frequency furnace. The temperature will rise in the crucible as indicated by the plate current ammeter on the induction furnace that must indicate a reading of at least 400 mA before complete combustion of sulfur can take place.

25.7.11 As sulfur dioxide is given off, the unit will begin titrating automatically. The titration is finished when the indicator light stops blinking for a period of time, or the iodate in the buret stops falling over a period of time.

25.7.12 Inspect the crucible for a proper burn. A rough, bumpy surface or appearance of non-combustion indicates that the furnace temperature was too low. Sticking of the porous cover to the crucible indicates that the furnace temperature may have been too hot. Both conditions indicate poor sulfur recovery and may be helped by a slight change in accelerator amounts.

25.8 *Calculation*:

25.8.1 Calculation of Furnace Factor *(F)*

$$F=\frac{R}{(A-B)/(W\times 2)} \tag{20}$$

where:

A = buret reading as % Sulfur (S),
B = buret reading for Blank determination,
R = % Sulfur (by Sodium Carbonate Fusion Method) of the reference material, and
W = weight of sample, g.

25.8.2 Calculate the percentage of sulfur in the sample by using furnace factor *F.*

$$\%\ S=F\times\frac{A-B}{W\times 2} \tag{21}$$

where:

A = buret reading as % Sulfur (S),
B = buret reading for Blank determination,
F = furnace factor, and
W = weight of sample, g.

25.9 *Precision and Bias*:

25.9.1 Nine laboratories cooperated in testing on three samples of high-calcium limestone to obtain the precision data for % sulfur given in 25.9.2 and 25.9.3.

25.9.2 The repeatability (Practice E 691 [r]) was found to be 0.0070 % sulfur.

25.9.3 The reproducibility (Practice E 691 [R]) was found to be 0.0120 % sulfur.

25.9.4 The user is cautioned to verify by the use of reference materials, if available, that the bias of this test method is adequate for the contemplated use.

26. Phosphorus by Molybdovanadate Method

26.1 *Scope*—This method is suitable for the determination of small amounts of phosphorous in lime and limestone samples. The procedure is based on the fact that phosphorous in its ortho form will combine with ammonium molybdovanadate to yield a yellow color that can be measured spectrophotometrically. Total phosphate is determined after a strong oxidation decomposition with perchloric acid.

26.2 *Summary of Test Method*—The sample is decomposed with perchloric acid, the solution filtered, SiO_2 expelled, and the insoluble residue fused with Na_2CO_3. Ammonium molybdovanadate which is then added reacts with the phosphorous in solution to form the heteropoly phosphomolybdovanadate complex. The absorbance of the solution is measured with a photometer at 430 nm and compared against standards similarly treated.

26.3 *Special Solutions*:

26.3.1 *Phosphorous Standard Stock Solution* (0.5 mg P/mL)—Weigh 1.0983 g of potassium dihyrogen phosphate, KH_2PO_4, into a 250-mL beaker and dampen with about 5 to 10 mL of water. Add 10 mL HNO_3 and 25 mL $HClO_4$(See Note 29), heat on a hot plate, and evaporate to heavy fumes of $HClO_4$. Cover and boil until the solution is colorless or slightly yellow (10 to 15 min). Cool the solution, transfer to a 500-mL volumetric flask, dilute to volume, and mix. Store in a borosilicate or plastic bottle with a screw cap.

26.3.2 *Phosphorous Working Standard* (0.05 mg P/mL)—Dilute 50 mL of stock solution 26.3.1 to 500 mL with distilled water. Store in a Pyrex or plastic bottle with screw cap.

26.3.3 *Ammonium Molybdovanadate Solution*:

26.3.3.1 Dissolve 1.25 g of ammonium metavanadate in 400 mL of 1 + 1 nitric acid in a 1 L volumetric flask.

26.3.3.2 Dissolve 50 g of ammonium molybdate in 400 mL of distilled water.

26.3.3.3 Pour solution from 26.3.4.2 into solution 26.3.4.1, mix, and dilute to volume with distilled water.

26.4 *Preparation of Standard Curve*:

26.4.1 To each of seven individual 50 mL volumetric flasks, add with a buret 0, 1, 2, 4, 6, 10, and 14 mL of phosphorous working standard solution corresponding to 0, 0.05, 0.10, 0.20, 0.30, 0.50, and 0.70 mg of phosphorous, respectively.

26.4.2 Add 1 mL of perchloric acid and dilute to about 20 mL with water. Add 10 mL of the molybdovanadate solution, swirling the contents of the flask during the addition. Dilute to volume with distilled water, mix well, and allow to stand for 10 min. The prepared standard solutions will contain 0 (blank), 1.0, 2.0, 4.0, 6.0, 10.0, and 14.0 micrograms (µg) P/mL.

26.4.3 Determine the absorbance of each standard solution in the spectrophotometer at a wavelength of 430 nm using the blank standard as the reference solution. Prepare a calibration curve by plotting absorbance versus concentration of phosphorous in µg/mL.

26.5 *Procedure*:

26.5.1 Weigh 5.0 g of prepared sample into a 250-mL beaker and dampen with about 5 to 10 mL of water. Add 10 mL HNO_3 and 25 mL $HClO_4$(See Note 29), heat on hot plate, and evaporate to heavy fumes of $HClO_4$. Cover and boil until solution is colorless or slightly yellow (10 to 15 min). Cool slightly and add 50 mL H_2O. Filter through retentive filter paper and wash thoroughly with hot H_2O (See Note 30). Reserve filtrate.

NOTE 29—If a special perchloric acid hood is not available, the use of perchloric may be omitted. Instead, add 10 mL HNO_3 and evaporate to dryness. Take up salts with 5 mL HCl, break up residue, and again evaporate to dryness. Boil up with 1 mL of HNO_3 and 20 mL of water, and filter, etc.

NOTE 30—The filter paper and silica residue must be washed free of perchlorate salts to prevent small explosions from occurring in the crucible when the filter paper is charred and ignited.

26.5.2 Place paper and contents in a platinum crucible and heat gently with a low flame until paper chars. Ignite at a higher temperature until ash is white. Cool, add 2 drops of $H_2SO_4(1 + 1)$ and 10 to 15 mL HF. Evaporate cautiously to dryness and heat in a muffle at 1000 °C for 2 min (See Note 31). Fuse residue with 0.5 g of Na_2CO_3, cool, add 5 mL H_2O and 1 mL $HClO_4$ and warm to dissolve. Combine the filtrates and transfer to a 100 mL volumetric flask. Dilute to volume and mix.

NOTE 31—The treatment of the residue with HF and H_2SO_4 may be omitted if the SiO_2 in the sample is low, <3 %.

26.5.3 Pipet 25 mL of solution into a 50 mL-volumetric flask and add 10 mL ammonium molydovanadate solution, dilute to volume and mix well. Allow to stand 30 min and measure the absorbance at 430 nm using the blank standard solution in the reference cell. Compare against a set of standards similarly treated.

26.6 *Calculation*:

26.6.1 Calculate % P_2O_5 as follows:

$$\% \; P_2O_5 = \frac{C \times D \times 2.2913}{W \times 10^4} \qquad (22)$$

where:

C = concentration of P in sample solution, µg/mL determined from calibration curve,
D = dilution factor, and
W = g of sample.

26.7 *Precision and Bias*:

26.7.1 The number of laboratories, materials, and determinations in this study does not meet the minimum requirements for determining precision prescribed in Practice E 691:

	Test Methods C 25	Practice E 691 Minimum
Laboratories	3	6
Materials	5	4
Determinations	4	2

26.7.2 The following precision statements are provisional. Within five years, additional data will be obtained and processed which does meet the requirements of Practice E 691.

26.7.2.1 Precision, characterized by repeatability, *Sr* and *r,* and reproducibility, *SR* and *R,* has been determined for the following test method and materials to be:

Precision Statement for Test Method:	% P_2O_5			Color	
Material	Average	*Sr*	*SR*	*r*	*R*
S-1145	0.0031	0.0010	0.0017	0.0029	0.0046
S-1142	0.0091	0.0019	0.0031	0.0053	0.0087
S-1141	0.0221	0.0014	0.0043	0.0040	0.0122
S-1144	0.0657	0.0063	0.0144	0.0175	0.0404
S-1143	0.1353	0.0077	0.0147	0.0215	0.0413

27. Manganese by the Periodate (Photometric) Method

27.1 *Scope*—In this method, periodate is the oxidizing agent used to convert manganous into permanganate ion whose color can then be read in a photometer at a wavelength of 545 nm. This method is capable of determining small amounts of Mn as low as 10 ppm.

27.2 *Summary of Test Method*—The same sample solution prepared in the determinations of phosphorous by molybdovanadate (See 26.5.1 to 26.5.2) can be used for the determination of manganese by periodate. The acid solution is oxidized to permanganate by potassium periodate. Photometric measurement is made at 545 nm.

27.3 *Special Solutions*:

27.3.1 *Manganese Standard Solution* (1 mL to 50 µg Mn)—Dissolve 0.0500 g pure manganese (Mn) metal in 20 mL $H_2SO_4(1 + 9)$ and dilute to 1 L with water.

27.3.2 *Nitric-Phosphoric Acid Mixture*—Add 800 mL HNO_3 and 200 mL H_3PO_4 to 400 mL of H_2O and dilute to 2 L.

27.4 *Preparation of Calibration Curve*:

27.4.1 Transfer 0, 1, 2, 3, 5 and 10 mL of manganese standard solution to six 150 mL beakers, respectively. Add 25 mL of acid mixture to each and heat but do not boil. While heating, add potassium periodate (KIO_3) crystals, a few milligrams at a time (about 0.3 g total), until the permanganic color is fully developed. Keep solution near boiling for 10 min after color develops; the total heating period should last about 30 min.

27.4.2 Allow to cool, transfer to a 50-mL volumetric flask, dilute to volume and mix. Read absorbance at 545 nm using the "0" standard (blank) in the reference cell and construct a calibration curve by plotting absorbance versus concentration of Mn in µg/mL.

27.5 *Procedure*:

27.5.1 Weigh 2.0 g of prepared sample into a 250-mL beaker and dampen with about 5 to 10 mL of water. Add 10 mL HNO_3 and 20 mL $HClO_4$(See Note 32), heat on hot plate, and evaporate to heavy fumes of $HClO_4$. Cover and boil until solution is colorless or slightly yellow (10 to 15 min). Cool slightly and add 50 mL H_2O. Filter through retentive filter paper and wash thoroughly with hot H_2O (See Note 30). Reserve filtrate.

NOTE 32—If a special perchloric hood is not available, omit the use of $HClO_4$. Instead, evaporate to dryness twice with nitric acid and finally boil with 10 mL HNO_3 and 50 mL H_2O.

27.5.2 Transfer paper and contents to a platinum crucible and heat until paper chars. Ignite at a higher temperature until ash is white. Cool, expel SiO_2 with HF and H_2SO_4, evaporate to dryness (See Note 31) and fuse residue with Na_2CO_3. Cool, add 10 mL H_2O and 2 mL HNO_3 and warm to dissolve. Combine solution with filtrate reserved in 27.5.1 and transfer to a 100 mL volumetric flask. Dilute to volume and mix.

27.5.3 Transfer an aliquot containing <500 µg Mn to a 150 mL beaker. Add 25 mL of acid mixture, heat to near boiling and develop the permanganate color by small additions of KIO_3 as directed in 27.4.1. Cool the solution, transfer to a 50 mL volumetric flask, dilute to volume and mix.

27.5.4 Record the absorbance at 545 nm using the blank standard solution in reference cell as in preparation of standard curve, and compare against a set of standards similarly treated.

27.6 *Calculation*:

27.6.1 Calculate the percent Mn as follows:

$$\% \text{ Mn} = \frac{C \times D}{W \times 10^4} \tag{23}$$

where:

C = concentration of Mn in sample solution µg/mL determined from calibration curve,

D = dilution factor, and

W = g of sample.

27.7 *Precision and Bias*:

27.7.1 The number of laboratories, materials, and determinations in this study does not meet the minimum requirements for determining precision prescribed in Practice E 691:

	Test Methods C 25	Practice E 691 Minimum
Laboratories	4	6
Materials	5	4
Determinations	4	2

27.7.2 The following precision statements are provisional. Within five years, additional data will be obtained and processed which does meet the requirements of Practice E 691.

