



Designation: C25 – 19<sup>ε</sup>1

# Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime<sup>1</sup>

This standard is issued under the fixed designation C25; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

<sup>ε</sup>1 NOTE—Editorially added research report to Section 21 in April 2024.

## 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, health, and environmental 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.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C07 on Lime and Limestone and are the direct responsibility of Subcommittee C07.05 on Chemical Tests.

Current edition approved May 1, 2019. Published July 2019. Originally approved in 1919. Last previous edition approved in 2017 as C25 – 17. DOI: 10.1520/C0025-19E01.

*Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- C50/C50M** Practice for Sampling, Sample Preparation, Packaging, and Marking of Lime and Limestone Products
- C51** Terminology Relating to Lime and Limestone (as Used by the Industry)
- C911** Specification for Quicklime, Hydrated Lime, and Limestone for Selected Chemical and Industrial Uses
- D1193** Specification for Reagent Water
- E29** Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E50** Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E70** Test Method for pH of Aqueous Solutions With the Glass Electrode
- E173** Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1997)<sup>3</sup>
- E177** Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E200** Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis
- E691** Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E832** Specification for Laboratory Filter Papers

## 3. Terminology

3.1 *Definitions:* Definitions—Unless otherwise specified, for definitions of terms used in these test methods refer to Terminology **C51**.

## 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.

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

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

## 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  $\pm 0.0002$  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.<sup>4</sup> 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, and so forth, 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 alkalis 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 **E832**, 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 ( $\mu\text{m}$ )	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

<sup>4</sup> Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

of intermittent operation at higher temperatures if required. It should have an indicating pyrometer accurate to  $\pm 25$  °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<sup>5</sup> 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.

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 **D1193** 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 <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )	99.5 %
Hydrochloric acid (HCl)	sp gr 1.19
Hydrofluoric acid (HF)	48 %
Nitric acid (HNO <sub>3</sub> )	sp gr 1.42
Perchloric acid (HClO <sub>4</sub> )	70 %
Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	85 %
Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	sp gr 1.84
Ammonium hydroxide (NH <sub>4</sub> OH)	sp gr 0.90

5.2.3.2 *Dilute Reagents*—The concentration of dilute acids and NH<sub>4</sub>OH 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<sub>2</sub>SO<sub>4</sub> (5 + 95) means 5 volumes of concentrated H<sub>2</sub>SO<sub>4</sub> (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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution (1 mL = 0.004 g Fe<sub>2</sub>O<sub>3</sub>). 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.

<sup>5</sup> *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.

## 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 **C50/C50M** 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 **E29**.

## 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 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 CRM 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 CRM. If the duplicate results do not agree within the permissible variation given in

**Table 1**, the determinations shall be repeated, following identification and correction of problems or errors, until a set of duplicate results do agree within the permissible variation.

**NOTE 2**—The term CRM refers to approved Certified Reference Materials listed in **Table 2**.

**NOTE 3**—There are no CRMs that are quicklime or hydrated lime as supplied. When analyzing a quicklime or hydrated lime the CRM in carbonate form needs to be converted to closely resemble the matrix of the product being tested. To accomplish this conversion, heat the chosen CRM 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 CRM unsuitable as a standard for carbon and sulfur determinations. For carbon and sulfur determinations use the appropriate CRM in its normal matrix.

7.1.4 The average of the results of acceptable duplicate determinations for each constituent may differ from the CRM certificate value by no more than the value shown in Column 3 of **Table 1**. When no CRM 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 CRM 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.

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, and so forth, 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.

**TABLE 1 Maximum Permissible Variations in Results<sup>A</sup>**

(Column 1) Constituent	(Column 2) Maximum Difference Between Duplicates	(Column 3) Maximum Difference of the Average of Duplicates from CRM Certificate Values <sup>B</sup>
Al as Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	0.10	±0.15
Si as SiO <sub>2</sub>	0.15	±0.30
Mn	0.05	±0.10
P	0.02	±0.05 <sup>C</sup>
Sr as SrO	0.05	
S	0.03	±0.05

<sup>A</sup> For demonstrating the performance of rapid test methods the CRM closest in overall composition to the limestone shall be used (see **Table 2**). In the case of quicklime or hydrated lime, the CRM 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**).

<sup>B</sup> Interelement corrections may be used for any standardization provided improved accuracy can be demonstrated.

<sup>C</sup> No CRM currently available.

