FERTILIZER METHODS

Chapter

SECONDARY/MICRONUTRIENT ANALYSIS

Subject

Dolomite/Limestone-AA

SCOPE: This is an analytical procedure for the determination of calcium carbonate and magnesium carbonate in dolomite and limestone.

PRINCIPLE:

In this method, total calcium and magnesium content is determined by atomic absorption (AA). For dolomite, the calcium concentration is converted to % calcium carbonate ($CaCO_3$) and magnesium concentration is converted to % magnesium carbonate ($MgCO_3$). Samples are digested in concentrated HC1 and brought to volume with deionized H_2O. Sample solutions are aspirated into a flame to disassociate the chemical compounds into free atoms. By measuring the amount of light absorbed, a quantitative determination of the amount of calcium or magnesium present can be made at the specific wavelength for calcium/magnesium.

The EDTA titration method (AOAC Colorimetric Method) is reviewed in this method.

SAFETY: Each laboratory is responsible for maintaining a current file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

APPARATUS & EQUIPMENT:

- Perkin Elmer AAnalyst 100 Atomic Absorption Spectrometer (or equivalent)
- Hamilton Digital Diluter (optional, or equivalent pipets)
- Volumetric flasks (Class “A” glassware) 200 mL, 1 L and 3 L
- Culture tubes (16 x 125 mm or equivalent)
- Vortex shaker
- Seraclear filters (Westco) or equivalent filter paper
- Pipets (Class "A") 2 mL, 3 mL, 10 mL and 20 mL
- Ultraviolet light source - calcium analysis (EDTA titration)
- Buret 50 mL
- Beakers 250 mL
- Magnetic stirrer and stirring bars

REAGENTS & CHEMICALS:

- Deionized H_2O
- Hydrochloric Acid (concentrated HCl)
- Calcium Stock Standard (1000 ppm-certified): Prepare a 20 ppm calcium standard by pipetting 20 mL of a 1000 ppm calcium standard into a 1 L volumetric flask and adding 200 mL of lanthanum oxide stock solution. Bring to volume with deionized H_2O and mix (AA analysis).
- Magnesium Stock Standard (1000 ppm-certified): Prepare a 2 ppm magnesium standard by pipetting 2 mL of a 1000 ppm magnesium stock standard into a 1 L volumetric flask and adding 200 mL of lanthanum oxide stock solution. Add 3 mL of the 1000 ppm calcium standard to the solution. Bring to volume with deionized H_2O and mix (AA analysis).
- NBS 88B Standard (dolomitic limestone): $\%CaCO_3$ - 53.45, $\%MgCO_3$ - 43.99. Weigh 0.5000 g of the dried (4 hours at 100^0C) NBS88B standard into a 200 mL volumetric flask, add 20 mL of conc. HC1 and digest for 30 minutes. Cool to room temperature, fill to volume with deionized H_2O and mix. Make a 1/10 dilution of this standard and bring to volume with deionized H_2O.
- NBS 1C Standard (limestone): $\%CaCO_3$ - 89.78. Weigh 0.5000 g of the dried (4 hours at 100^0C) NBS 1C standard into a 200 mL volumetric flask, add 20 mL of conc. HC1 and digest for 30 minutes. Cool to room temperature, fill to volume with deionized H_2O and mix. Make a 1/10 dilution of this standard and bring to volume with deionized H_2O.
- 0.4% EDTA Standard Solution: Dissolve 4 g of ethylenediamine tetraacetic acid, tetrasodium salt in 1 L of deionized water and mix thoroughly.
- $CaCO_3$ Buffer Solution: Dissolve 840 g KOH and 198 g KCN in 2 L of deionized H_2O and dilute to a total volume of 3 L with deionized H_2O.
- $MgCO_3$ Buffer Solution: Dissolve 202.2 g NH_4C1 and 60 g KCN in 1200 mL of deionized H_2O, add 1.71 L of NH_4OH and dilute to 3 L with deionized H_2O.
- Calcine Modified II Indicator Powder: Calcine + Bromthymol Blue + Potassium Chloride. Purchased from GFS Chemicals.
- Erichrome Black-T Indicator Solution: Dissolve 0.2 g of the indicator powder in 50 mL of absolute methyl alcohol containing 2 g of hydroxylamine hydrochloride. Make fresh indicator solution every month.
- Lanthanum Oxide (La_2O_3) Stock Solution: Dissolve 117.3 g of La_2O_3 (99.99%) in 500 mL of conc. HC1 and bring to volume with deionized H_2O in a 2 L volumetric flask. Cool to room temperature, fill to volumetric mark and mix.
- Lanthanum Oxide (La_2O_3) Working Diluent: Dilute 600 mL of the lanthanum oxide stock solution with deionized H_2O to make a final volume of 3 L.

SAMPLE HANDLING: For samples having a considerable amount of "free-floating" trash in the flask, pour a portion of the sample into a culture tube and filter solution through a seraclear filter.

SAMPLE PREPARATION:

Take a 100 g portion from original sample and dry at 106°C for 4 hours. Do not dry over 106°C. The moisture factor is recorded in the gypsum moisture log as well as on the sample work card. Transfer dried portion (100 g) to a clean, dry 8 ounce sample bottle and regrind sample.

Weigh 0.5000 g of dried sample into a 200 mL volumetric flask.

Add 20 mL of concentrated HCl to each sample and digest sample for 30 minutes (do not allow sample to go dry). Add approx. 15 mL of 1:1 (v/v) HC1/ deionized H_2O to sample if it is close to dryness.

Cool to room temperature, bring to volume with deionized H_2O and shake.

SAMPLE ANALYSIS:

Atomic Absorption (AA)

Make appropriate dilution and analyze on AA:

Element	Dilution
Ca	1/50
Mg	1/250 (first take 1/10 dilution and then a 1/25 dilution of the 1/10 dilution)

Samples and standards (NBS std.) are diluted with lanthanum oxide (La_2O_3) working diluent solution.

Blanks used in atomic absorption calibration are treated with same dilution as the Ca analysis.

The following AA spectrometer parameters are used for Ca/Mg analysis (listed under the instrument conditions for calcium and magnesium methods): **Burner Head Angle** - 30^0/Straight, **Acetylene Flow** - 1.6/1.2 (liters/min), **Air Flow** - 14.0/14.2 (liters/min), **Bandwidth(nm)** - 0.7/0.7, **Wavelength** - 422.7/285.1.

EDTA TITRATION:

Pipet a 10 mL aliquot from the sample into a 250 mL beaker for the calcium titration. Pipet a 10 mL aliquot from the sample into a 250 mL beaker for the magnesium titration.

Add 100 mL of deionized H_2O to each beaker.

For calcium titration, add 10 mL of $CaCO_3$ buffer solution and 35 mg of calcine indicator. This should produce a green fluorescent color. Place under a UV light

source and titrate with the standardized EDTA solution while stirring. The endpoint is the point where all fluorescent color is completely gone.

For magnesium titration, add 7 mL of the $MgCO_3$ buffer solution and 10 drops of the Erichrome black-T indicator. This solution should give a wine red color. Titrate with the EDTA titration, while stirring, to an endpoint of permanent pure blue color.

For EDTA Titration: To standardize the EDTA solution for calcium and magnesium titration, take two 10 mL aliquots of the NBS 88B and 1C standard from the calcium standard prep and titrate it as described under sample analysis. The calcium titration gives the **Titer Ca value** for a dolomite and limestone. Take two 10 mL aliquots of the NBS 88B from the calcium standard prep again and titrate it as described under sample analysis for the magnesium titration. This gives the **Titer Mg value** (see EDTA titration analysis).

CALCULATIONS:

AA ANALYSIS:

$\%CaCO_3$ found = (NBS factor) x [ppm reading (for sample)] x 0.5000 / (sample weight)
NBS factor = 53.45 or 89.78/ [ppm reading from AA analysis (NBS std)]

$\%MgCO_3$ found = (NBS factor) x [ppm reading (for sample)] x 0.5000 / (sample weight)
NBS factor = 43.99/ [ppm reading from AA analysis (NBS std)]

NOTE: Remember to use the correct NBS factor for a dolomite or limestone sample.

EDTA TITRATION ANALYSIS:

$\%\ CaCO_3$ = (titer Ca) (mL EDTA) (200 mL/10 mL) (100.09/40.08) * 100 / (0.5 g)
= (titer Ca) (mL EDTA) (9.982)

$\%\ MgCO_3$ = (titer Mg) [(mL EDTA Ca+Mg)- (mL EDTA Ca)] (200mL/10mL) (84.32/24.32) * 100 / (0.5 g)
= (titer Mg) (net mL of EDTA titration)(13.870)

CORRECTION FACTOR FOR MOISTURE FOUND IN SAMPLE
Analytical results reported are "dry basis." If the sample "as received" contains more moisture than the maximum guaranteed (**15**%), analytical results shall be corrected for the amount of moisture present in excess of the guarantee.

$$\frac{100 - \%\ \text{Moisture "as received"}}{100 - \%\ \text{Moisture "guaranteed"}} = \mathbf{W}\ \text{(correction factor)}$$

MECHANICAL TEST FACTORS (See Appendix – SOP Sample Preparation)

Applicable only to sieve tests below guarantee.

(a) Correction for 50 mesh sieve test:
% passing 50 mesh sieve =
% guarantee
(b) Correction for 20 mesh sieve:
% passing 20 mesh sieve =
% guarantee
(c) Correction for 8 mesh sieve test:
% passing 8 mesh sieve =
% guarantee

MOISTURE TEST CORRECTION FOR PURPOSE OF PENALTY ASSESSMENTS

The percentage calcium carbonate or magnesium carbonate found is converted to "corrected basis" by multiplying by the factor "**W**" above as applicable, i.e.:

$\%CaCO_3$ or $MgCO_3$ x W = $\%CaCO_3$
or $\%MgCO_3$ corrected for purposes of penalty assessment

APPROVAL:

Approved by:  **Date: 5/13/03**
Signature

Bureau Chief
Title

METHOD REVISION HISTORY:

Version	Date	Description	Author
Original	5/12/03	Original	W. Bell

REFERENCE:

AOAC 16th Edition, *Method 965.09*