



Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) and Atomic Absorption (AA)¹

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1. Scope

1.1 The following test method covers the use of inductively coupled plasma-atomic emission spectroscopy (ICP) and atomic absorption spectroscopy (AA) in the analysis of major and trace elements in limestone and lime (calcined limestone).

1.2 Table 1 lists some of the elements that can be analyzed by this test method and the preferred wavelengths. Also see U.S. EPA Method 200.7 and 200.9.

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.*

2. Referenced Documents

2.1 ASTM Standards:

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

D 1193 Specification for Reagent Water³

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁴

E 863 Practice for Describing Atomic Absorption Spectrometric Equipment⁴

E 1479 Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers⁴

2.2 U.S. EPA Standards:

Methods for the Determination of Metals in Environmental Samples; U.S. EPA Methods 200.2, 200.7 and 200.9; Smoley, C. K., 1992⁵

Method 6010, Inductively Coupled Plasma Method, SW-846, Test Methods for Evaluating Solid Waste⁶

3. Terminology

3.1 Definitions—Definitions for terms used in this test

¹ This test method is under the jurisdiction of ASTM Committee C07 on Lime and is the direct responsibility of Subcommittee C07.05 on Chemical Uses.

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² Annual Book of ASTM Standards, Vol 04.01.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 03.05.

⁵ Available from CRC Press, 2000 Corporate Blvd., N. W., Boca Raton, FL 33431.

⁶ Available from U.S. Government Printing Office, Washington, DC 20402.

TABLE 1 Elements and Some Suggested Wavelengths^A

Major Elements	ICP Wavelength, nm	AA Wavelength, nm
Calcium	317.933 (315.887) ^B	422.7
Magnesium	279.079 (285.213)	285.2
Silicon	251.611 (288.160)	251.6
Aluminum	308.215 (309.271)	309.3
Iron	259.940	248.3
Manganese	257.610	279.5
Sodium	588.995 (589.59)	589.0
Potassium	766.491	766.5
Phosphorus	214.914 (213.618)	... ^C
Strontium	421.552	460.7
Trace Elements	ICP Wavelength, nm	AA Wavelength, nm
Antimony	206.833	217.6
Arsenic	193.696	193.7
Barium	455.403 (493.409)	553.6
Beryllium	313.042	234.9
Boron	249.773	249.8
Cadmium	226.502 (228.80)	228.8
Chromium	267.716 (205.552)	357.9
Cobalt	228.616	240.7 (242.5)
Copper	324.754	324.8
Lead	220.353	217.0 (283.3)
Molybdenum	202.030 (203.844)	313.3
Nickel	231.604 (221.647)	232.0
Selenium	196.090	196.0
Silver	328.068	328.1
Sulfur	180.731 (180.669)	... ^C
Thallium	190.864	276.8
Tin	189.989	235.5 (286.3)
Vanadium	292.402	318.4
Zinc	213.856 (202.551)	213.9

^A The suggested wavelengths may vary for your particular instrument.

^B Numbers in parentheses are alternate wavelengths.

^C Not recommended or not used.

method can be found in Terminologies C 51 and E 135.

3.2 Additional Definitions:

3.2.1 *total recoverable, n*—trace element concentration in an unfiltered sample after heating in acid.

3.2.2 *total digestion, n*—complete digestion of a sample, including silica and silicate minerals, using the fusion-flux method.

4. Summary of Test Method

4.1 A sample, digested by either fusion or acid, is atomized and passed into an excitation medium (a plasma in the case of ICP; a flame in the case of AA). The resulting ions are analyzed

by atomic spectroscopy. Elemental concentrations are determined by graphically relating the emission/absorption at specific wavelengths for an unknown sample to analytical curves made from reference standards of known composition.

5. Significance and Use

5.1 The presence and concentration of elements in lime and limestone is important in determining product quality and its suitability for various uses. This test method provides a means of measuring the major and trace element concentration in lime and limestone.

6. Interferences

6.1 *Chemical*—Chemical interferences, most common in AA, arise from the formation of molecular compounds that cause absorbances at the wavelength of interest. This molecular band spectral overlap can be minimized by buffering the sample with matrix modifiers (a Lanthanum additive, for example), using standard additions techniques, matrix matching or by careful selection of operating conditions (for example, using a hotter nitrous oxide/acetylene flame, selecting an alternate wavelength).

6.2 *Physical*—Physical interferences are the result of the inconsistencies in the introduction of the sample into the instrument, namely the transport and atomization/nebulization of the sample. These inconsistencies are a function of changing viscosity and surface tension, and are found primarily in samples of high-dissolved solids or high-acid concentrations. Physical interferences can be reduced by diluting the sample and by the use of a peristaltic pump.

