



Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone¹

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1. Scope

1.1 This test method covers the X-ray emission spectrometric analysis of limestone, quicklime, hydrated lime, and hydraulic lime using wavelength dispersive instruments.

1.2 The values stated in SI units are to be regarded as the standard.

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.* Specific precautionary statements are given in Section 10.

2. Referenced Documents

2.1 ASTM Standards:

C 25 Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime²

C 50 Methods for Sampling, Inspection, Packing, and Marking of Lime and Limestone Products²

C 51 Terminology Relating to Lime and Limestone (As Used by the Industry)²

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals³

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials³

E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves³

E 456 Terminology Relating to Quality and Statistics⁴

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

E 1060 Practice for Interlaboratory Testing of Spectrochemical Methods of Analysis⁵

E 1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis⁵

2.2 NIST Documents:⁶

ANSI-NIST Handbook 114

NIST Standards Catalog

3. Terminology

3.1 Definitions:

3.1.1 *emission spectroscopy*—unless otherwise specified, for definitions of terms used in this test method pertaining to emission spectroscopy, refer to Terminology E 135.

3.1.2 *lime*—unless otherwise specified, for definitions of terms used in this test method pertaining to lime, refer to Terminology C 51.

3.1.3 *statistical*—unless otherwise specified, for definitions of terms used in this test method pertaining to statistics, refer to Terminology E 456.

4. Summary of Test Method

4.1 A briquetted powder specimen or a fused-glass disk specimen is irradiated by a high-energy X-ray beam. The secondary X rays produced are dispersed by means of crystals, and the intensities are measured by suitable detectors at selected wavelengths. Data are collected based on the time required to reach a fixed number of counts, total count for a fixed time, or integration of voltage for a fixed time. Concentrations of the elements are determined by relating the measured radiation of unknown specimens to analytical curves prepared from reference materials of known composition.

5. Significance and Use

5.1 This procedure is suitable for manufacturing control and verifying that the product meets specifications. It provides rapid, multi-element determinations with sufficient accuracy to ensure product quality and minimize production delays. The analytical performance data included may be used as a benchmark to determine whether similar X-ray spectrometers provide equivalent precision and accuracy, or whether the performance of a particular X-ray spectrometer has changed.

6. Interferences

6.1 Interelement effects or matrix effects may exist for some of the elements listed. One way to compensate for these effects is to prepare a series of calibration curves to cover the

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² *Annual Book of ASTM Standards*, Vol 04.01.

³ *Annual Book of ASTM Standards*, Vol 03.05.

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

⁵ *Annual Book of ASTM Standards*, Vol 03.06.

⁶ Available from National Institute for Standards and Technology (NIST), Gaithersburg, MD 20899.

designated concentration ranges. The composition of the specimen being analyzed must match closely the composition of the reference materials used to prepare the calibration curve. Mathematical corrections, derived from empirical relationships or fundamental parameter calculations, may be used alternatively. Any of these are acceptable, providing that the analytical accuracy required by this test method is achieved.

6.2 Calcium is the primary component of the matrix analyzed by this test method. The analyst must be aware of all possible interferences and matrix effects of this element. Orders of all wavelengths may cause interference, for example, the effect of $\text{CaK}\beta_1$ (2nd order) on $\text{PK}\alpha_1$.

6.3 Contamination from the grinding apparatus is an ever-present source of interference of which the analyst must always be cognizant. For example, stainless steel will impart iron, chrome, and nickel to the prepared sample.

6.4 Spectral interferences from the X-ray tube may also occur, for example, line overlap from $\text{CrK}\beta_1$ on $\text{MnK}\alpha_1$ caused by a chrome target tube.

7. Apparatus

7.1 Specimen Preparation Equipment:

7.1.1 *Jaw Crusher*, for initial crushing of lumps.

7.1.2 *Plate Grinder or Pulverizer*, with one static and one rotating disk for further grinding.