**TABLE 2 Approved CRM List**

CRM	Al as % Al <sub>2</sub> O <sub>3</sub>	Ca as % CaO	Mg as % MgO	Fe as % Fe <sub>2</sub> O <sub>3</sub>	Si as % SiO <sub>2</sub>	% Mn	% P	Sr as % SrO	% S	Ti as % TiO <sub>2</sub>	K as % K <sub>2</sub> O	Na as % Na <sub>2</sub> O	% LOI
ECRM 752-1 <sup>A</sup>	0.120	55.400	0.150	0.045	0.700	0.008	NC <sup>B</sup>	0.019	0.007	0.009	0.020	NC	43.40
IPT 35	0.240	53.800	0.700	0.140	1.980	0.009	0.003	0.040	NC	0.013	0.100	0.004	43.00
IPT 44	0.330	50.500	2.930	0.300	2.690	0.012	0.006	0.040	NC	0.019	0.120	0.002	42.90
IRSID 701-1 <sup>C</sup>	0.550	52.700	0.600	1.040	1.990	0.022	0.022	NC	0.04	0.030	NC	NC	NC
NIST 1c <sup>C</sup>	1.300	50.300	0.420	0.550	6.840	0.019	0.017	0.030	NC	0.070	0.280	0.020	39.90
NIST 88B	0.336	30.120	21.030	0.277	1.130	0.012	0.002	0.008	NC	(0.016) <sup>D</sup>	0.103	0.029	(46.98)
BCS 368	0.170	30.800	20.900	0.230	0.920	0.050	NC	0.009	NC	<0.01	(0.024)	<0.01	46.70
IRSID 702-1	0.400	30.050	20.510	0.629	2.220	0.10	0.024	NC	0.027	0.022	NC	NC	NC
GBW 07214 <sup>C</sup>	0.017	54.950	0.670	0.071	0.380	0.007	0.0011	NC	0.020	NC	NC	NC	43.57
GBW 07215 <sup>C</sup>	0.500	51.560	2.670	0.292	1.170	0.014	0.0013	NC	0.196	NC	NC	NC	43.22
GBW 07216 <sup>C</sup>	0.027	36.550	16.590	0.226	0.092	0.022	0.0018	NC	0.014	NC	NC	NC	46.23
GBW 07217 <sup>C</sup>	0.295	30.600	20.730	0.376	0.960	0.048	0.0012	NC	0.174	NC	NC	NC	46.30
GBW 03106	0.640	50.380	2.280	0.290	4.380	0.0055	0.006	NC	0.006	0.034	0.14	0.07	41.58
GBW 03108	0.880	47.490	3.630	1.970	3.840	0.15	0.017	NC	0.036	0.14	0.23	0.024	41.52
IPT 48	0.170	31.000	21.200	0.170	0.450	0.011	0.010	0.009	NC	0.006	0.026	0.013	46.90
NIST 1d	0.526	52.85	0.301	0.319	4.08	0.0209	0.0413	0.0303	0.1028	(0.0306)	0.1358	0.0109	(41.57)
GBW 07214a	0.093	55.34	0.29	0.085	0.22	0.0039	0.0011	NC	0.043	NC	0.02	(0.007)	43.61
GBW 07215a	0.77	51.2	2.29	0.446	1.8	0.0108	0.0013	NC	0.302	NC	0.168	0.025	42.57
GBW 07216a	0.024	35.02	17.88	0.495	0.049	0.015	0.0012	NC	0.0093	NC	0.001	0.013	46.32
GBW 07217a	0.017	32.11	20.37	0.224	0.021	0.0248	0.001	NC	0.018	NC	0.0011	0.023	46.89
BCS 513	0.108	55.59	0.182	0.0275	0.228	0.0074	NC	0.0176	0.0097	NC	0.015	NC	43.61
IPT 122	1.24	32	17.5	0.65	4.3	0.0333	0.0306	0.018	NC	0.06	0.43	0.019	43.3
JLS-1	0.0207	55.09	0.606	0.0178	0.12	0.00162	0.019	0.0349	0.0123	(0.002)	0.00297	0.002	(43.82)
JDo-1	0.0174	33.96	18.47	0.0222	0.216	0.0051	0.022	0.0137	(0.0095)	(0.00133)	0.00232	0.013	(47.1)

<sup>A</sup> This CRM is still available but its named has been changed from BCS 393.

<sup>B</sup> NC = Not Certified.