6.3 *Spectral*—Spectral interference, most common in ICP, consists of overlapping and unresolved peaks. Computer software, along with the analysis of the suspected interfering element, can compensate for this effect. Using an alternate wavelength is also a solution. Another spectral interference is caused by background, both stray light and continuous spectrum (continuous argon spectrum, for example). Background correction adjacent to the analyte line will correct background spectral interference.

7. Apparatus

7.1 Spectrometer.

7.1.1 *Inductively Coupled Plasma Emission Spectrometer (ICP)*—Either a scanning sequential or multi-element simultaneous type ICP, with resolution appropriate for the elements to be analyzed. The optical path may be in air, vacuum or an inert gas. A detailed description of an ICP is given in Practice E 1479.

7.1.2 *Atomic Absorption Spectrometer (AA)*—An atomic absorption spectrometer consisting of single or double beam optics, a monochromator, photomultiplier detector, adjustable slits, a wavelength range from 190 to 800 nm, and provisions for interfacing with either a strip chart recorder or a computer. A simultaneous background correction system is also recommended. A detailed description of an AA is given in Practice E 863.

7.1.2.1 *Hollow Cathode Lamps*—Single hollow cathode lamps, one for each element. Multi-element hollow cathode lamps can be used but spectral interferences are possible.

8. Reagents

8.1 *Purity of Reagents*—Reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society as a minimum when such specifications are available.⁷ The high sensitivity of both the ICP and AA may require reagents of high purity. It is recommended that the reagents be of sufficiently high purity so as not to lessen the accuracy of the determination.

8.2 *Purity of Water*—At minimum, water should conform to Type II of Specification D 1193.

8.3 *Stock Solutions*—Standard stock solutions may be purchased or prepared from high purity metals or metal salts (Method 6010, SW-846; EPA Method 200.7 and 200.9). Salts should be dried at 105°C for 1 h, unless otherwise specified.

8.4 *Multi-element Calibration Standards*—ICP calibration is most often performed using multi-element calibration standards prepared from single element stock solutions. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Standards are combined in such a way that they are chemically compatible (no precipitation occurs) and do not cause spectral interferences. An example of multi-element combinations is given in EPA Method 200.7.

8.5 *Interference Check Sample*—Interference check samples are made from single element stock solutions at a concentration level equal to that of the samples to be analyzed.

8.6 *Calibration Blank*—A calibration blank is prepared at the same acid strength as that of the samples to be analyzed; usually 5 or 10 %. To prepare a 10 % nitric acid calibration blank, add one volume of nitric acid to nine volumes of water. This same blank can be used as the rinse solution for flushing the system between standards and samples.

8.7 *Reagent Blank*—The reagent blank contains all the reagents in the same concentrations (including nitric acid) as the samples to be analyzed. The reagent blank is carried through the same processes as a sample for analysis.

8.8 *Nitric Acid*—High purity nitric acid is recommended.

8.9 *Lithium Tetraborate (Li₂B₄O₇) Powder or Lithium Metaborate (LiBO₂) Powder.*

8.10 *Non-Wetting Agent*—Saturated solution of Hydrogen Bromide (HBr), Potassium Bromide (KBr) or Potassium Iodide (KI) as a non-wetting agent to prevent the flux from sticking to the crucible.

8.11 *Lanthanum Chloride (LaCl₃) Powder*—Lanthanum is added to samples for AA analysis as a releasing agent (for Calcium) and ionization suppressant (for Aluminum). When added to the sample solution, Lanthanum will preferentially react with potential interferents and “release” the analyte. In addition, the Lanthanum will preferentially ionize relative to Aluminum, aiding in the number of ground state Aluminum atoms. A typical Lanthanum additive is prepared by dissolving

⁷ *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

175 g LaCl₃ in 1 L of water (equivalent to 100 g/L Lanthanum).

9. Preparation of Apparatus

9.1 Prepare and operate the spectrometer in accordance with the manufacturer's instructions. The present method assumes that good operating procedures are followed. Design differences between spectrometers make it impractical to specify the required steps in detail here.

10. Calibration and Standardization

10.1 Allow a warm-up time of at least 30 min. Operate the spectrometer according to the operation manual for the instrument.

10.2 Calibrate the instrument by aspirating the blank and standards. A 10 % by volume HNO₃ rinse solution is aspirated for a minimum of 60 s between each standard. Most new systems are controlled by computer. The computer will establish the slope, intercept and correlation coefficients for each element. Some suggested wavelengths are given in Table 1 and EPA Methods 200.2, 200.7, and 200.9.