7.1.3 *Rotary Disk Mill or Shatter Box*, with hardened grinding containers and timer control for final grinding.

7.2 Briquetting Equipment:

7.2.1 *Briquetting Press*, capable of providing pressures up to 550 MPa (80 000 psi). The press shall be equipped with a mold assembly that provides a briquet compatible with the X-ray specimen holder.

7.3 Fusion Equipment:

7.3.1 *Furnace or Gas Burners*, with a timer, capable of heating the sample and flux to at least 1000°C and homogenizing the melt.

7.3.2 Fusion Crucibles:

7.3.2.1 *Vitreous Carbon or Graphite*, 20 to 30-mL capacity, with a flat bottom 30 to 35 mm in diameter.

7.3.2.2 *Platinum/Gold, 95 % platinum/5 % gold alloy*, 30 to 35-mL capacity.

7.3.2.3 *Platinum/Gold Casting Dish, 95 % platinum/5 % gold alloy*, 30 to 35-mL capacity, with a flat bottom 30 to 35 mm in diameter.

7.3.3 *Polishing Wheel*, suitable for polishing the fusion disk to obtain a uniform surface for irradiation. The analyst should be aware at all times of possible contamination from the polishing media used for surfacing the disk (6.3).

7.4 Excitation Source:

7.4.1 *X-Ray Tube Power Supply*, providing constant potential or rectified power of sufficient energy to produce secondary radiation of the specimen for the elements specified. The generator may be equipped with a line voltage regulator and current stabilizer.

7.4.2 *X-Ray Tubes*, with targets of various high-purity elements, capable of continuous operation at required potentials and currents, and that will excite the elements to be determined.

7.5 *Spectrometer*, designed for X-ray emission analysis and

equipped with specimen holders and a specimen chamber. The chamber may contain a specimen spinner, and it must be equipped for vacuum operation.

7.5.1 *Analyzing Crystals*—Flat or curved crystals with optimized capability for diffraction of the wavelengths of interest.

7.5.2 *Collimator*, for limiting the characteristic X rays to a parallel bundle when flat crystals are used in the instrument. A collimator is not necessary for curved crystal optics.

7.5.3 *Detectors*, sealed or gas flow, proportional type, Geiger counters, scintillation counters or equivalent.

7.5.4 *Vacuum System*, providing for the determination of elements whose radiation is absorbed by air (atomic number below 20). The system shall consist of at least one vacuum pump, gage, and electrical controls to provide automatic pumpdown of the optical path and maintain a controlled pressure, usually 13 Pa or less.

7.6 *Measuring System*, consisting of electronic circuits capable of counting or integrating pulses received from the detectors. The counts, count rate, or integrated voltages may be displayed on meters, recorders, digital counters, or voltmeters. The counts, count rates, or integrated voltages can also be presented to a computer or programmable calculator for conversion to percent concentration. Pulse height analyzers may be required to provide more accurate measurements for some measurements.

8. Reagents and Materials

8.1 *Purity and Concentration of Reagents*—The purity and concentration of chemical reagents shall conform to the requirements prescribed in Practices E 50.

8.2 *Binders*—Various binders have been used successfully to prepare briquettes suitable for presentation to the instrument. As a general rule, the binder should not contain an element that will be determined. In addition, the sample to binder ratio must be present in the analytical sample as in the reference materials that were used to establish the calibration.

8.3 *Fluxes*—Various fluxes have been used successfully to prepare fusion disks. The flux must be capable of dissolving or dispersing the analyzed elements in an homogeneous and reproducible fashion in the melt. The prepared disks must then be suitable for presentation to the instrument.

8.4 *Detector Gas (P-10)*, consisting of a mixture of 90 % argon and 10 % methane for use with gas flow proportional counters only.

9. Reference Materials

9.1 Certified reference materials are available from the National Institute for Standards and Technology (NIST) and other international certification agencies. Refer to Test Methods C 25 for a current listing.

9.2 Reference materials with matrixes similar to that of the test specimen and containing varying amounts of the elements to be determined may be used provided that they have been analyzed in accordance with ASTM standard test methods.

9.3 Standard additions method or spiked samples may also be used to create standards for which appropriate reference materials are not available for an element desired to be analyzed. The matrix material must match that of the test specimen.

10. Safety Precautions

10.1 Occupational health and safety standards for ionizing radiation shall be observed at all X-ray emission spectrometer installations. It is also recommended that operating and maintenance personnel follow the guidelines of safe operating procedures given in current handbooks and publications from the original equipment manufacturer, NIST, U.S. Government Printing Office, or similar handbooks on radiation safety. See NIST Standards Catalog and ANSI-NIST Handbook 114.

10.2 *Personnel*—X-ray equipment shall be used only under the guidance and supervision of a responsible, qualified person.

10.3 *Monitoring Devices*—Either film badges or dosimeters shall be worn by all operating and maintenance personnel. Periodic radiation surveys of the equipment for leaks and excessive scattered radiation shall be made by a qualified person using an ionization chamber detector to meet local, state, and federal radiation standards. The personal film badge survey record, the radiation survey record, and an equipment maintenance record shall be available upon request.

10.4 Special precautions for operators and maintenance personnel shall be posted at the equipment site.

10.5 Radiation caution signs shall be posted near the X-ray equipment and at all entrances to the radiation area.

10.6 Fail-Safe “X-ray on” warning lights shall be used on the equipment.

11. Sampling

11.1 Gross sample is to be taken in accordance with Methods C 50.

11.2 Sample preparation is to be performed in accordance with Methods C 50 and Test Methods C 25.

11.3 Special preparation may be required to grind the analytical sample finer than is required in 11.2.

12. Preparation of Reference Materials and Test Specimens

12.1 Treat reference materials and specimens exactly the same way throughout the procedure. Either briquetted powder or fused disk specimens may be used.

13. Preparation of Apparatus

13.1 Prepare and operate the spectrometer in accordance with the manufacturer’s instructions, using the parameters given in Table 1. Once established, control all instrument parameters closely to ensure repeatable analyses.

14. Calibration and Standardization

14.1 *Calibration (Preparation of Analytical Curves)*—Select a sufficient number of reference materials to cover the concentration ranges of the elements sought. Average duplicate intensity measurements of each reference material, and establish a calibration curve for each element in accordance with Practice E 305. Establish the curve by a least squares or multiple regression fit of the X-ray intensity measurements versus the corresponding weight percent concentrations of the element in the reference materials.

14.2 *Standardization (Analytical Curve Adjustment)*—Verify that the calibration curve for each element has not drifted using a control reference material. Drift is indicated by

TABLE 1 Analytical Lines and Crystals

Element	Wavelength, Å	Crystals
Sodium	11.91	TLAP, multilayer
Magnesium	9.889	ADP, TLAP, RAP, multilayer
Aluminum	8.338	PET, EDdT, RAP
Silicon	7.126	PET, EDdT, RAP, InSb
Phosphorus	6.155	Ge, PET
Sulfur	5.373	Ge, PET, NaCl
Chlorine	4.729	PET, Ge
Potassium	3.742	LiF 200, PET
Calcium	3.359	LiF 200, PET
Titanium	2.750	LiF 200, LiF 220
Manganese	2.103	LiF 200, LiF 220
Iron	1.937	LiF 200, LiF 220
Strontium	0.8766	LiF 200, LiF 220
Barium	2.775	LiF 200, LiF 220
Lead	1.175	LiF 200, LiF 220

a change in counts that exceeds the normal variation of counts for that element. A change of 1 % or greater usually signifies that the calibration curve for that element has drifted and should thus be adjusted. Re-measure the reference materials to verify that acceptable analyses are obtained after the adjustments are made.

15. Procedure

15.1 *Excitation*—Introduce the specimen into the specimen chamber, using care not to contaminate the surface to be excited. Produce the secondary fluorescence using the equipment used in 7.4.

15.2 *Radiation Measurements*—Obtain and record the counting rate measurement for each element. Either fixed count or fixed time modes may be used. A predetermined minimum count rate is obtainable only after unacceptable long counting times for lime materials, with the exception of the major oxides (Si, Fe, Al, Ca, and Mg). A minimum counting time of 60 s is acceptable.

15.3 *Spectral Interferences*—Some X-ray spectrometers will not resolve radiation completely from several line overlaps. Care must therefore be exercised in these cases. Alternate wavelengths without interference may be used. Otherwise, mathematical calculations must be used to correct for the interferences.

NOTE 1—If a goniometer is used, the setting for the 2θ peak must be determined experimentally within each laboratory. Periodic checks to verify the setting are advisable.

15.4 *Replicate Measurements*—Make a minimum of two measurements on each test specimen. The performance of an X-ray spectrometer is not improved significantly by making multiple measurements on the same surface of the same specimen; however, for those elements not having sufficient counts in the predetermined time, the statistics near the detection limit will improve with multiple exposures. Confidence in the accuracy of analysis will also improve by analyzing more than one specimen.

16. Calculation of Results

16.1 Determine the concentration of the various elements using the radiation measurements for the test specimen and the appropriate analytical curves.

16.2 If mathematical corrections must be made to correct

the concentrations for interelement effects, any one of a number of correction procedures may be used. Refer to the equipment manufacturer's manual for the instrument being used. Computers are normally interfaced to the X-ray spectrometers in laboratories using such correction systems. Refer to Guide E 1361 for a guide to interelement corrections.

NOTE 2—With computer-controlled X-ray spectrometers that convert output signals automatically to percent concentrations and make interelement corrections, calculated results are usually printed without operator involvement.

17. Precision and Bias

17.1 *Precision*—An acceptable number of laboratories tested this test method in accordance with Practice E 1060. Precision data are provided in the annex.

17.1.1 *Repeatability (R1)*—Calculations for within-laboratory precision are listed in the annex.

17.1.2 *Reproducibility (R2)*—Calculations for between-laboratory precision are listed in the annex.

17.2 *Bias (Accuracy)*—Bias data calculated in accordance with Practice E 1060 are included in the annex.

18. Keywords

18.1 chemical analysis; hydrated lime; hydraulic lime; limestone; quicklime; wavelength dispersive; X-ray spectrometric

ANNEX

(Mandatory Information)

A1. HIGH CALCIUM LIMESTONE BY THE BRIQUETTE METHOD

A1.1 Summary of Test Method:

A1.1.1 A briquetted powder specimen of high calcium limestone is prepared and irradiated as directed in Test Method C 1271.

A1.2 Provisions:

A1.2.1 There are no special provisions in the test method that are not referred to in Test Method C 1271.

A1.3 Precision and Bias:

A1.3.1 Round Robin—An interlaboratory study, consistent with the guidelines of Practice E 691, was conducted in 1997. Five high calcium limestone materials were analyzed by eight laboratories performing replicate measurements on four briquettes.

A1.3.2 Precision—The relative precision of this test method, characterized by repeatability (S_r and r) and reproducibility (S_R and R) has been determined for the materials and elements to be:

A1.3.2.1 Silicon as % Silicon Dioxide (% SiO₂):

Material	Average	S_r	S_R	r	R
S-1143	0.054	0.012	0.022	0.034	0.062
S-1145	0.156	0.009	0.048	0.026	0.133
S-1142	0.627	0.011	0.070	0.032	0.197
S-1141	0.875	0.026	0.084	0.071	0.234
S-1144	1.866	0.062	0.091	0.174	0.254

A1.3.2.2 Iron as % Ferric Oxide (% Fe₂O₃):

Material	Average	S_r	S_R	r	R
S-1143	0.0244	0.0013	0.0156	0.0038	0.0436
S-1145	0.0359	0.0018	0.0067	0.0050	0.0188
S-1141	0.1357	0.0023	0.0062	0.0064	0.0173
S-1142	0.1917	0.0021	0.0168	0.0058	0.0469
S-1144	0.8792	0.0137	0.0388	0.0383	0.1087

A1.3.2.3 Aluminum as % Aluminum Oxide (% Al₂O₃):

Material	Average	S_r	S_R	r	R
S-1143	0.0463	0.0015	0.0259	0.0042	0.0724
S-1145	0.0736	0.0040	0.0330	0.0111	0.0924
S-1142	0.1142	0.0030	0.0321	0.0083	0.0899
S-1141	0.1159	0.0036	0.0330	0.0102	0.0924
S-1144	0.4404	0.0163	0.0444	0.0457	0.1244

A1.3.2.4 Calcium as % Calcium Oxide (% CaO):

Material	Average	S_r	S_R	r	R
S-1144	53.347	0.150	0.295	0.421	0.826
S-1141	53.683	0.159	0.428	0.446	1.199
S-1142	54.304	0.127	0.359	0.356	1.006
S-1145	55.599	0.110	0.371	0.307	1.039
S-1143	55.837	0.143	0.284	0.401	0.794

A1.3.2.5 Magnesium as % Magnesium Oxide (% MgO):

Material	Average	S_r	S_R	r	R
S-1143	0.176	0.015	0.085	0.042	0.238
S-1145	0.216	0.006	0.085	0.017	0.237
S-1144	0.637	0.007	0.024	0.021	0.067
S-1142	0.919	0.010	0.039	0.028	0.109
S-1141	1.406	0.049	0.106	0.138	0.298

A1.3.2.6 Manganese as % Manganese (% Mn):

Material	Average	S_r	S_R	r	R
S-1145	0.0024	0.0003	0.0016	0.0009	0.0044
S-1143	0.0035	0.0003	0.0015	0.0009	0.0041
S-1142	0.0170	0.0036	0.0046	0.0101	0.0128
S-1141	0.0248	0.0003	0.0021	0.0007	0.0059
S-1144	0.0900	0.0004	0.0196	0.0011	0.0550

A1.3.3 Repeatability—The difference in absolute value between test results of the averages of two briquettes of the same sample, carried out separately and consecutively, in the same laboratory by the same operator using the same apparatus, may be expected to occur with a probability of approximately 0.95 (95 % confidence level). The repeatability limit for this test method is the following:

Silicon as % Silicon Dioxide (% SiO ₂)	0.009 + 0.081 x
Iron as % Ferric Oxide (% Fe ₂ O ₃)	0.0015 + 0.0411 x
Aluminum as % Aluminum Oxide (% Al ₂ O ₃)	0.1038 x
Calcium as % Calcium Oxide (% CaO)	0.386
Magnesium as % Magnesium Oxide (% MgO)	0.0751 x
Manganese as % Manganese (% Mn)	0.0027

where: x is the average of test results from two briquettes.

A1.3.4 Reproducibility—The difference in absolute value of replicate determinations, carried out in different laboratories using samples taken at random from a single sample prepared from the same bulk sample after the last stage of reduction, may be expected to occur with a probability of approximately 0.95 (95 % confidence level). The reproducibility limit for this test method is the following:

Silicon as % Silicon Dioxide (% SiO ₂)	0.109 + 0.093 x
Iron as % Ferric Oxide (% Fe ₂ O ₃)	0.0227 + 0.0963 x
Aluminum as % Aluminum Oxide (% Al ₂ O ₃)	0.0768 + 0.1104 x
Calcium as % Calcium Oxide (% CaO)	0.973
Magnesium as % Magnesium Oxide (% MgO)	0.1781 + 0.0174 x
Manganese as % Manganese (% Mn)	0.588 x

where: x is the average of test results.

A1.3.5 Bias—Certified reference materials are used for the calibration of this test method. No bias is expected for the method.

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