27.7.2.1 Precision, characterized by repeatability, *Sr* and *r,* and reproducibility, *SR* and *R,* has been determined for the following test method and materials to be:

Precision Statement for Test Method:		% Mn		Color	
Material	Average	*Sr*	*SR*	*r*	*R*
S-1145	0.0011	0.0004	0.0005	0.0011	0.0014
S-1143	0.0025	0.0005	0.0007	0.0014	0.0020
S-1142	0.0147	0.0010	0.0010	0.0028	0.0028
S-1141	0.0271	0.0012	0.0024	0.0034	0.0066
S-1144	0.1096	0.0072	0.0108	0.0200	0.0304

28. Available Lime Index

28.1 *Scope*—The available lime index of high-calcium quicklime and hydrated lime designates those constituents that enter into the reaction under the conditions of this specified test method, otherwise known as the "rapid sugar test method." The interpretation of results obtained by this test method shall be restricted by this definition.

28.2 *Summary of Test Method*—The sample is slaked and dispersed with water. The lime is solubilized by reaction with sugar to form calcium sucrate which is then determined by titration against standard acid using phenolphthalein as the indicator.

28.3 *Special Solutions*:

28.3.1 *Hydrochloric Acid, Standard* (1.000 *N*)—Prepare a solution by diluting 83 mL of HCl to 1 L with CO_2-free water. Standardization of sock solution should be performed on a regular basis at a minimum of once per month. For precision and bias information on standardization with Na_2CO_3 or Tris-(Hydroxymethyl) Amino-Methane see Practice E 200.

28.3.2 *Standardization of HCl with* Na_2CO_3:

28.3.2.1 Transfer approximately 20 g of primary standard anhydrous sodium carbonate (Na_2CO_3) to a platinum dish or crucible, and dry at 250 °C for 4 h. Cool in a desiccator.

28.3.2.2 Weigh accurately 4.4 g to the nearest 0.1 mg of the dried Na_2CO_3 and transfer to a 500-mL flask. Add 50 mL of CO_2-free water, swirl to dissolve the carbonate, and add two drops of a 0.1 % solution of methyl red in alcohol. Titrate with the HCl solution to the first appearance of a red color, and boil the solution carefully, until the color is discharged (See Note 29). Cool to room temperature, and continue the titration, alternating the addition of HCl solution and the boiling and cooling to the first appearance of a faint red color that is not discharged on further heating.

28.3.2.3 *Calculation*—Calculate normality as follows:

$$A = (B \times 18.87)/C \tag{24}$$

where:

A = normality of the HCl solution,

B = Na_2CO_3 used, g, and

C = HCl solution consumed, mL.

NOTE 33—This titration can also be performed potentiometrically with the aid of a glass electrode and a calomel electrode.

28.3.3 *Standardization of HCl with TRIS (THAM)—[Tris-(Hydroxymethyl) Amino-Methane]*:

28.3.3.1 Transfer an appropriate amount of primary standard tris-(hydroxymethyl) amino-methane to suitable dish or crucible and dry in a vacuum at 70 °C for 24 h (refer to Practice E 200). As an alternative, Tris can also be dried at 105 °C (± 5 °C) for 2 h in a regular laboratory drying oven. Cool in a desiccator to room temperature.

28.3.3.2 *Preparation of Mixed Indicator*—Mix 100 mg of Bromocresol Green with 2 mL 0.1 *N* NaOH and dilute with CO_2-free water to 100 mL. Dissolve 100 mg of Alizarin Red S in 100 mL CO_2-free H_2O. Mix equal portions of Bromocresol Green and Alizarin Red S solutions to form mixed indicator.

28.3.3.3 Weigh approximately 8 g of TRIS to the nearest 0.1 mg and dissolve in 50 mL of CO_2-free water. Add 6 drops of mixed indicator (See Note 30) and titrate to a bright yellow end-point with acid.

NOTE 34—This titration can also be performed potentiometrically using a suitable pH meter to a pH of 4.70.

28.3.3.4 *Calculation*—Calculate normality as follows:

$$A = B/(0.121136 \times C) \tag{25}$$

where:

A = normality of the HCl solution,
B = Tris-(Hydroxymethyl) Amino-Methane used, g,
C = HCl solution consumed, mL.

28.3.4 *Phenolphthalein Indicator (4 %)*—Dissolve 4 g of dry phenolphthalein in 100 mL of 95 % alcohol.

28.3.5 *Sucrose Solution*—(40 g of pure cane sugar in solid form may be used per sample in place of a sugar solution.) Prepare a 40 % solution (w/v) using pure cane sugar and CO_2-free water in a large beaker and stir until dissolved. Add several drops of phenolphthalein indicator solution. Add 0.1 N NaOH solution dropwise with stirring until a faint pink color persists. Stock solution of sugar may be made for convenience; however, it should not be stored for more than two days. As an alternative the acidity of each lot of sugar can be determined, and a correction applied to the titration.

28.4 *Procedure*:

28.4.1 *Procedure for Quicklime*:

28.4.1.1 The sample as received at the laboratory shall be thoroughly mixed and a representative sample with minimum weight of 100 g shall be taken and pulverized to pass a No. 50 sieve for analysis. Weigh rapidly 2.804 g of the finely pulverized sample, brush carefully into a 500-mL Erlenmeyer flask containing about 40 mL of CO_2-free water (See Note 35), and immediately stopper the flask.

NOTE 35—Water should not be added to the sample because, especially with quicklime, there is a tendency for the material to cake and form lumps difficult to completely dissolve in the sugar solution later. On the other hand, if the lime is added to a little water, a better dispersion of the fine particles occurs, leading to a more rapid dissolution of the sample. It is possible that in the case of quicklime, some slaking action occurs to facilitate the dispersion and solution.

28.4.1.2 Remove the stopper. Place the flask on a hot plate and immediately add 50 mL of boiling CO_2-free water to the flask. Swirl the flask and boil actively 1 min for complete slaking. Remove from the hot plate, stopper the flask loosely, and place in a cold-water bath to cool to room temperature.

28.4.1.3 Add 100 mL of the neutralized sugar solution (or approximately 40 g of pure cane sugar). Stopper the flask, swirl, and let stand for 15 min to react. (Reaction time should not be less than 10 min nor more than 20 min.) Swirl at 5-min intervals during reaction. Remove stopper, add 4 to 5 drops of 4 % phenolphthalein indicator solution and wash down the stopper and sides of the flask with CO_2-free water.

28.4.1.4 When titrating (See Note 36), first add about 90 % of the acid requirement from a 100-mL buret. Finish the titration, more carefully at approximately one drop per second, to the first disappearance of the pink color, which persists for 3 s. Note the endpoint and ignore any further return of color.

NOTE 36—A mechanical stirrer may be used during the titration if desired. Put a clean magnetic stirrer bar into the flask and place the flask on the magnetic stirrer. Adjust to stir as rapidly as possible without incurring any loss by spattering. Unless the operator is familiar with previous analyses of the lime under test, and in cases where the available lime content varies to extremes, it is good practice to run a preliminary test by slow titration to determine the proper amount of acid required to neutralize the sample.

28.4.2 *Procedure for Hydrated Lime*—The procedure for determining $Ca(OH)_2$ is the same as for CaO with the exception that cold CO_2-free water is used and the boiling and cooling steps are omitted.

28.5 *Calculation*:

28.5.1 Calculate for CaO as follows:

$$\text{Available lime (CaO), } \% = N \times V \times 2.804/W \tag{26}$$

where:

N = normality of acid solution,
V = standard HCl used (1.000 N), mL,
W = weight of sample, g, and
2.804 = CaO, g, equivalent to 1 mL of standard acid × 100, or 1 mL of standard HCl = 1 % CaO if exactly 2.804 g of sample is used.

28.5.2 Calculate for $Ca(OH)_2$ as follows:

$$\text{Available lime } [Ca(OH)_2], \% = N \times V \times 3.704/W \tag{27}$$

where:

N = normality of acid solution,
V = standard HCl (1.000 N), mL,
W = weight of sample, g, and
,mdit> 3.704 = $Ca(OH)_2$, g, equivalent to 1 mL of standard acid × 100 or 1 mL of standard HCl = 1.32 % $Ca(OH)_2$ when exactly 2.804 g of sample is used.

28.6 *Precision and Bias*:

28.6.1 Twenty-four laboratories cooperated in the testing of three high calcium quicklimes and one high calcium hydrated lime thereby obtaining the repeatability (*r*) and reproducibility (*R*) (Practice E 691) data contained in Table 4.

28.6.2 The user is cautioned that the repeatability and reproducibility are considered adequate for the purposes of the test method. However, higher levels of MgO and nonreactive CaO increase the value of the repeatability (within lab) slightly and the reproducibility value (between labs) noticeably.

28.6.3 Due to the lack of a recognized industry standard, the bias of this test method has not been determined.

29. Free Silica

29.1 *Scope*—Free silica is usually present in the acid-insoluble residue of lime and limestone samples. This method is applicable to the determination of free silica when it exceeds 0.05 %.

TABLE 4 Precision Data (Results in % Available CaO)

Material	Average	*r*	*R*
Hydrated lime	71.967	0.367	0.963
Magnesian quicklime	88.495	0.479	1.784
Shaft kiln quicklime	94.393	0.398	1.405
Rotary kiln quicklime	94.438	0.337	1.092

29.2 *Summary of Test Method*—After dissolution of a large sample of lime or limestone, the insoluble matter including SiO_2 is separated, ashed, and the oxides fused with pyrosulfate. The silicic acid liberated from the clay minerals in the insoluble matter is dissolved in a hot solution of sodium hydroxide but the free silica is unaffected.

29.3 *Procedure*:

29.3.1 Weigh 5.0 g of the prepared sample in a 400-mL beaker, add 25 mL of HCl (1 + 1), and heat to a boil. Using a retentive paper, filter the insoluble matter including SiO_2 and wash several times with hot water. Discard the filtrate.

29.3.2 Place the paper containing the insoluble matter in a platinum crucible and char the paper without inflaming at low heat. Increase the heat to burn off the carbon, but do not exceed 600 ± 50 °C. Cool, add approximately 10 g of fused and powdered $KHSO_4$ or $K_2S_2O_7$ in the platinum crucible, and blend thoroughly with a small spatula. Fuse thoroughly over a gas burner, first by gradual heating to prevent loss of SO_3. When the fusion becomes quietly molten, finish the fusion at a dull red heat not over 800 °C.

NOTE 37—Do not continue heating to a point where salts begin to freeze on top of the melt and on the sides of the crucible because of the difficulty of subsequent solution.

29.3.3 Cool the crucible and its contents and dissolve the melt by heating with 150 to 200 mL of water in a 400-mL beaker. To the warm solution, cautiously add approximately 12 g of NaOH pellets a few at a time to dissolve the precipitated silicic acid (See Note 37). Digest on a hot plate for 30 min at 80 to 90 °C.

NOTE 38—Free silica is not transformed to silicic acid by the fusion and is not affected by the caustic treatment.

29.3.4 Filter quickly, using a retentive paper; thoroughly scrub and wash the beaker with hot water. Wash the filter paper and its contents ten times with hot water; five times with hot dilute HCl (1 + 1) to dissolve iron and other contaminants of the free silica, and finally five times with hot water or until free of acid. Transfer the paper and residue to a tared platinum crucible, ignite at 1000 °C to constant weight, cool in a dessicator, and weigh as free silica.

29.3.5 To the ignited and weighed residue add 2 drops of $H_2SO_4(1 + 1)$ and approximately 10 mL of HF, evaporate to dryness, ignite and weigh (See Note 34). If the mass of the residue exceeds 0.001 g, the determination may have been improperly accomplished. Replicate determinations should then be made to verify the validity of the results, or the residue examined by X-ray diffraction to determine whether refractory or highly insoluble minerals are present.

NOTE 39—Occasionally the free silica is contaminated by compounds not decomposed during fusion or dissolved in the subsequent treatments. The residue then is treated with HF and sulfuric and SiO_2 expelled.

29.4 *Calculation*—Calculate the percent free silica as follows:

$$\text{Free silica, }\% = (A - B)/W \times 100 \tag{28}$$

where:

A = crucible + insoluble residue, g,
B = crucible minus SiO_2, g, and
W = sample, g.

29.5 *Precision and Bias*—The precision and bias of this test method have not been determined.

30. Unhydrated Oxides Calculated on As-Received Basis

30.1 *Scope*—From the analytical determinations made in accordance with the preceding sections, it is possible to calculate combined water, $CaCO_3$, and $CaSO_4$ in samples of lime and hydrated lime. Unhydrated oxides of MgO in hydrated lime can also be calculated.

30.2 *Summary of Test Method*—Determine the percent of free water, LOI, CO_2, SO_3, CaO, and MgO in accordance with the preceding sections. Calculate combined H_2O, calcium carbonate, calcium sulfate, and unhydrated magnesium oxide using the following procedures.

30.3 *Procedure*:

30.3.1 Calculate percentage of combined water in quicklime from the loss on ignition and CO_2 determinations, as follows:

$$\text{Combined } H_2O,\ \% = \%\ \text{LOI} - \%(CO_2 + \text{FM}) \tag{29}$$

30.3.2 Calculate the percentage of combined water in hydrated lime from the LOI, CO_2, and free moisture (FM) determinations as follows:

$$\text{Combined } H_2O,\ \% = \%\ \text{LOI} - \%(CO_2 + \text{FM}) \tag{30}$$

30.3.3 Calculate the percent unhydrated oxides on the as-received basis as follows (See Notes 40-42):

NOTE 40—The calculations involved in determining the percentage of unhydrated oxides on the as-received basis are illustrated in Table 5.

NOTE 41—This method for calculating the percentage of hydrated oxides is intended primarily for use with Type S hydrated lime.

NOTE 42—It is recognized that the results from this method of calculation may not be in strict accord with the actual composition of the material. Experience indicates, however, that these results provide an index to the performance of the material in practice. The value obtained by this calculation shall be reported to the nearest 0.5 %.

30.3.3.1 Calculate the CaO equivalents of the CO_2 and SO_3 as follows:

$$CO_2 \times 1.275 = \text{equivalent CaO } (A) \text{ as } CaCO_3 \tag{31}$$

$$SO_3 \times 0.700 = \text{equivalent CaO} (B) \text{ as } CaSO_4 \tag{32}$$

TABLE 5 Example of Calculation, Unhydrated Oxides

Compound	Values Determined From Chemical Analysis, %	Residual Values	Factors	Calculated Values, %
CO_2	0.40		× 1.275	= equivalent CaO = 0.51
SO_3	0.48		× 0.700	= equivalent CaO = 0.34
CaO	42.79 – (0.51 + 0.34 = 0.85)	= 41.94	× 0.3213	= equivalent H_2O = 13.48
H_2O	25.09 – 13.48	= 11.61	× 2.238	= equivalent MgO = 25.98
MgO	30.68 – 25.98			= unhydrated MgO = 4.70

30.3.3.2 Subtract the sum of these CaO equivalents from the total CaO:

$$\text{Total CaO} - (A+B) = \text{hydrated CaO}(C) \quad (33)$$

30.3.3.3 Calculate the H_2O equivalent of the remaining CaO as follows:

$$\text{Hydrated CaO } (C) \times 0.3213 = \text{equivalent } H_2O \ (D) \text{ as } Ca(OH)_2 \quad (34)$$

30.3.3.4 Subtract this value for H_2O (D) from the combined water as calculated in 30.3.1 and 30.3.2.

$$\text{Combined water} - H_2O \ (D) = \text{equivalent } H_2O \ (E) \text{ as } Mg(OH)_2 \quad (35)$$

30.3.3.5 Calculate the MgO equivalent of the remaining water (E) as follows:

$$H_2O \ (E) \times 2.238 = \text{equivalent MgO } (F) \text{ as } Mg(OH)_2 \quad (36)$$

30.3.3.6 Subtract this MgO equivalent (F) from the total MgO as determined from preceding sections to obtain the percentage of unhydrated MgO on the as-received basis.

$$\text{Total MgO} - \text{MgO equivalent } (F) = \textit{unhydrated MgO} \quad (37)$$

31. Calcium and Magnesium Oxide (Alternative EDTA Titration Method)

31.1 *Scope*—This test method is a rapid EDTA complexometric method for determining calcium and magnesium in lime and limestone products. Ordinarily the EDTA procedure is designed to follow routine separations, that is, single dehydration of silica and a single precipitation with NH_4OH of the combined oxides of iron and aluminum. For expediency, the assays can be run directly without prior separation of the combined oxides of iron and aluminum by using the complexing action of EDTA at appropriate pH levels.

31.2 *Summary of Test Method*:

31.2.1 In this test method, calcium and magnesium are determined by EDTA titration after separation of silica and the NH_4OH group during a routine analysis of lime and limestone. The assays may also be made after a direct HCl decomposition followed by removal of the silica and insoluble.

31.2.2 If interfering elements are present in large enough quantities to cause problems, the interferences may be suppressed by the addition of complexing or masking agents such as triethanolamine or cyanide.

31.2.3 For the determination of calcium, the solution is adjusted to a pH of 12 to 12.5 with KOH solution and titrated with EDTA to a blue end point using hydroxy naphthol blue as the indicator. Both CaO and MgO are then titrated from a solution buffered to pH 10 with $NH_3 \cdot NH_4Cl$ using Calmagite as the indicator. MgO is calculated by subtracting the EDTA equivalent to CaO present from the EDTA equivalent to CaO + MgO.

31.3 *Reagents*:

31.3.1 *EDTA Solution* (0.4 %)—Dissolve 4 g of disodium dihydrogen ethylenediamine tetraacetic acid in water and dilute to 1 L.

31.3.2 *Potassium Hydroxide, Standard Solution* (1 *N*)—Dissolve 56 g of KOH in 1 L of distilled water.

31.3.3 *Ammonia Buffer* (pH 10.5)—Dissolve 67.5 g of NH_4Cl in 300 mL of distilled water, add 570 mL of NH_4OH, and dilute to 1 L.

31.3.4 *Hydroxy Naphthol Blue* (calcium indicator)—Disodium salt of 1-(2-naphthol azo-3,6 disulfonic acid)2 naphthol-4-sulfonic acid on suitable carrier.

31.3.5 *Calmagite* (magnesium + calcium indicator)—1-(hydroxyl-4-methyl-2 phenylazo)-2 naphthol-4 sulfonic acid on a suitable carrier.

NOTE 43—Both the hydroxy naphthol blue and Calmagite indicators are manufactured by Mallinckrodt Chemical Works, St. Louis, MO. Each indicator is a diluted mixture of dye plus an inert carrier.

31.3.6 *Hydrochloric Acid* (1 + 1).

31.3.7 *Hydrochloric Acid* (1 + 9).

31.3.8 *Triethanolamine* (1 + 2).

31.3.9 *Potassium Cyanide Solution* (20 g/L)—Dissolve 2 g of KCN in 100 mL of water.

31.3.10 *Calcium Standard Solution* (1.00 mg CaO/mL)—Weigh 1.785 g of $CaCO_3$, primary standard grade. Dissolve in HCl (1 + 9) and dilute to 1 L with distilled water.

31.3.11 *Magnesium Standard Solution* (1.00 mg MgO/mL)—Dissolve 0.603 g of magnesium metal turnings in HCl and dilute to 1 L with distilled water.

31.4 *Apparatus*:

31.4.1 *Magnetic Stirrer* with light.

31.4.2 *Stirring Bar,* TFE-fluorocarbon-covered.

31.5 *Standardization*:

31.5.1 *Calcium*—Pipet 10 mL of standard CaO solution into an Erlenmeyer flask and add 100 mL of distilled water. To prevent precipitation of calcium, add about 10 mL of EDTA titrating solution. Adjust to pH 12 to 12.5 with about 15 mL of 1 *N* KOH solution and stir. Add 0.2 to 0.3 g of hydroxy naphthol blue indicator (See Note 44) and complete titration to a clear blue end point (See Note 45). Titrate three or more aliquots and use the average to calculate the titer of the CaO solution.

$$\text{CaO titer, mg/mL} = 10 \text{ mg CaO standard/mL EDTA titration} \quad (38)$$

NOTE 44—The amount of indicator is usually a matter of individual preference, but if Mallinckrodt reagents are used, the recommended dosages are considered the proper amounts to add for easy end point detection.

NOTE 45—The use of a magnetic stirrer with light may be very helpful in detecting the color change. The end point is the first definite blue color that remains stable for at least 30 s.

31.5.2 *Magnesium*—Pipet 10 mL of the 1.00-mg/mL standard MgO solution into an Erlenmeyer flask and add 100 mL of distilled water. Adjust to pH 10 with 10 mL of the ammonium chloride-ammonium hydroxide buffer solution, and add 0.3 to 0.4 g of Calmagite indicator (See Note 44). Titrate with disodium EDTA, noting the color change from a red to deep blue end point (See Note 45). Titrate three or more aliquots and use the average to calculate the magnesium titer.

$$\text{MgO titer, mg/mL} = 10 \text{ mg MgO standard/mL EDTA titration} \quad (39)$$

31.6 *Procedure*:

31.6.1 If using limestone, dry the sample at 110 °C to constant weight and cool to room temperature.

31.6.2 Weigh 0.5 g of the dry sample into a 250-mL beaker, add 10 mL of HCl (1 + 1), and carefully evaporate to dryness on hot plate. Dissolve residue in 25 mL of HCl (1 + 9), dilute to about 100 mL with water, and digest at low heat for 15 min. Cool, transfer to a 250-mL volumetric flask, dilute to volume, mix, and let settle or filter using a medium textured paper.

31.6.3 Alternatively, if the standard procedure has been used to determine the silica and insoluble and iron and aluminum, the filtrate remaining after the precipitation of the iron and aluminum with ammonia can be used for the Ca and Mg EDTA determination. Continue the analysis as follows: Acidify the filtrate with HCl, transfer to a 250-mL volumetric flask, dilute to volume with distilled water, and mix.

31.6.4 *Calcium Oxide*:

31.6.4.1 Pipet a 20-mL aliquot from the 250-mL volumetric flask and transfer to an Erlenmeyer flask. Dilute to 150 mL with water, adjust the pH to 12 with about 30 mL of 1 *N* KOH solution, and stir.

NOTE 46—Precipitation of calcium hydroxide can be prevented, if necessary, by adding one half to one third of the estimated volume of disodium EDTA solution before the addition of the potassium hydroxide. Presence of a large precipitate can cause loss of sharpness in the end point.

31.6.4.2 If the sample is known to contain significant quantities (>1 %) of iron, manganese, and heavy metals (See Note 47), add 2 to 3 drops of 2 % potassium cyanide solution, or 10 mL of triethanolamine.

NOTE 47—If silica and phosphate or excessive amounts (>5 %) of iron and aluminum are present, they should first be removed by a double ammonia precipitation as in the standard procedure.

Warning—Cyanides should be used with utmost care because they can be very toxic compounds. They should be kept basic and prescribed disposal procedures used. Waste cyanide solutions must not be poured down laboratory sinks. Such solutions can be rendered relatively harmless by making them strongly basic, pH 12 or higher, with sodium hydroxide, adding calcium hypochlorite, and letting the solution stand for 24 h.

31.6.4.3 Add 0.2 to 0.3 g of hydroxy naphthol blue indicator (See Note 39) and titrate as in 36.5.1 to a clear blue end point (See Note 45).

31.6.4.4 *Calculation*:

$$\text{CaO, \%} = \text{CaO titer} \times \text{mL EDTA} \times 1.25/\text{weight of sample, g} \tag{40}$$

31.6.5 *Magnesium Oxide*:

31.6.5.1 Pipet a 20-mL aliquot of the acid solution from the 250-mL volumetric flask and transfer to an Erlenmeyer flask. Dilute with 100 mL of water, add about 20 mL of ammonia buffer to pH 10, and stir.

31.6.5.2 Add 2 to 3 drops of 2 % potassium cyanide solution, or 10 mL of triethanolamine and 1 drop of triethanolamine (**Warning**—See 31.6.4.2) (See Note 47). Add EDTA standard solution equivalent to calcium titration; then add approximately 0.4 g of Calmagite indicator (See Note 39).

TABLE 6 Precision of Calcium Oxide

Sample Tested	CaO Found	Repeatability 1 sigma	Reproducibility 1 sigma
A-1a	53.48	0.31	0.27
A-2b	30.98	0.28	0.41
L-1	53.92	0.29	0.26
P-1a	53.88	0.31	0.28
Pooled	. . .	0.30	0.31

TABLE 7 Precision of Magnesium Oxide

Sample Tested	MgO Found	Repeatability Within Laboratories	Reproducibility Between Laboratories
A-1a	1.58	0.19	0.18
A-2b	21.58	0.24	0.41
L-1	0.58	0.21	0.22
P-1a	1.45	0.23	0.24
Pooled	. . .	0.22	0.28

31.6.5.3 Titrate to a blue end point with the 0.4 % EDTA solution (See Note 45).

31.6.5.4 The titration determines both the calcium and magnesium present in solution. Subtraction of the EDTA titration obtained for calcium from the total titration gives the titration value for magnesium.

31.6.5.5 *Calculation*:

$$\text{mL EDTA solution equivalent to MgO} = (\text{mL EDTA solution used in CaO} + \text{MgO titration}) - \text{mL} - \text{mLEDTA solution used in CaO titration}) \tag{41}$$

$$\text{MgO, \%} = \text{mL EDTA equivalent to MgO} \times \text{MgO EDTA titer} \times 1.25/\text{weight of sample, g} \tag{42}$$

31.7 *Precision and Bias:*[7]

31.7.1 The precision of this test method was tested by ten laboratories using three limestone and one dolomite reference samples. The results shown in Tables 6 and 7 are summarized as follows:

31.7.1.1 The overall precision (1 sigma) between laboratories (reproducibility) for CaO is ± 0.31 absolute units.

31.7.1.2 The overall precision (1 sigma) between laboratories for MgO is ± 0.28 absolute units.

31.7.1.3 The overall precision (1 sigma) within laboratories (repeatability) for CaO is ± 0.24 absolute units.

31.7.1.4 The overall precision (1 sigma) within laboratories for MgO is ± 0.22 absolute units.

32. Total Carbon by the Direct Combustion-Thermal Conductivity Cell Method

32.1 This test method covers the determination of carbon in lime and hydrated lime samples having a carbon concentration in the range from 0.005 to 5 %.

32.2 *Summary of Test Method*—All the carbon in the sample is converted to CO_2 by combustion in a stream of purified oxygen using an induction furnace. Under some conditions, CO is formed and a catalyst furnace is used to convert it to CO_2. The products of combustion are swept into the carbon analyzer where the CO_2 is selectively absorbed by a molecular sieve. The CO_2 is later released and swept by a fresh stream of oxygen past a thermal conductivity cell which senses the amount of CO_2 present. The signal from the sensor is amplified and electronically converted to % C which is displayed on a digital readout panel.

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: C07-1000.

32.3 *Apparatus*:

32.3.1 *Combustion Furnace and Carbon Determinator*—This unit is commercially available.

32.3.2 *Crucibles*—Use crucibles recommended by the manufacturer of the instrument.

32.3.3 *Oxygen Cylinder with Two-Stage Regulator.*

32.3.4 *Purifying Train,* consisting of a sulfuric acid tower, an absorption bulb containing Ascarite and another absorption bulb containing Anhydrone. A flowmeter precedes the induction furnace assembly.

32.3.5 *Catalyst Furnace,* to convert CO to CO_2.

32.3.6 *Combustion Tube with Built-In Jet.*

32.4 *Reagents*:

32.4.1 *Iron Chip Accelerator,* low-carbon.

32.4.2 *Copper-Tin Accelerator.*

32.5 *Preparation of Apparatus*:

32.5.1 Assemble the apparatus. Start the flow of oxygen at 1500 mL/min and the carrier gas flow at the rate recommended by the manufacturer of the apparatus.

32.5.2 Test the furnace and the analyzer to ensure the absence of leaks and make the required electrical power connections. Prepare the induction furnace and analyzer for calibration and sample analysis according to the manufacturer's manual of instructions.

32.5.3 After the instrument has been prepared for calibration, check the CO_2 collection time which should have an 80 to 90-s time duration. The collection time can be checked by operating without a sample. If it is outside of this range, make the necessary adjustment of the collect relay as provided for in the manual of instructions.

32.6 *Calibration*:

32.6.1 Select NIST steel calibration standards containing approximately 0.02 to 1 % carbon (See Note 48).

NOTE 48—The accuracy of this test method is dependent to a large extent on the accuracy of the methods used to certify the carbon concentration in the calibration standards as well as upon their homogeneity. Tests made on NIST steel standards have shown that they are sufficiently homogeneous to permit the use of samples as small as 20 mg.

32.6.2 Condition the analyzer if more than 2 h have elapsed since the last sample was run and determine the blank reading as follows:

32.6.2.1 Load into a crucible 1.5 g of iron chip accelerator and 1 g of tin-coated copper.

32.6.2.2 Proceed as directed in 32.7.1 to 32.7.4.

32.6.2.3 Repeat 32.6.2.1 and 32.6.2.2 a sufficient number of times to establish that low and consistent blank readings are obtained.

32.6.2.4 The normal blank reading should be 0.007 to 0.009. If it is out of this range, determine the cause, correct it, and repeat the steps as directed in 32.6.2.1 through 32.6.2.2.

32.6.3 *Calibration Curve*:

32.6.3.1 The calibration of the analyzer should be done using carbon standards that bracket the percent carbon in the samples estimated from previous tests, using the following guidelines:

% Carbon in Sample	High-Carbon Standard, %	Low-Carbon Standard, %
0.5–1	1.0	0.4
0.2–0.5	0.6	0.2
0.1–0.2	0.2	0.1
0.02–0.1	0.1	0.01

32.6.3.2 Treat each standard as directed in 32.7.1 to 32.7.4.

32.6.3.3 Select two standards, one slightly higher and the other slightly lower than the carbon concentration of the sample.

32.6.3.4 Run the high standard first and observe the reading. The carbon reading should be within ± 1 % of the standard carbon value plus the blank (See Note 49). If it is within this range, proceed to 32.6.3.7.

NOTE 49—For example, with a blank reading of 0.009, a carbon standard which has a standardized value of 0.428 % should read 0.433 to 0.441.

32.6.3.5 If the reading is out of this range, run a duplicate sample.

32.6.3.6 If the second sample has approximately the same value as the first sample, adjust the slope control (See Note 50) to bring the reading to within the tolerance of the standard.

NOTE 50—Not all manufacturers may have this particular feature in their instrument, in which case the manual of instructions supplied with each instrument should be adhered to very closely and the instructions followed.

32.6.3.7 Run a carbon standard that has a carbon value lower than the sample as directed in 32.6.3.1 to 32.6.3.3.

32.6.3.8 The reading should be within +1 % of the carbon value plus the blank (See Note 50).

32.6.3.9 If the reading is within tolerance range, proceed to sample analysis, 32.7.1 to 32.7.4.

32.6.3.10 If the reading is out of the tolerance range, run a duplicate sample. If the second sample has the same out of tolerance value as the first sample, repeat 32.6.3.4 to 32.6.3.9, readjusting the slope control to bring the high standard within the tolerance of the standard.

32.6.3.11 If the standards are still out of line, refer to the manufacturer's manual for instruction, determine the cause, correct it, and repeat the standardization procedure, 32.6.3.2 to 32.6.3.8.

32.7 *Procedure*:

32.7.1 Stabilize the furnace and analyzer as directed in 32.5.1 to 32.5.3.

32.7.2 Weigh duplicate samples to the nearest 1 mg, using the following guidelines:

Carbon Content, %	Sample Weight, g
0 to 0.1	1.000
0.1 to 2	0.500
2 to 5	0.250

32.7.3 Transfer the sample to a combustion crucible, add 1.5 g of iron chip accelerator and 1 g of the tin-coated copper accelerator. Place the crucible on the furnace pedestal, raise the pedestal into position, and lock the system. Start the flow of oxygen at 1500 mL/min, and flush the system for 30 s.

32.7.4 Start the cycle timer which energizes the furnace and starts the programmer, after having set it to provide a combustion cycle of 1 min. Using the variable transformer, manually control the plate current within the range from 350 to 450 mA. When the cycle is complete, remove and discard the crucible. Record the reading.

32.8 *Calculation*—Subtract the value found for the blank in 32.6.2.3 from the reading found in 32.7.4 and record the net reading. Calculate the percentage of carbon as follows:

$$\text{Carbon, \%} = A/B \qquad (43)$$

where:

A = net carbon content, %, and

B = sample mass, g.

32.9 *Precision and Bias*—The precision and bias of this test method have not yet been determined.

33. Calcium Carbonate Equivalent

33.1 *Scope*—The calcium carbonate equivalence (CCE) test is used to determine the neutralizing capability of a calcareous material and to report this value in terms of percent calcium carbonate equivalents (% $CaCO_3$).

33.2 *Significance and Use*—Calcareous materials such as crushed limestone, hydrated lime and pulverized slags (from the production of steel) have been used extensively as soil modifiers or agricultural liming materials. A measure of their neutralizing capability can be determined through the use of this method of test. Not all neutralizing components of acalcareous material may be beneficial, therefore, the chemical analysis is suggested.

33.3 *Apparatus*:

33.3.1 *pH Metre,* conforming to Sections 4 and 5 of Test Method E 70.

33.3.2 *Mechanical Stirrer.*

33.3.3 *Sieve,* No. 60 (250-µm).

33.4 *Reagents*:

33.4.1 *Preparation of Mixed Indicator*—Mix 100 mg of Bromocresol Green with 2 mL of 0.1 *N* NaOH and dilute with CO_2-free water to 100 mL. Dissolve 100 mg of Alizarin Red S in 100 mL CO_2-free H_2O. Mix equal portions of Bromocresol Green and Alizarin Red S solutions to form mixed indicator.

33.4.2 *Hydrochloric Acid,* Standard (1.0 *N*)—Prepare a 1.0 *N* solution of hydrochloric acid (HCl) and standardize. Refer to available lime index test method for procedure on standardization of hydrochloric acid. For further information on preparation and standardization of solutions see Practice E 200.

33.4.3 *Phenolphthalein Indicator Solution* (1 g/100 mL)—Dissolve 1.0 g phenolphthalein in 100 mL of alcohol.

33.4.4 *Sodium Hydroxide Standard Solution* (0.5V AN)—Dissolve 20 g of sodium hydroxide (NaOH) in 150 mL of carbon dioxide—free water. Cool the solution to 25 °C and dilute to 1 L. Prepare free from carbonates and store in a polyethylene bottle provided with a siphon tube and with guard tubes containing soda-lime, or other suitable device, to prevent absorption of carbon dioxide (CO_2) from the air:

33.4.4.1 Standardize against 1.0 *N* hydrochloric acid with three 50 mL aliquots using phenolphthalein solution as indicator. Take the average of the three results as the normality of the Sodium Hydroxide Standard Solution.

$$\text{Normality (NaOH)} = \frac{V_2 N_2}{V_1} \qquad (44)$$

where:

V_1 = volume of NaOH Standard Solution,

V_2 = volume of HCl used to neutralize NaOH, and

N_2 = normality of HCl Standard Solution.

33.5 *Preparation of Sample*:

33.5.1 Weigh and dry the limestone and slag samples to constant weight at a temperature of 110 ± 5 °C. Record the as-received and dry weights in order to calculate moisture content. Use lime samples as received. Grind the sample to pass a No. 60 (250-µm) sieve, mix thoroughly, and store in airtight containers.

33.6 *Procedure*:

33.6.1 *Indicator Titration Method*—Using Table 8 as a guide (See Note 51), weigh the material, to the nearest 0.1 mg, and place into a 500-mL Erlenmeyer flask; add 100 mL of 1.0 *N* HCl and boil gently for 5 min. Cool, and titrate the excess acid with 0.5 *N* NaOH solution using phenolphthalein as indicator. Calculate CCE as described in 33.6.3.

33.6.2 *Potentiometric Titration Method* (applicable to agricultural liming materials containing large amounts of ferrous iron or coloring matter, but not to silicate materials)—Proceed as in 33.6.1 through "Cool. . .". Transfer to a 400-mL beaker and insert glass and calomel electrodes of a pH metre and a

TABLE 8 Recommended Sample Weight[A]

Sample Type	Formula	Purity, %	Theoretical C.C.E.	Sample Weight, g
Magnesium oxide	MgO	97	248.33	1.9
Dolomitic lime	CaO MgO	97	207.69	2.3
Calcium oxide	CaO	97	178.48	2.6
Dolomitic Type N hydrate	Ca(OH)2 MgO	98	175.01	2.6
Dolomitic Type S hydrate	Ca(OH)2 Mg(OH)2	98	151.21	3.0
Calcium hydroxide	Ca(OH)2	98	135.11	3.4
Dolomitic limestone	CaCO3 MgCO3	97	108.56	4.3
Calcium carbonate	CaCO3	97	100.00	4.6

[A] For those materials not listed in Table 8: To determine the amount of 1.0 *N* HCl required for neutralization, a preliminary titration using 2 g of sample (weighed to the nearest 0.1 mg) should be performed to a yellow end point using mixed indicator. Using the following formula, determine the sample weight need for testing and proceed to 33.6.1.

$$Wr\text{, grams (g)} = \frac{Wu * 100}{Vu + 10}$$

where:

Wr = sample weight required for testing, g,

Wu = sample weight used in preliminary titration, g, and

Vu = volume of 1.0N HCl used in preliminary titration, mL.

mechanical stirrer. Stir at a moderate speed to avoid splash. Deliver from a buret the 0.5 *N* NaOH solution rapidly to pH 5, then dropwise until the solution attains pH 7 and remains constant for 1 min while stirring. Report as $CaCO_3$ equivalent as described in 33.6.3.

33.6.3 Calculation of Percent Calcium Carbonate Equivalence:

33.6.3.1 *Dry Basis*:

$$\%\ CaCO_{3(dry)} = \frac{5.0045\ (V_1N_1 - V_2N_2)}{W} \tag{45}$$

where:
V_1 = HCl solution used, mL,
N_1 = normality of HCl solution,
V_2 = NaOH solution required for titration of excess acid, mL,
N_2 = normality of NaOH solution, and
W = sample weight, g.

33.6.3.2 *As-received basis (limestone only)*:

$$\%\ CaCO_{3(as\ received)} = [1 - (A - B/A)] \times \%\ CaCO_{3(dry)} \tag{46}$$

where:
A = as received sample weight from 33.5.1, and
B = dry sample weight from 33.5.1.

34. pH of Alkaline Earth Solutions

34.1 *Scope*—This method covers the electrometric pH analysis of solutions made from a variety of lime, hydrate, and limestone-bearing materials.

34.2 *Summary of Test Method*—In this test method a sample of material is mixed with CO_2-free deionized water so that the pH of the solution is determined electrometrically. To ensure that an accurate measurement of pH is obtained for samples with a pH greater than 11.5, it is critical that all samples and buffer solutions be at 25.0 °C when measured.

34.3 *Special Apparatus*:

34.3.1 *pH Metre*—A commercially available pH metre capable of calibration with a minimum of two different buffers (See Note 51).

NOTE 51—It is necessary that the pH metre be equipped with a combination pH electrode as well as a temperature compensation probe. It is strongly recommended that a combination pH and temperature compensation probe be used.

34.3.2 *Constant Temperature Water Bath*—The water bath should be large enough to hold all samples and buffer solutions necessary to perform this method.

34.4 *Special Solutions*:

34.4.1 *Potassium Chloride Solution (0.2 M)*—Dry reagent grade KCl crystals at 110 °C for 1 h. Dissolve 14.91 g of the dry KCl in CO_2-free deionized water and dilute to 1 L.

34.4.2 *Sodium Hydroxide Solution (0.2 M)*—Dissolve 8.00 g of NaOH in CO_2-free deionized water and dilute to 1 L. Standardize this solution with potassium acid phthalate using phenolphthalein as the indicator.

34.4.3 *Hydroxide-Chloride Buffer Solution (pH 13.0 at 25.0 °C)*—Dilute 25.0 mL of the KCl solution and 66.0 mL of the NaOH solution to 100 mL with CO_2-free deionized water.

34.4.4 *Phenolphthalein Indicator*—Dissolve 4 g of dry phenolphthalein in 100 mL of 95 % alcohol.

34.4.5 Commercially available pH buffer solutions, pH 7 and pH 10.

34.5 *Standardization of Sodium Hydroxide Solution*:

34.5.1 *Initial Standardization*—Transfer 50.0 mL of the sodium hydroxide solution to be standardized to a well rinsed 50-mL Class A buret by means of a pipette. Accurately weigh out 8.0 ± 0.1 g of reagent grade potassium hydrogen phthalate which has been dried in an oven at 110 °C for 1 h. Record the weight to the nearest 0.1 mg, then quantitatively transfer the weighed material into a 400-mL beaker. Add 185 mL of CO_2-free deionized water which is at a temperature of 26.0 ± 2.0 °C. Stir this mixture gently until all of the crystals dissolve. Add five drops of the phenolphthalein indicator solution and proceed to titrate the prepared standard with the sodium hydroxide solution to be standardized. Titrate to an endpoint of light pink which will persist for at least 6 s.

34.5.2 *Calculation of Sodium Hydroxide Normality*—The normality of the sodium hydroxide solution can be calculated from the following equation:

$$\text{Normality of NaOH} = \frac{\text{Wt. of potassium hydrogen phthalate}}{\text{mL of NaOH} \times \text{factor of } 0.204228} \tag{47}$$

This preliminary standardization may reveal the necessity for either dilution with CO_2-free deionized water or the 0.2 molarity specified.

34.5.3 *Correction if Base is "too weak"*—If the molarity (normality) is determined to be too weak, it can be adjusted by the addition of additional sodium hydroxide. An example of this calculation follows. If 1.0 L of 0.1979 N solution needs to be strengthened to 0.2000 N, calculate how many grams of sodium hydroxide need to be added as follows:

$$\begin{gathered} 1.0\ \text{L} \times 0.1979\ \text{M} = 0.1979\ \text{mole} \\ 0.2\ \text{M} - 0.1979\ \text{M} = 0.0021\ \text{M} \\ \text{NaOH} = 39.997\ \text{g/mole} \\ 39.997\ \text{g/mole} \times 0.0021\ \text{mole} = 0.0830\ \text{g needed} \end{gathered} \tag{48}$$

After the addition of additional sodium hydroxide is completed, recheck the standardization as specified in section 34.4.

34.5.4 *Correction if Base is "too strong"*—If the molarity (normality) is determined to be too strong, it can be adjusted by the addition of CO_2-free deionized water. An example of this calculation follows. If 1.0 L of 0.2019 N solution needs to be weakened to 0.2000 N, calculate how many millilitres of CO_2-free deionized water need to be added as follows:

$$\begin{gathered} 1.0\ \text{L} \times 0.2019\ \text{M} = 0.2019\ \text{mole} \\ 0.2019 - 0.200 = 0.0019\ \text{L or } 1.9\ \text{mL of } CO_2- \\ \text{free deionized water needed} \end{gathered} \tag{49}$$

After the addition of additional CO_2-free deionized water is completed, recheck the standardization as specified in section 34.5.

34.6 *Calibration of pH Metre*—Due to the wide variety of commercially available pH equipment, a detailed calibration procedure cannot be incorporated into this test method. Follow the manufacturer's instructions for calibration of your particular equipment.

34.6.1 Using the appropriate combination of the commercially available pH 7 and pH 10.0 buffers, and the Hydroxide-Chloride buffer (pH 13.0), choose the pair of buffers which best brackets the pH of the sample being tested. Standardize your pH metre in accordance with the manufacturer's instructions. For samples with pH less than 11.5, the temperature of the samples and buffers should be kept at 25.0 ± 3.0 °C (See Note 53).

NOTE 52—For alkaline solutions in this pH range the temperature does not cause errors to the extent that it does with samples with a pH in excess of 11.5, therefore the temperature is not as critical.

For samples with a pH greater than 11.5, it is imperative that all solutions be at 25.0 ± 0.1 °C while they are being measured. If all buffers and test solutions are not within this range, due to the high pH being measured, large errors in the measured pH will occur. This can easily be accomplished by the use of a constant temperature water bath (See Note 54).

NOTE 53—In strongly alkaline solutions, especially above pH 12, the concentration of hydroxide ions is so high that the small amount of hydrogen ions produced by the ionization of water is sufficient to change the pH appreciably with temperature.

34.7 *Procedure—Materials with pH Less than 11.5*:

34.7.1 Weigh 10.0 g of the prepared sample and record the weight to the nearest 0.1 mg. Quantitatively transfer the weighed material into a 250-mL Erlenmeyer flask containing 200 mL of CO_2-free deionized water. Add a magnetic stir bar, immediately stopper the flask with a rubber stopper, and stir for 30 min.

34.7.2 Let the solution stand for at least 30 min to allow the suspended material to settle out from the suspension, as well as to allow the sample temperature to stabilize at 25.0 ± 3.0 °C. A constant temperature water bath may be necessary to obtain the desired temperature range.

34.7.3 Once the temperature of the sample is stabilized at 25.0 ± 3.0 °C, using a 50-mL transfer pipette, transfer 50 mL of the settle solution to a 100-mL beaker containing a magnetic stir bar.

34.7.4 Slowly stir the sample solution using a magnetic stirrer. Using a previously standardized pH metre, standardized in accordance with section 34.6, quickly measure the pH of the sample. Report the pH to four significant figures.

34.8 *Procedure—Materials with pH of 11.5 and greater*:

34.8.1 Weigh 10.0 g of the prepared sample and record the weight to the nearest 0.1 mg. Quantitatively transfer the weighed material into a 250-mL Erlenmeyer flask containing 200 mL of CO_2-free deionized water. Add a magnetic stir bar, immediately stopper the flask with a rubber stopper, and stir for 30 min.

34.8.2 Place the sample solution into a constant temperature water bath set at 25.0 °C. Let the solution stand for at least 30 min to allow the suspended material to settle out from the suspension as well as to allow the sample temperature to stabilize at 25.0 ± 0.1 °C.

34.8.3 Once the temperature of the sample is stabilized at 25.0 ± 0.1 °C, using a 50-mL transfer pipette, transfer 50 mL of the settled solution to a 100-mL beaker containing a magnetic stir bar.

34.8.4 Slowly stir the sample solution using a magnetic stirrer. Using a previously standardized pH metre, standardized in accordance with section 34.6, quickly measure the pH of the sample solution (See Note 53). It is imperative that the temperature of the test solution remain at 25.0 ± 0.1 °C during the pH measurement. If needed, the pH measurement should be carried out in a constant temperature water bath. Report the pH to four significant figures.

34.9 *Precision and Bias*:

34.9.1 The number of laboratories, materials, and determinations in this study does meet the minimum requirements for determinating precision prescribed in Practice E 691:

	Test Methods C 25	Practice E 691 Minimum
Laboratories	7	6
Materials	12	4
Determinations:	3	2

34.9.2 *Precision Statement for Test Method: pH*—Precision, characterized by repeatability, *Sr* and *r,* and reproducibility, *SR* and *R,* has been determined for the following materials to be:

Materials	Average	*Sr*	*SR*	*r*	*R*
Sample A kiln dust	12.3817	0.0069	0.2791	0.0194	0.7814
Sample B waste lime	12.2998	0.0297	0.4004	0.0831	1.1210
Sample C dolo hydrate	12.4073	0.0123	0.2408	0.0345	0.6741
Sample D dolo lime	12.3942	0.0177	0.2785	0.0495	0.7799
Sample E –325 stone	11.2199	0.0274	0.3355	0.0766	0.9393
Sample F cyclone dust	12.4090	0.0164	0.2336	0.0459	0.6541
Sample G bottom ash	12.1948	0.0120	0.4049	0.0336	1.1338
Sample H fly ash	9.6776	0.0557	0.3821	0.1559	1.0699
Sample I fly ash	11.3193	0.0143	0.2191	0.0402	0.6136
Sample J hydrate	12.4111	0.0244	0.2994	0.0684	0.8384
Sample K h. hyd. lime	12.5477	0.0069	0.1875	0.0193	0.5249
Sample L quicklime	12.4331	0.0260	0.1767	0.0728	0.4949

35. Total Carbon and Sulfur by the Combustion/Infrared Detection Method

35.1 *Scope*:

35.1.1 This test method is for the determination of carbon or sulfur, or both, in lime and limestone. This test method has also been adapted for use with kiln flue dusts. This test method covers the determination of carbon and sulfur in an acceptable concentration range from 0.01 to 13 % carbon and from 0.005 to 3 % sulfur.

35.1.2 Hydrated lime, hydroxides, and samples with high moisture cannot be suitably analyzed for sulfur using an induction furnace unit. Significant portions of SO_2 will be trapped in the dust filter which will be moist due to the water released or produced from the combustion. These samples must be analyzed on a resistance-furnace-type unit. Carbon results will not be similarly effected. Because of the high moisture content in the post-combustion gases, moisture filters must be checked often, and when needed, changed.

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

35.2 *Summary of Test Method*:

35.2.1 A sample of lime, limestone, or kiln flue dust is weighed into a ceramic crucible, accelerators are added, and the crucible is placed in the furnace. In a pure oxygen environment at the high temperatures generated by the furnace, the sample is fluxed and oxidized converting carbon into CO/CO_2 and sulfur into SO_2. The combustion gases are swept through a drying tube to remove the combustion moisture and then swept toward the analyzer. In the analyzer, the gas stream passes through the carbon and sulfur infrared detection cells where measurement occurs.

35.2.2 Both carbon and sulfur are calibrated against a reference material or standard with known carbon and sulfur concentrations. This is to compensate for characteristics of a given apparatus, and for the blank due to accelerators and crucibles.

35.3 *Apparatus*:

35.3.1 *Furnace*:

35.3.1.1 *Induction*—The induction furnace works by supplying power to an inductor coil, which interacts with the sample and accelerators in a ceramic crucible. The power can be controlled by the voltage to the coil and the accelerators used in combusting the sample. Some instruments are supplied with a rheostat used to control the power input to the induction coil. This is used to avoid heating some types of samples too rapidly during the early stages of combustion. Combustion takes place in an oxygen stream, which carries the combustion products through various dust and moisture traps to a detector.

35.3.1.2 *Resistance*—The resistance furnace is an open-ended combustion system that provides an oxygen environment in two separate areas. A purge flow of oxygen around the front of the combustion area provides an oxygen blanket to keep the atmosphere out while acting as a primary source for combustion. The second oxygen flow is delayed to start after the majority of the sample has been combusted and provides a direct lance flow of oxygen onto the sample to combust the remaining sample material.

35.3.2 *Detector*—The detector shall consist of one or more infrared solid-state absorption detectors for carbon or sulfur, or both. The detector may be packaged with the furnace unit as long as interference does not occur during analysis.

NOTE 54—Halogens can be a source of problems. If they are, or are suspected to be, present, it is suggested that a halogen trap be used.

35.3.3 *Combustion Crucibles*—The crucibles must be of adequate thickness and capacity to retain the molten slag and have a sulfur blank as low and consistent as possible.

Warning—There is an explosion hazard associated with the analysis of coal and coke in an induction furnace. Flammable gasses may collect in the IR cell within the closed system. These types of materials should be analyzed in a resistance furnace. See the manufacturer's instructions and cautions before analyzing any samples.

Warning—It is extremely dangerous to change the oscillator tube in the induction furnace electrical cabinet. This should only be done by trained personnel. Serious injury or death can result. See manufacturer's instructions and cautions before attempting to change the oscillator tube.

35.4 *Reagents*—Use reagents recommended by the instrument manufacturer or their equivalent.

35.5 *Calibration*:

35.5.1 *Calibration Standard*—This test method and instrument must be calibrated daily or as indicated by check standards by using a standard of known carbon and sulfur content.

35.5.2 *Check Standard*—The instrument calibration must be validated on a regular basis (See 35.6.3.6) using a check standard. The check standard is used to determine the shift-to-shift variations in the test method and to verify that the electronics are working properly. The check and calibration standard cannot be the same standard. The standards must have a known carbon or sulfur content, or both, either as determined by a reference method, such as the Total Gravimetric Sulfur Method (See Section 24), or certified upon purchase traceable to a nationally recognized standard.

35.6 *Procedure*:

35.6.1 *Instrumental Setup*—Clean and perform routine maintenance on furnace and detector units in accordance with recommended procedures in the manufacturer's operating manual. It is recommended that a minimum of three conditioning samples be analyzed before instrument calibration.

35.6.2 *Calibration Procedure*:

35.6.2.1 Prepare blanks, analyze, reset instrument blank values, and record results. Check with previous blank values and if necessary repeat. Prepare calibration samples, analyze, reset instrument values, and record results.

35.6.2.2 It is recommended that a check standard be prepared and analyzed on a routine basis (See 35.6.3.6). This is to verify that routine samples tested during a specific interval are accurate according to the last instrument calibration.

35.6.2.3 Run laboratory samples as specified in 35.6.3.

35.6.3 *Sample Procedure*:

35.6.3.1 Weigh samples to the nearest 0.1 mg in accordance with the manufacturer's instructions for a specific instrument.

NOTE 55—It has been found through round-robin studies that the practice of pre-igniting samples at 1000 °C causes erratic recovery of sulfur. This practice should not be used.

35.6.3.2 Place the sample in the instrument and perform the analysis.

35.6.3.3 Analysis time is generally 65 s. This can be determined by watching the integration time of materials, and finding out what is a normal time for the type of sample you are running. If analysis time for sulfur exceeds the normal expected time, then changing of the Anhydrone tube is recommended as moisture absorption/desorption of SO_2 may be occurring. Be cautious about the variability of instruments and materials. It is possible to have bimodal curves that indicate a late release of sulfur. When in doubt, check the instrument with a material of known concentration.

NOTE 56—An anhydrone tube that has collected moisture or particulates may "cake" and cause your analysis time to increase. When operating the instrument, you can also expect the analysis time to increase due to dust and moisture from combustion of the sample. The tube should be cleaned, or replaced, at regular intervals.

35.6.3.4 Inspect the crucible for a proper burn. A rough, bumpy surface or appearance of noncombustion indicates that the furnace temperature was too low.

35.6.3.5 After each analysis, record results and continue. It is recommended that samples be saved until results can be verified by a check standard.

35.6.3.6 Analyze the check standard after a minimum of every 10 samples to verify instrument performance. If the analysis of the check standard is not within tolerance (See Note 57), then find the cause and recalibrate.

NOTE 57—For purposes of this procedure, tolerance can be defined as results which meet the published certified value of the standard within the published standard deviation of the standard's certified value. The use of NIST traceable standards or comparable is recommended.

35.7 *Precision and Bias*—The precision and bias of this test method have not yet been determined.

36. Keywords

36.1 alternative method; aluminum; available lime index; calcium; carbon; carbon dioxide; chemical analysis; free moisture, lime; free moisture, limestone; free silica; hydrated lime; instrumental analysis; iron; limestone; loss on ignition, (LOI); magnesium; manganese; methods, classical; methods, historical; oxides; oxides, unhydrated; phosphorus; quicklime; reference method; silicon dioxide; Standard Reference Material (SRM); strontium; sulfur

APPENDIXES

(Nonmandatory Information)

HISTORICAL ASTM METHODS

X1. TOTAL IRON BY THE POTASSIUM PERMANGANATE TITRATION METHOD

INTRODUCTION

The following test methods have been published as information only and are a collection of classical methods that had historically been widely used by the industry. Because they are presently of limited use, they have been deleted from the main body of reference test methods. Since some laboratories may still wish to perform these analyses, they have been placed in these appendixes. The precision and bias testing has not been performed for these methods. Therefore, users are advised to develop their own laboratory precision and to check against standard reference materials. Subcommittee C07.05 encourages comments and evaluation of these methods.

X1.1 *Scope*—This test method permits a more accurate analysis of the trace amounts of iron that may be present because a larger sample is used.

X1.2 *Summary of Test Method*—The sample is dissolved in HCl and the SiO_2 is dehydrated and separated from the soluble salts by filtration. The small amount of iron left in the insoluble residue is dissolved with sulfuric acid after SiO_2 is expelled with HF, and the recovered iron is combined with the bulk of the iron in the main filtrate. Iron is reduced with $SnCl_2$ and titrated with $KMnO_4$ solution.

X1.3 *Special Solutions:*

X1.3.1 *Manganese Sulfate Solution* (70 g/L)—Dissolve 70 g of crystalline manganese sulfate ($MnSO_4$) in 500 mL of water. Add 140 mL H_3PO_4 and 130 mL H_2SO_4. Dilute to 1 L.

X1.3.2 *Potassium Permanganate, Standard Solution* (0.05 *N*):

X1.3.2.1 Dissolve 1.60 g of potassium permanganate ($KMnO_4$) in 1 L of water and boil gently in a flask for 20 to 30 min. Cool, dilute again to 1 L, stopper, and allow to stand for several days in the dark. Filter through purified asbestos or a wad of glass fiber and standardize against the National Institute of Standards and Technology's standard sample 40C, sodium oxalate ($Na_2C_2O_4$), or equivalent in accordance with X1.3.2.2 through X1.3.2.4.

NOTE X1.1—Alternatively, potassium dichromate may be used in place of potassium permanganate as in the procedure of 13.4.

X1.3.2.2 Transfer 0.15 g of the standard sodium oxalate, dried at 105 °C, to a 400-mL beaker. Add 250 mL of diluted H_2SO_4(5 + 95), which has been previously boiled for 10 min and cooled to 27 ± 3 °C. Stir until the oxalate has dissolved. Add 40 to 42 mL of the standard $KMnO_4$ solution at the rate of 25 to 30 mL/min, while stirring slowly. Let stand until the pink color disappears (about 60 s).

NOTE X1.2—If the pink color should persist because of the addition of too much $KMnO_4$ solution, discard and begin again, adding a few millilitres less of the $KMnO_4$ solution initially.

X1.3.2.3 Heat the contents of the beaker to 60 °C and complete the titration at this temperature by adding $KMnO_4$ solution until a slight pink color persists for 30 s. Add the last 0.5 to 1 mL dropwise, allowing each drop to become decolorized before the next one is added.

X1.3.2.4 One millilitre of standard $KMnO_4$ solution will be approximately equivalent to 0.004 g of ferric oxide (Fe_2O_3). Determine the exact Fe_2O_3 equivalent of the solution from the following:

$$N=(W/V)\times 14.925 \tag{X1.1}$$

where:

N = normality of $KMnO_4$ solution,

W = sodium oxalate, g,
V = $KMnO_4$ solution used to titrate the sodium oxalate solution, mL, and
14.925 = sodium oxalate equivalent to 1 mL of 1 *N* $KMnO_4$ solution, g.

Fe_2O_3 equivalent of $KMnO_4 = N \times 0.07984$, where $0.07984 =$ g Fe_2O_3 equivalent to 1 mL of 1 *N* $KMnO_4$ solution.

X1.4 *Procedure:*

X1.4.1 Weigh 2 to 5 g (depending upon the amount of iron present) of the properly prepared sample into a beaker and add 25 mL of HCl (1 + 1). After the reaction ceases, evaporate the solution to dryness. Add 50 mL of HCl (1 + 4), heat to dissolve the salts, filter the insoluble matter including SiO_2 using a medium-textured paper, then wash the paper and contents several times with hot water. Retain the filter paper. Heat the solution to boiling, add a few drops of methyl red indicator, and precipitate the iron by adding enough NH_4OH to change the color of the indicator from red to distinct yellow. Allow the precipitate to settle slightly, filter, and wash using hot water. Dissolve contents of the paper by placing paper and contents in 50 mL of hot HCl (1 + 3). Filter into a clean beaker and wash. Reserve filtrate.

X1.4.2 Place the paper containing the insoluble matter from the evaporated HCl solution in a platinum crucible. Char the paper without inflaming, at low heat, increase the heat to ash the paper, and ignite at 1000 °C for 15 min. Cool, add 1 mL of H_2SO_4 and 10 to 15 mL of HF, and evaporate to fumes of sulfur trioxide. Cool, dilute the contents of the crucible with water, and warm to dissolve salts. Transfer the acidified solution to the main solution containing the bulk of the iron.

X1.4.3 Heat the solution to near boiling. Reduce the iron by adding $SnCl_2$ dropwise from a pipet, while swirling the beaker constantly, until the yellow color of the ferric iron just disappears (See Note 21). Add 2 or 3 drops of $SnCl_2$ in excess, but no more. Cool the beaker quickly in running water, then add all at once 10 mL of $HgCl_2$ solution. Stir and allow to stand for 3 to 5 min (See Note 22). Transfer with washing to a 600-mL of 1-L beaker containing 300 mL of cold water and 25 mL of the $MnSO_4$ solution. Titrate with standard 0.05 *N* $KMnO_4$ solution, added very slowly while stirring constantly, until a permanent pink end point is obtained. A blank should also be determined.

X1.5 *Calculation*—Calculate the percent iron oxide (Fe_2O_3) to the nearest 0.01 % as follows:

$$Fe_2O_3, \% = (A \times B)/C \times 100 \quad (X1.2)$$

where:
A = 0.05 *N* $KMnO_4$ solution used in titration, mL,
B = Fe_2O_3 equivalent of $KMnO_4$, and
C = sample weighed, g.

X1.6 *Precision and Bias*—The precision and bias of this test method have not been determined.

X2. STRONTIUM OXIDE BY THE GRAVIMETRIC SULFATE (ETHER) METHOD

X2.1 *Scope*—There may be certain applications that require a separate determination of strontium content or an exact determination of calcium. This test method is designed to determine the SrO present which will allow a correction for the percent CaO as obtained in previous sections.

X2.2 *Summary of Test Method*—The alkaline earth oxides are converted to nitrates. The different solubilities of calcium and strontium nitrate in absolute alcohol and ether are used to separate the two metals from each other. After filtration, the strontium nitrate precipitate is dissolved with water and the strontium precipitated with H_2SO_4 filtered, ignited, and weighed as strontium sulfate ($SrSO_4$).

X2.3 *Procedure:*

X2.3.1 Transfer the weighed oxides obtained in the gravimetric determination of calcium oxide (See Section 5.1.4) to a small flask of 20-mL capacity and dissolve in HNO_3. Evaporate to dryness and heat at 150 to 160 °C. Treat the thoroughly dried nitrates with as little (rarely over 2 mL) of a mixture of equal parts of absolute alcohol and ether as may be needed to dissolve the calcium salt, hastening solution by occasional, gentle agitation. After standing overnight in the stoppered flask, collect the insoluble matter on the smallest possible filter and wash with more of the above mixture of alcohol and ether.

Warning—Ethers tend to form peroxides by air oxidation on standing which are highly explosive. Peroxide containing ethers should not be distilled unless the peroxide is first destroyed by a suitable agent such as sodium sulfate or ferrous sulfate and should not be allowed to stand indefinitely in the laboratory.

X2.3.2 Let the filter air dry, then pass a few millilitres of hot water through the filter to dissolve the strontium nitrate. A few tenths of a milligram of residue may remain, consisting of material other than lime or alkaline earth, whose mass should therefore be deducted from the mass of the lime determined by the gravimetric method (See Section 16).

NOTE X2.1—This correction is unnecessary if it can be shown that the impurities are derived from the glass of the small flask in which the nitrates of calcium and strontium were evaporated.

X2.3.3 To the solution of strontium nitrate, in a small beaker add a few drops of H_2SO_4 and a quantity of alcohol equal to the volume of the nitrate solution. The precipitate of strontium sulfate is allowed to develop and settle at room temperature for a period of 12 h.

X2.3.4 Filter the $SrSO_4$ on a small filter paper, and wash with 50 % alcohol. Ignite at low temperature, cool, moisten with dilute H_2SO_4(1 + 1), evaporate to dryness, again ignite, and weigh as strontium sulfate ($SrSO_4$). The sulfate may be tested spectroscopically for traces of calcium and barium if it is considered necessary.

X2.4 *Calculation:*

X2.4.1 Calculate the mass of strontium oxide as follows:

$$\text{SrO, \%} = (A/B) \times 56.41 \tag{X2.1}$$

where:

A = mass of $SrSO_4$,
B = original mass of sample, g, and
56.41 = molecular ratio of SrO to $SrSO_4 \times 100$.

X2.4.2 Deduct the percent SrO from the percent CaO determined in Section 17.

X2.5 *Precision and Bias*—This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

X3. PHOSPHORUS BY THE TITRIMETRIC METHOD

X3.1 *Scope*—This is a titrimetric test method for determining phosphorus in samples of limestone, quicklime, or lime hydrate. A fairly large sample weight is required because this test method is not sensitive enough for an accurate analysis at the low levels of phosphorus frequently encountered in limestone rock.

X3.2 *Summary of Test Method*—The sample is dissolved in dilute nitric acid, the solution filtered, the residue fused with a little sodium carbonate and its nitric acid solution added to the other. An HF-HNO_3 treatment is included if the rock contains more than 3 % SiO_2. Ammonium molybdate is added to the nitric acid solution to precipitate phosphorus as ammonium phosphomolybdate. The phosphomolybdate is dissolved in an excess of a standard solution of sodium hydroxide which is then back-titrated with standard acid in the presence of phenolphthalein indicator.

X3.3 *Special Solutions:*

X3.3.1 *Ammonium Molybdate Solution:*

X3.3.1.1 *Solution A*—Add 400 mL of nitric acid to 600 mL of water. Mix and cool.

X3.3.1.2 *Solution B*—Dissolve 118 g of 85 % molybdic acid with 400 mL of water and add 80 mL of NH_4OH. Cool.

X3.3.1.3 Add Solution B to Solution A slowly with constant stirring, let solution stand for 24 h. Filter immediately before using.

X3.3.2 *Potassium Nitrate Solution* (10 g/L)—Dissolve 10 g of potassium nitrate (KNO_3) in water freshly boiled to expel CO_2 and cooled. Dilute to 1 L.

X3.3.3 *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 $Ba(OH)_2$ (See Note X3.1). Shake the solution frequently for several hours and filter it. Store in a stoppered flask protected from the CO_2 of the air by means of a guard tube packed with Ascarite. Standardize against standard acid phthalate such as NIST Standard Sample No. 84 or benzoic acid, NIST Standard Sample No. 39 furnished by the National Institute of Standards and Technology[4] , as follows:

NOTE X3.1—$Ba(OH)_2$ precipitates the carbonate as insoluble $BaCO_3$.

X3.3.3.1 Lightly crush 5 to 6 g of standard acid potassium phthalate to a fineness of approximately 10 mesh and dry for 2 h at 100 °C. Place in a small glass-stoppered container and cool in a desiccator.

X3.3.3.2 Accurately weigh about 1 g of the dried standard and transfer it to a 500-mL Erlenmeyer flask.

X3.3.3.3 Add 50 mL of CO_2-free distilled water and swirl gently to dissolve. Add 3 drops of phenolphthalein indicator and titrate with the sodium hydroxide to the first pink color.

X3.3.3.4 Calculate the normality of NaOH as follows:

$$N = W/V \times 204.228 \tag{X3.1}$$

where:

N = normality of NaOH solution,
W = grams of potassium acid phthalate,
V = millilitres of NaOH used, and
204.228 = gram equivalent weight of potassium acid phthalate.

X3.3.3.5 Calculate the phosphorus pentoxide (P_2O_5) equivalent (See Note X3.2) of the NaOH solution in grams per millilitre as follows:

$$E = N \times 0.003086 \tag{X3.2}$$

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 X3.2—Phosphorus reacts to form ammonium phosphomolybdate $2(NH_4)_3PO_4 \cdot 12MoO_3$. The precipitate reacts with the NaOH solution thus:

2(NH4)3PO4 · 12MoO3 + 46NaOH = 2(NH4)2HPO4
+ (NH4)2MoO4 + 23Na2MoO4 + 22H2O

The equivalent weight of P_2O_5(0.003086) is obtained by dividing the molecular weight of P_2O_5(141.96) by 46 (for 46 moles of 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 be followed closely as prescribed.

X3.3.4 *Sulfuric Acid, Standard* (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 H_2SO_4 solution used in titration.

X3.4 *Procedure:*

X3.4.1 Dissolve 10 g of the prepared sample by adding 80 mL of dilute HNO_3(1 + 1) and heating on hot plate. Add 350 mg of ferric nitrate salt ($Fe(NO_3)3 \cdot 9\ H_2O$) (See Note X3.3) and 15 g of ammonium chloride (NH_4Cl), make ammoniacal, then add 5 mL of NH_4OH (1 + 1) in excess. Heat to boiling, filter on medium-textured paper and wash with diluted NH_4OH (5 + 95). Discard the filtrate.

NOTE X3.3—Small amounts of phosphorus in the sample can be concentrated very easily this way. The iron combines with the phosphate to form $FePO_4$ that is very insoluble in NH_4OH and affords the analyst the opportunity to separate it from major matrix elements.

X3.4.2 Place the precipitating beaker under the funnel and punch a small hole in the tip of the filter cone by pushing a platinum wire through it. Pour 25 mL of hot HNO_3(1 + 4) through the paper and wash free of iron with hot 5 % HNO_3. Discard the paper.

X3.4.3 Evaporate the nitric acid of solution to dryness and to the dry salts add 30 mL of aqua regia mix (160 mL of HNO_3 + 40 mL HCl (1 + 1). Boil on hot plate until reddish-brown fumes cease to come off and for several minutes thereafter. Add 100 mL of water and boil.

X3.4.4 Filter into a 500-mL Erlenmeyer flask and wash with hot water. Ignite the residue, cool, add 1 mL of HNO_3 and 10 mL of HF and evaporate to dryness (See Note X3.4). Evaporate twice with nitric acid to expel all the HF. Fuse residue with a pinch of Na_2CO_3(0.5 g), dissolve in dilute nitric acid, and add to the filtrate in the Erlenmeyer flask.

NOTE X3.4—The treatment of the residue with HF and HNO_3 may be omitted if the SiO_2 in the sample is low, <3 %.

X3.4.5 Neutralize the nitric acid solution with NH_4OH until iron hydroxide just begins to form. Reacidify with nitric acid slowly until precipitate just dissolves, then add 1 mL of HNO_3 for every 100 mL of solution. Heat the solution to 40 °C and add 40 mL of ammonium molybdate ($(NH_4)_2MoO_4$) (filtered). Stopper the flask, shake for several minutes, and allow to settle overnight (12 h).

X3.4.6 Filter through a retentive paper. Wash the flask and precipitate five times with 15-mL portions of a 1 % solution of KNO_3 and then wash the paper ten times with 10-mL portions of the same solution. The paper should be carefully washed each time from the rim downward and then allowed to drain completely before washing with the next portion of wash solution. (The wash solution must be free of CO_2.)

X3.4.7 Return the paper and precipitate to the flask, add about 75 mL of CO_2-free water, and add enough standard sodium hydroxide solution to decompose the precipitate and leave approximately 2 mL in excess. Record the millilitres of NaOH solution added.

X3.4.8 Stopper the flask and shake to disintegrate the paper. Wash the stopper and sides of the flask with CO_2-free water, add 6 drops of phenolphthalein indicator solution, and titrate the excess sodium hydroxide with standard H_2SO_4 until the pink color of indicator just disappears. Record the millilitres of standard acid.

X3.5 *Calculation:*

NOTE X3.5—Titanium and vanadium interfere in this determination but should not be encountered in significant amounts in this class of material.

X3.5.1 Calculate the percent P_2O_5 as follows:

$$P_2O_5,\ \% = \{E(V_1 - V_2R)\}/W \times 100 \quad (X3.3)$$

where:

E = P_2O_5 equivalent of the NaOH solution, g/mL,
V_1 = NaOH solution used, mL,
V_2 = H_2SO_4 solution used, mL,
R = ratio in strength of the NaOH solution to the H_2SO_4 solution, and
W = mass of sample, g.

X3.6 *Precision and Bias*—The precision and bias of this method have not been determined.

X4. MANGANESE BY THE BISMUTHATE METHOD

X4.1 *Scope*—This is the standard titrimetric method that may be used to determine manganese in lime and limestone samples when the concentration of manganese is at least 0.05 %.

X4.2 *Summary of Test Method*—After dissolution of the sample, bivalent manganese is oxidized to permanganic acid by the use of sodium bismuthate ($NaBiO_3$) in nitric acid solution, filtering, washing with nitric acid, adding a measured excess of ferrous sulfate and then determining this excess by titration with a standard solution of permanganate.

X4.3 *Apparatus:*

X4.3.1 *Filtering Crucible*—An asbestos Gooch crucible or a fritted glass crucible of fine porosity.

X4.4 *Reagents:*

X4.4.1 *Sodium Bismuthate*—The sodium bismuthate shall contain enough active oxygen to correspond to at least 75 % $NaBiO_3$.

X4.4.2 *Ferrous Ammonium Sulfate Solution* (12 g/L)—Dissolve 12 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 1 L of cool H_2SO_4(5 + 95).

X4.4.3 *Standardization of Ferrous Ammonium Sulfate Solution*—Measure into a 250-mL Erlenmeyer flask, 50 mL of cold nitric acid (3 + 97). Add about 0.5 g of sodium bismuthate ($NaBiO_3$), agitate, dilute with 50 mL of HNO_3(3 + 97) and filter through asbestos or a fritted glass crucible. To the filtrate add 50 mL of the ferrous ammonium sulfate solution and titrate with standard $KMnO_4$ solution to pink color. Determine the ratio (R) of the standard $KMnO_4$ solution to the standard ferrous ammonium sulfate solution by dividing the volume of $KMnO_4$ solution by the volume of $Fe(NH_4)_2(SO_4)_2$ solution used in the titration.

X4.4.4 *Nitric Acid* (3 + 97).

X4.4.5 *Potassium Permanganate Standard Solution* (0.05 *N*)—The same solution as prepared in the Total Iron, Standard Method, Section 13.

X4.5 *Procedure:*

X4.5.1 Dissolve 10 g of the sample in 100 mL of diluted $HNO_3(1 + 1)$, filter, and wash the residue with hot water. Ignite the residue in platinum, fuse with a little Na_2CO_3, and add the nitric acid solution of the melt to the main filtrate.

X4.5.2 Dilute the solution to 150 mL and add 0.5 g of sodium bismuthate. Heat for a few minutes or until the pink color has disappeared and MnO_2 has precipitated. If MnO_2 does not precipitate, add more bismuthate.

X4.5.3 Clear the solution by slowly adding ferrous ammonium sulfate solution (12 g/L) until the MnO_2 dissolves. Boil to expel brown fumes, cool to 10 to 15 °C, add 0.5 to 1.5 g of $NaBiO_3$(or an amount equal to at least 26 times the weight of manganese present), and agitate vigorously for 1 min. Add 50 mL of cold $HNO_3(3 + 97)$ and filter through a Gooch crucible or fritted glass crucible of fine porosity. Wash with 50 mL of cold $HNO_3(3 + 97)$ or until the washings run colorless.

X4.5.4 Add enough ferrous ammonium sulfate solution (12 g/L) from a buret to discharge completely the permanganate color and then add 1.0 to 2.0 mL in excess. Record the buret reading. Titrate the excess ferrous with 0.05 *N* $KMnO_4$ solution to a faint pink end point.

X4.6 *Calculation*—Calculate the percentage of manganese as follows:

$$\text{Mn, \%} = (V_1 R - V_2) N / W \times 1.0988 \tag{X4.1}$$

where:

V_1 = $Fe(NH_4)_2(SO_4)_2$ solution used, mL,
R = ratio in strength of $KMnO_4$ solution to the $Fe(NH_4)_2(SO_4)_2$ solution,
V_2 = $KMnO_4$ solution used, mL,
N = normality of $KMnO_4$ solution,
W = mass of sample, g, and
1.0988 = manganese equivalent of $KMnO_4 \times 100$.

X4.7 *Precision and Bias*—The precision and bias of this test method have not been determined.

X5. FERROUS IRON BY TITRATION WITH POTASSIUM PERMANGANATE

X5.1 *Scope*—The determination of ferrous iron in carbonate rocks is difficult if not impossible in the presence of carbonaceous matter. Nevertheless, acceptable results are sometimes obtainable if there is not much of such matter, and if it does not give a colored solution with acid. But even then, it is only the soluble iron, existing chiefly if not wholly as carbonate, that is determinable.

X5.2 *Summary of Test Method*—The limestone sample is decomposed with dilute sulfuric acid in a steam or CO_2 atmosphere and the soluble ferrous iron is titrated with $KMnO_4$. In the absence of carbonaceous matter, it is possible to determine ferrous iron in the insoluble residue. Metallic iron, if introduced by grinding media, will also be determined as ferrous iron, and precautions should be taken to avoid this contaminate.

X5.3 *Special Solutions:*

X5.3.1 Potassium Permanganate, *Standard Solution* (0.05 *N*)—Prepare as in Total Iron, Standard Method (See Section 13).

X5.3.2 *Diphenylamine Sulfonate Indicator Solution*—Dissolve 0.2 g of sodium diphenylamine sulfonate in 100 mL of water.

X5.3.3 *Potassium Dichromate, Standard Solution* (0.028 *N*)—Weigh 2.728 g of dry National Institute of Standards and Technology potassium dichromate ($K_2Cr_2O_7$) or other pure, dry $K_2Cr_2O_7$ and dilute to 2 L in a volumetric flask. The solution contains the equivalent of 0.002 g FeO/mL.

X5.4 *Procedure:*

X5.4.1 *In Absence of Carbonaceous Matter:*

X5.4.1.1 Weigh several grams of prepared sample into a flask of about 250-mL capacity, add 25 mL of water, and boil water until air is expelled. While still boiling, add diluted $H_2SO_4(1 + 1)$ a little at a time until effervescence ceases, then add a few millilitres in excess (See Note X5.1). Calcium sulfate precipitates, but the iron will remain in solution. Remove the flame and tightly insert a stopper through which passes a small stopcock funnel. When the flask is cool, or nearly so, pour cold water into the funnel and cautiously open the cock so the water may be drawn into the flask. Keep filling the funnel as fast as it empties until the solution in the flask amounts to 100 to 150 mL (See Note X5.2). Immediately titrate the iron solution in the flask with 0.05 *N* $KMnO_4$ solution (See Note X5.3). The ferrous iron thus found is mostly, if not altogether, that existing as carbonate.

Warning—The contents of the flask may erupt violently unless this addition is made with care.

NOTE X5.1—With a carbonate that is wholly decomposable without the aid of heat, solution may be accomplished in a flask filled with CO_2, using cold acid. This mode of acid decomposition lessens the danger of attacking silicates if these are present.

NOTE X5.2—Such precaution to exclude air is hardly necessary, in most cases; however, since in the presence of H_2SO_4 the oxidation of ferrous iron is exceedingly slow. It is ordinarily quite sufficient to equalize the internal and external pressures by opening the cock, removing the stopper, and pouring in cold water.

NOTE X5.3—If MnO_2 is absent, the potassium dichromate method of titration may be substituted and HCl used instead of H_2SO_4. In this case, there is no separation of an insoluble calcium salt which renders easier the subsequent determination of iron in the insoluble residue.

X5.4.2 *Ferrous Iron in the Insoluble Residue in Absence of Carbonaceous Matter:*

X5.4.2.1 Filter the titrated solution (See X5.4.1.1) through a medium-sized, hardened filter. Transfer the residue completely to the paper and wash with hot water. Rinse the contents of the paper into a large platinum crucible (80 to 100-mL capacity) with a snugly fitting cover of transparent polypropylene and having a plastic tube for the introduction of CO_2 and a small plastic funnel for the addition of acid and the escape of vapors and steam.

X5.4.2.2 Add 18 mL of $H_2SO_4(1 + 1)$ and air-free water until the crucible is at least half full. Drop in a small coil of platinum wire to prevent bumping, fit the cover tightly, and pass CO_2 through for at least 10 min as the mixture is gradually brought to boiling. Stop the stream of gas as soon as steam escapes, immediately add 7 mL of HF through the funnel, and boil gently for 10 to 15 min, or until decomposition is complete.

X5.4.2.3 Prepare an 800-mL beaker containing 500 mL of air-free water, 12 g of boric acid, and 20 mL of $H_2SO_4(1 + 3)$. Quickly transfer the crucible cover and contents to the 800-mL beaker. With the aid of a stirring rod, remove the crucible and cover from the beaker and rinse it off with water. Add 3 to 5 drops of sodium diphenylamine sulfonate indicator and titrate with the $K_2Cr_2O_7$ standard solution to a purple color that persists for 20 to 30 s.

NOTE X5.4—Potassium dichromate is preferred because it reacts much less rapidly on organic matter than permanganate.

X5.4.3 *Ferrous Iron in Presence of Insoluble Carbonaceous Matter:*

X5.4.3.1 Weigh 2 to 5 g of prepared sample into a flask of about 250-mL capacity, pass in a stream of CO_2 through a delivery tube and introduce dilute $H_2SO_4(1 + 1)$ till effervescence ceases, then add a few more millilitres in excess. Heat if necessary to decompose the limestone (See Note X5.5) and filter quickly (See Note X5.6) through asbestos or sintered glass fiber (in an atmosphere of carbon dioxide if much iron is present). Wash the filter and the residue a few times with water and titrate the filtrate at once with 0.05 *N* $KMnO_4$ solutions. Discard the residue (See Note X5.7).

NOTE X5.5—Heat is not needed with limestone if active agitation is used; but with dolomites, heat is necessary.

NOTE X5.6—It is important to allow the acid to act no longer than is necessary and to filter quickly.

NOTE X5.7—A determination of the ferrous iron in the insoluble matter is usually not worth attempting because of the admixed organic matter.

X5.5 *Calculation*—Calculate the percent FeO as follows:

$$\text{FeO, \%} = V \times N \times 7.184/W \tag{X5.1}$$

where:

V = titrant ($KMnO_4$ or $K_2Cr_2O_7$), mL,
N = normality of $KMnO_4$ or $K_2Cr_2O_7$ solution,
W = weight of sample, g, and
7.184 = equivalent weight of FeO × 100.

X5.6 *Precision and Bias*—The precision and bias of this test method have not been determined.

X6. TEST METHOD FOR FREE CALCIUM OXIDE IN HIGH-CALCIUM HYDRATED LIME[8]

X6.1 Scope

X6.1.1 This test method covers the determination of the amount of free calcium oxide (CaO) in high-calcium hydrated lime capable of being hydrated by steam at atmospheric pressure.

X6.2 Summary of Test Method

X6.2.1 This test method is based on the principle of gain in weight of CaO when it is hydrated to form calcium hydroxide ($Ca(OH)_2$).

X6.2.2 The sample is dried, subjected to steam at atmospheric pressure, again dried, and the gain in weight calculated to CaO.

X6.3 Apparatus

X6.3.1 *Drying Oven,* thermostatically controlled, CO_2-free atmosphere.

X6.3.2 *Analytical Balance.*

X6.3.3 *Steam Bath,* as shown in Fig. X6.1.

X6.4 Procedure

X6.4.1 Weigh a clean, dry, 10-mL Erlenmeyer flask on an analytical balance.

NOTE X6.1—Once started, complete the test without interruption.

X6.4.2 Add to the flask, by means of a widestem funnel, 3 to 5 g of the lime to be tested. Reweigh to get the exact sample weight.

NOTE X6.2—The flask should be kept stoppered at all times, except when weighing, drying, or steaming.

X6.4.3 Place the flask in the drying oven that has been previously heated to 120 °C, and maintain at this temperature for 30 min. Remove, stopper, cool in a desiccator, and weigh.

NOTE X6.3—Oven atmosphere can be kept CO_2 free by placing therein a container of soda lime, quicklime, or other suitable CO_2-absorbing medium.

X6.4.4 Place the flask and the sample in a vigorously boiling steam bath and steam for 30 min. Protect the flask in the steam bath by a drip shield during the steaming period. Remove the flask to the oven, dry for 30 min at 120 °C, stopper, cool in a desiccator, and weigh.

X6.4.5 Record all weighings to the fourth decimal place.

X6.5 Calculation

X6.5.1 Calculate the percentage of water and CaO as follows:

$$\text{Free water, \%} = [(W_1 - W_2)/S] \times 100 \tag{X6.1}$$

$$\text{Free CaO, \%} = \frac{(W_3 - W_2) \times 3.114}{S} \times 100$$

where:

W_1 = weight of sample and flask before drying,
W_2 = weight of sample and flask after drying,
W_3 = weight of sample and flask after steaming and drying, and
S = weight of sample.

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[8] This test method was taken from the Appendix of Specification C 911.

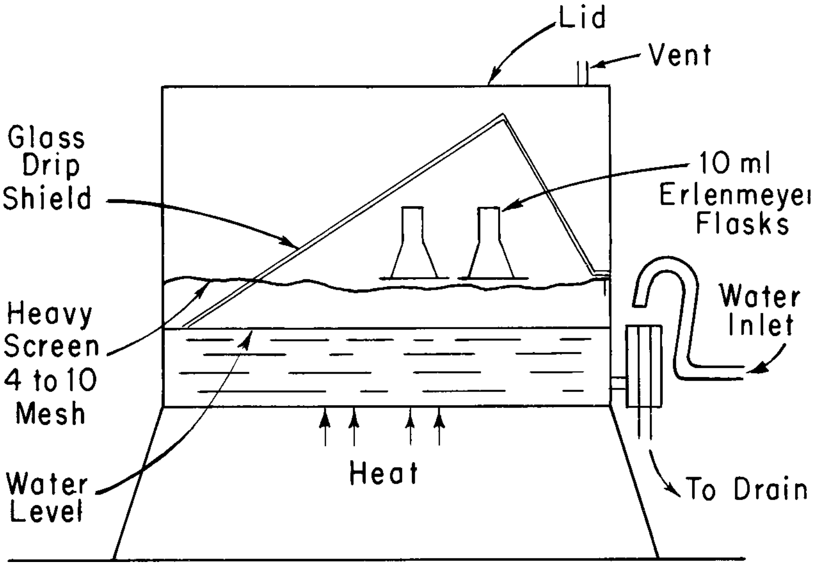

FIG. X6.1 Steam Chamber

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