<sup>C</sup> This CRM is no longer commercially available but use of private stock is allowed.

<sup>D</sup> ( ) = not certified; data for information only.

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 CRM 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 CRM 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 CRM, or an accepted value of a known secondary standard differs from the value obtained by the test method in question by more than twice the value 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<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>) 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, and so forth.

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<sub>2</sub>.

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<sub>3</sub>) and perchloric (HClO<sub>4</sub>) acids and evaporated to fumes of HClO<sub>4</sub>.

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<sub>4</sub>) is an extremely reactive liquid. When using HClO<sub>4</sub>, 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<sub>3</sub>) to the sample prior to fuming with HClO<sub>4</sub>. All evaporations involving HClO<sub>4</sub> 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 E50.

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<sub>3</sub> 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<sub>4</sub> 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<sub>2</sub>.

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

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

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<sub>2</sub> 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<sub>2</sub> from the insoluble residue with hydrofluoric acid and the percent SiO<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub>.

**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<sub>2</sub>.

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

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

where:

A = mass of ignited residue, g (insoluble matter including SiO<sub>2</sub>),

B = mass of ignited residue less SiO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub>) (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.

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

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

where:

A = insoluble matter including SiO<sub>2</sub>, %, and

**TABLE 3 Precision Summary of Classical Test Methods**

Section	Test Method	Average, <sup>A</sup> % Found	Range, <sup>A</sup> % Found	Repeatability (R <sub>1</sub> , E173)	Reproducibility (R <sub>2</sub> , E173)
8	Insol + SiO <sub>2</sub> (Standard)	...	...	...	...
9	Insol + SiO <sub>2</sub> (Optional)	1.405	0.09–6.40	0.184	0.351
10	SiO <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	0.180	0.05–0.36	0.064	0.183
15	Al <sub>2</sub> O <sub>3</sub>	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

<sup>A</sup> Average and range of the limestones tested.



$B = \text{SiO}_2, \%$ .

### 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 ( $\text{TiO}_2$ ), phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), and manganese oxide ( $\text{Mn}_3\text{O}_4$ ) 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  $\text{Fe}_2\text{O}_3$ . 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  $\text{Al}_2\text{O}_3$  analysis.

12.2 *Summary of Test Method*—In this test method, aluminum, iron, titanium, and phosphorus are precipitated from the filtrate after  $\text{SiO}_2$  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  $\text{SiO}_2$  (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  $\text{SiO}_2$ , 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  $\text{NH}_4\text{OH}$  (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 ( $\text{NH}_4\text{Cl}$ ) (see **Note 16**).

**NOTE 14**—The  $\text{NH}_4\text{OH}$  used to precipitate the hydroxides must be free of any dissolved carbon dioxide ( $\text{CO}_2$ ).

**NOTE 15**—At the neutral point, it usually takes 1 drop of  $\text{NH}_4\text{OH}$  (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  $\text{NH}_4\text{OH}$  (1 + 1).

**NOTE 16**—Two drops of methyl red indicator solution should be added to the  $\text{NH}_4\text{Cl}$  solution in the wash bottle followed by  $\text{NH}_4\text{OH}$  (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  $\text{NH}_4\text{OH}$  (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  $\text{NH}_4\text{OH}$  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  $\text{NH}_4\text{Cl}$ . 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:

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

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 ( $\text{FeS}_2$ ) 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  $\text{Fe}_2\text{O}_3$  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 ( $\text{K}_2\text{Cr}_2\text{O}_7$ ).

### 13.3 *Special Solutions:*

13.3.1 *Stannous Chloride Solution (50 g/L)*—Dissolve 5 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  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  $\text{SnCl}_2$  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  $\text{HgCl}_2$  in 100 mL of water.

13.3.4 *Potassium Dichromate, Standard Solution (0.05 N)*—Dry pure crystals of  $\text{K}_2\text{Cr}_2\text{O}_7$  at 110 °C, then pulverize and dry at 180 °C to constant weight. Dissolve 2.4518 g of pulverized  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and dilute to 1 L. This is a primary standard, 1 mL = 0.0040 g  $\text{Fe}_2\text{O}_3$ .

### 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 ( $\text{K}_2\text{S}_2\text{O}_7$ ). 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  $\text{H}_2\text{SO}_4$  (5 + 95). Add 5 mL of  $\text{H}_2\text{SO}_4$  (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  $\text{SiO}_2$  can then be added to the mass of  $\text{SiO}_2$  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  $\text{SiO}_2$  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  $\text{SnCl}_2$  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  $\text{SnCl}_2$  was added and the analysis must be repeated.