10.3 A peristaltic pump is recommended for aspirating standards and samples. The peristaltic pump will reduce physical interferences caused by changes in specimen viscosity and concentration (transport processes).

11. Sample Preparation

11.1 *Major Elements*—Samples for major element analysis are prepared for total digestion using lithium tetraborate or lithium metaborate as a flux. Major elements include Calcium, Magnesium, Silicon, Aluminum, Iron, Manganese, Sodium and Potassium. Trace elements such as Lead, Arsenic, Selenium and Antimony will partially volatilize using this fusion method and it is therefore not recommended for trace element analysis.

11.1.1 Take a representative minus 100 mesh sample split and dry at 105°C for 2 h.

11.1.2 Weigh 0.25 g of dried sample in a graphite or platinum crucible. Then weigh 1.00 g of lithium metaborate in the crucible. Add a few drops of non-wetting agent if needed. Mix the sample and lithium metaborate (the flux) well. Cover the mixed sample-lithium metaborate with an additional 0.50 g of lithium metaborate. This will give a total sample-flux ratio of 1:6.

11.1.3 Place a lid (optional) on the crucible prepared in 11.1.2 and place in a muffle furnace at 1000°C for 30 min. Gently agitate the molten contents of the crucible at least once during the 30 min heating.

11.1.4 Add 12.5 mL of concentrated nitric acid and 40 mL of water to a clean 250 mL wide-mouth plastic bottle.

11.1.5 When the 30 min heating in 11.1.3 is complete, quickly pour molten contents of the crucible into the plastic bottle described in 11.1.4. The water will bubble and sizzle. Quickly put the lid on the plastic bottle and shake. To aid in digestion place the bottle in a warm ultrasonic bath.

11.1.6 The contents of the plastic bottle can either be quantitatively transferred to a 250 mL volumetric flask and diluted to volume or diluted to volume by weight (that is, 1 mL = 1 g) in the same 250 mL plastic bottle it was digested in. Keep in mind, however, that the standards need to be made in

the same manner as the samples. Add 10 mL Lanthanum additive to samples for AA analysis (10 mL addition is part of the dilution to volume). Filtering is not necessary.

11.2 *Trace Elements*—Samples for trace element analysis are prepared using hydrochloric acid (1:5 or 1+4) and nitric acid (1:2 or 1+1). The trace elements concentrations determined by this method are termed "total recoverable" (that is, components not digested in hot acid are not recovered). Trace elements include, but are not limited to, Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Silver, Strontium, Thallium, Tin, Vanadium, and Zinc.

11.2.1 Take a representative minus 100 mesh sample split and dry at 105°C for 2 h.

11.2.2 Weigh 1.00 g of dried sample and transfer to a clean beaker.

11.2.3 Add 10 mL of dilute hydrochloric acid (see 11.2) and 4 mL of dilute nitric acid (see 11.2). In the case of limestone, add the acids slowly so that the powdered sample will not splatter on the sides of the beaker during its effervescent reaction with the acid. Cover the sample (a ribbed watch glass is best) and place on a hot plate. Heat at approximately 85°C for 30 min. Boiling should be kept to a minimum. After 30 min allow the sample to cool. Then quantitatively transfer the liquid and any undissolved residue to a 100 mL volumetric flask. Dilute to volume.

12. Procedure

12.1 Aspirate the specimens prepared in Section 11 into the AA or ICP using the same conditions used during calibration.

12.2 Analyze the instrument check standards, blanks and internal control samples at a 10 % or better frequency. The results on the instrument check standards are to be within 10 %, and the internal control specimens should fall within established limits of deviation. If the results exceed these limits, investigate the cause and take corrective action.

12.3 It is recommended that 10 % of the samples analyzed be duplicates. Process duplicates through the same dissolution and analysis procedures as any other sample. The results should fall within established limits of deviation. If the results exceed these limits, investigate the cause and take corrective action. The applicability of duplicate analysis data as a measure of analytical and sampling reproducibility assumes specimen homogeneity.

12.4 Analyze an interference check specimen at the beginning and the end of each specimen run or a minimum of twice per 8 h work shift, whichever is more frequent. This check specimen should contain, in relatively high concentration, those elements which are expected to be present at significant levels in the samples and which are known interfering species. All other elements should be present at relatively low levels in order to assess the quality of interference corrections.

12.5 Use the background and interference corrected data to calculate the concentration of each element. This calculation, including the dilution factor, is performed by the computer.

13. Precision and Bias

13.1 Participation in a round robin is anticipated.

14. Keywords

14.1 atomic absorption; atomic emission spectroscopy; digestion; dissolution; inductively coupled plasma; lime; limestone; spectrometer; trace elements

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