13.4.4 Add 5 mL of  $\text{H}_3\text{PO}_4$  and 3 drops of sodium diphenylamine sulfonate indicator.

13.4.5 Titrate with standard 0.05 N  $\text{K}_2\text{Cr}_2\text{O}_7$  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:*

$$\text{Fe}_2\text{O}_3, \% = (A/C) \times B \times 100 \quad (6)$$

where:

A =  $\text{K}_2\text{Cr}_2\text{O}_7$  used in titration, mL,

B = 0.004 ( $\text{Fe}_2\text{O}_3$  equivalent of  $\text{K}_2\text{Cr}_2\text{O}_7$ ), 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.<sup>6</sup> 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  $\text{SiO}_2$ , ignited in a platinum crucible and treated with HF and  $\text{H}_2\text{SO}_4$  to expel the  $\text{SiO}_2$  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 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.

<sup>6</sup> Sandel, E. B., *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience Publications, 1959.

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<sub>2</sub>O<sub>3</sub>)—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<sub>2</sub>O<sub>3</sub>)—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<sub>2</sub>O<sub>3</sub>.

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<sub>4</sub>OH (1 + 1) until the congo red indicator turns bright red, then add 1 drop of NH<sub>4</sub>OH (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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>4</sub>OH (1 + 1) until the congo red indicator turns a bright red, then add one drop of NH<sub>4</sub>OH (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<sub>2</sub>O<sub>3</sub> as follows:

$$\% \text{Fe}_2\text{O}_3 = \frac{C \times D}{W \times 10^4} \quad (7)$$

where:

*C* = concentration of Fe<sub>2</sub>O<sub>3</sub> 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 E691:

	Test Methods	Practice E691
	C25	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 E691.

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 <sub>2</sub> O <sub>3</sub>		Color		
	Average	<i>Sr</i>	<i>SR</i>	<i>r</i>	<i>R</i>
Material					
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<sub>2</sub>O<sub>3</sub>. When phosphorus or titanium are determined, their oxides must also be deducted.

15.2 *Procedure*—Subtract the percent Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>. In special cases where P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> need to be reported, a correction for these oxides must be made.

15.3 *Calculation*—Calculate the percent Al<sub>2</sub>O<sub>3</sub> as follows:

$$\text{Al}_2\text{O}_3, \% = A - B \quad (8)$$

where:

*A* = combined oxides (Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>), %, and

*B* = Fe<sub>2</sub>O<sub>3</sub>, %.

#### 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  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , filtered, ignited to the oxide, and redissolved with HCl. Any of the  $\text{NH}_4\text{OH}$  group of metals that escaped precipitation before may be recovered at this point by the addition of a small amount of  $\text{NH}_4\text{OH}$  and boiling. Any precipitate that separates out is assumed to be  $\text{Al}(\text{OH})_3$  and after ignition to  $\text{Al}_2\text{O}_3$  this amount is added to the mass of  $\text{Al}_2\text{O}_3$  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  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  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  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  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  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  (see Note 22). Reserve filtrate for the magnesium determination.

NOTE 22—Hot solutions should be avoided when washing the  $\text{CaC}_2\text{O}_4$  precipitate. One litre of hot water will dissolve 5 mg of CaO. One litre of cold 0.1 %  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  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  $\text{NH}_4\text{OH}$  till the color of indicator changes to yellow. Heat just to boiling. If a small amount of  $\text{Al}(\text{OH})_3$  separates, filter it, wash with a hot 2 % solution of  $\text{NH}_4\text{Cl}$ , ignite, weigh, and add this to the mass of  $\text{Al}_2\text{O}_3$  determined in 15.2.

16.4.3 Heat the filtrate to boiling and add slowly, while stirring, 35 mL of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  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:

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

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 ( $\text{KMnO}_4$ ) 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 ( $\text{Na}_2\text{C}_2\text{O}_4$ ) 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  $\text{H}_2\text{SO}_4$  (5 + 95) freshly boiled for 10 to 15 min and cooled to  $27 \pm 3$  °C. Stir until the oxalate has dissolved. Add 40 to 42 mL of the standard  $\text{KMnO}_4$  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  $\text{KMnO}_4$  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  $\text{KMnO}_4$  solution from the following: