FERTILIZER METHODS

Chapter

SECONDARY/MICRONUTRIENT ANALYSIS

Subject

Dolomite, Limestone or Gypsum ~ ICP

SCOPE: This is an automated analytical procedure for the determination of total magnesium in dolomite and limestone and the determination of total calcium in dolomite, limestone and gypsum samples by inductively coupled plasma optical emissions spectrometer (ICP-OES).

PRINCIPLE: ICP-OES determination of total magnesium and calcium in fertilizer is achieved by measuring the amount of light emitted by the analyte or analytes in an inductively coupled plasma. A quantitative determination of the amount of analyte or analytes present can be made at the specific wavelength or wavelengths emitted by each analyte. Dolomite, limestone and gypsum samples are prepared by digesting the dried sample with 20 mL of certified American Chemical Society (A.C.S.) grade concentrated hydrochloric acid for 30 minutes. The solution is brought to volume, filtered, diluted and analyzed using Yttrium as the internal standard. In dolomite and limestone samples, the calcium content is converted to percent calcium carbonate ($CaCO_3$) and the magnesium is converted to percent magnesium carbonate ($MgCO_3$). In gypsum samples, the calcium content is converted to percent calcium sulfate ($CaSO_4$). The total calcium found in the gypsum sample often comes from multiple sources (calcium sulfate as well as calcium carbonate etc.). Therefore, the lower of the two values (total calcium or combined sulfur), after conversion, is used as the true calcium sulfate result. The ethylenediaminetetraacetic acid (EDTA) titration method is reviewed at the end of this method.

SAFETY: Each laboratory is responsible for maintaining a current file of the Occupational Safety and Health Administration (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:

- Balance, (accuracy to 0.001 g)
- UV lamp (Model: UVGL – 58) or equivalent
- Hamilton digital diluter (Microlab 500) or equivalent
- Vortex shaker (Fisher Vortex Genie 2) or equivalent
- Hydrochloric acid fume hood

- Hotplate (Thrifty Model #3) or equivalent
- Peristaltic pump (Perkin-Elmer) or equivalent
- Air compressor
- Chiller (Neslab CFT – 33) or equivalent
- Auto sampler (Perkin-Elmer AS-93 plus) or equivalent
- Perkin-Elmer WinLab 32 software or equivalent
- Inductively coupled plasma optical emissions spectrometer (Perkin-Elmer ICP-OES 3300 DV) or equivalent
- Volumetric flask, 200 mL, 1 L & 3 L (class "A")
- Beakers, 250 mL
- Graduated cylinder, 50 mL (class "A")
- Bottle, 8-ounce
- Burette, 50 mL (class "A")
- Pipets as required (class "A")
- Nalgene plastic bottle or equivalent
- Stopper, for 200 mL volumetric flask
- Disposable culture tube (16 x 125 mm) or equivalent
- Disposable centrifuge tube (50 mL) or equivalent
- Filter paper (Whatman 113V grade or better)
- Pump tubes
  A. Red-Red (0.045 ID) or equivalent
  B. Black-Black (0.030 ID) or equivalent
  C. Purple-Purple (0.110 ID) or equivalent

REAGENTS & CHEMICALS:

- Deionized (D.I.) water q.s.
- Tetrasodium EDTA Certified A.C.S. grade or equivalent
- Hydrochloric acid (HCl) Certified A.C.S. grade or equivalent – Caution: Strong acid. Avoid breathing vapors and skin contact. Use in a fume hood and wear protective equipment
- NBS 88B Standard (dolomite) - % $CaCO_3$ = 53.45, % $MgCO_3$ = 43.99

  Weigh 0.500 g of the dried (4 hours at 100°C) NBS 88B standard into a 200 mL volumetric flask, add 20 mL of concentrated HCl and digest for 30 minutes. Cool to room temperature, fill to volume with deionized water and mix well. Make a 1/10 dilution of this standard and bring to volume with deionized water.
- NBS 1C Standard (limestone) - % $CaCO_3$ = 89.78

  Weigh 0.500 g of the dried (4 hours at 100°C) NBS 1C standard into a 200 mL volumetric flask, add 20 mL of concentrated HCl and digest for 30 minutes. Cool to room temperature, fill to volume with deionized water and mix well. Make a 1/10 dilution of this standard and bring to volume with deionized water.

- Stock standards

  A. Calcium stock standard - 1000 ppm Ca in 2% Nitric acid.
  B. Copper stock standard - 1000 ppm Cu in 2% Hydrochloric acid
  C. Iron stock standard - 1000 ppm Fe in 2% Hydrochloric acid
  D. Magnesium stock standard - 1000 ppm Mg in 2% Nitric acid
  E. Manganese stock standard – 1000 ppm Mn in 2% Nitric acid
  F. Molybdenum stock standard – 1000 ppm Mo in distilled water
  G. Yttrium stock standard – 1000 ppm Y in 2% Nitric acid
  H. Zinc stock standard – 1000 ppm Zn in 2% Hydrochloric acid
  I. Quality check 1 stock standard – 1000 ppm (Al, Ca, Co, Cu, Fe, Mn, Mo, Zn) in 1% Hydrochloric acid
  J. Quality check 2 stock standard – 100 ppm (Ca, Co, Cu, Fe, Mg, Mn, Mo, Zn) in 5% Nitric acid
  K. Laboratory internal standard – 2000 ppm (Ca, Cu, Fe, Mg, Mn, Zn), 500 ppm Mo in 5% Hydrochloric acid

- Calibration standard FSF ICP #4

Calcium stock standard	5.0 g
Copper stock standard	2.5 g
Iron stock standard	5.0 g
Magnesium stock standard	5.0 g
Manganese stock standard	2.5 g
Molybdenum stock standard	2.5 g
Zinc stock standard	2.5 g
2% Hydrochloric acid	75.0 g

  Weigh 5.0 g each of Calcium stock standard, Iron stock standard, Magnesium stock standard and 2.5 g each of Copper stock standard, Manganese stock standard, Molybdenum stock standard, and Zinc stock standard into a 150 mL Nalgene plastic bottle. Weigh 75.0 g of 2% hydrochloric acid into the bottle and mix well.

- Calibration standard FSF ICP #3

Calibration standard FSF ICP #4	20.0 g
2% Hydrochloric acid	80.0 g

  Weigh 20.0 g of calibration standard FSF ICP #4 and 80.0 g of 2% hydrochloric acid into the 150 mL Nalgene plastic bottle. Mix well.

- Calibration standard FSF ICP #2

Calibration standard FSF ICP #3	25.0 g
2% Hydrochloric acid	75.0 g

  Weigh 25.0 g of calibration standard FSF ICP #3 and 75.0 g of 2% hydrochloric acid into the 150 mL Nalgene plastic bottle. Mix well.

- Calibration standard FSF ICP #1

Calibration standard FSF ICP #2	20.0 g
2% Hydrochloric acid	80.0 g

  Weigh 20.0 g of calibration standard FSF ICP #2 and 80.0 g of 2%

hydrochloric acid into the 150 mL Nalgene plastic bottle. Mix well.

- Quality check standard 1 (QC 1)

  Quality check 1 stock standard 1.0 g
  2% Hydrochloric acid 99.0 g
  Weigh 1.0 g of quality check 1 stock standard and 99.0 g of 2% hydrochloric acid into the 150 mL Nalgene plastic bottle. Mix well.

- Quality check standard 2 (QC 2)

  Quality check 2 stock standard 1.0 g
  2% Hydrochloric acid 99.0 g
  Weigh 1.0 g of quality check 2 stock standard and 99.0 g of 2% hydrochloric acid into the 150 mL Nalgene plastic bottle. Mix well.

- Potassium cyanide (KCN) Certified A.C.S. grade or equivalent
- Potassium hydroxide (KOH) Certified A.C.S. grade or equivalent
- Ammonium chloride (NH_4Cl) Certified A.C.S. grade or equivalent
- Ammonium hydroxide (NH_4OH) Certified A.C.S. grade or equivalent
- $CaCO_3$ buffer solution

  KOH 840.0 g
  KCN 198.0 g
  Deionized water 2.0 L
  Weigh 840 g of KOH and 198 g of KCN into 2 L of deionized water. Dissolve and bring to volume (3 L) with deionized water and mix well.

- $MgCO_3$ buffer solution

  NH_4Cl 202.2 g
  KCN 60.0 g
  Deionized water 1200 mL
  NH_4OH 1710 mL
  Weigh 202.2 g of NH_4Cl and 60.0 g of KCN into 1200 mL of deionized water. Dissolve and add 1710 mL of NH_4OH and bring to volume (3 L) with deionized water and mix well.

- Calcine modified II indicator powder (GFS)
- Methyl alcohol
- Eriochrome Black-T, indicator grade (ACROS)
- 3% Hydroxylamine hydrochloride (Lab. Chem, Inc.)
- Eriochrome Black-T indicator solution

  Eriochrome Black-T 0.2 g
  Methyl alcohol 50 mL
  3% Hydroxylamine hydrochloride 2.0 g
  Weigh 0.2 g of Eriochrome Black-T indicator in 50 mL of absolute methyl

alcohol containing 2 g of hydroxylamine hydrochloride. Mix well. Make fresh indicator solution every month.

- 0.4 % EDTA Standard solution

Tetrasodium EDTA	4.0	g
Deionized water	1.0	L

  Weigh 4.0 g of tetrasodium EDTA to 1.0 L of deionized water. Dissolve and mix well.
- 2% Hydrochloric acid solution

Hydrochloric acid	20	mL
Deionized water	980	mL

  Add 20 mL hydrochloric acid to 400 mL deionized water and dilute to 1 liter.
- 1:1 Hydrochloric acid/water (v/v) solution

Hydrochloric acid	250	mL
Deionized water	250	mL

  Add 250 mL hydrochloric acid to 250 mL deionized water.

SAMPLE HANDLING:

Note: The moisture content is calculated back into the final percent found calculation. Grind the dried portion of the sample to obtain a uniform sample.

SAMPLE PREPARATION:

1. 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 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.
2. Weigh 0.5 g of sample and internal standard solution directly into 200 mL volumetric flask.
3. Add 20mL of concentrated hydrochloric acid directly to each sample and digest sample for 30 minutes on hotplate (do not allow the sample to go dry). Add approximately 15 mL of 1:1 HCl/water (v/v) to sample if it is close to dryness.
4. Allow sample to cool to room temperature and bring to volume with deionized water and shake well.
5. An internal standard is weighed with each set to check the method and dilution steps.
6. Filter the samples with (Whatman Filter paper 113V grade or better) if needed.
7. Make appropriate dilutions and analyze in ICP-OES.

SAMPLE ANALYSIS:

See: BUREAU OF FEED, SEED & FERTILIZER LABORATORIES, STANDARD OPERATING PROCEDURES, SYSTEM START-UP

PERKIN-ELMER ICP-OES 3300 DV

QA/QC:

The correlation coefficient (calibration standard) should be 0.999 or better.

CALCULATIONS:

Dolomite & Limestone

$CaCO_3$ found (%) =

NBS factor * [ppm reading (ICP)] * (flask volume) * dilution factor * 100/ (sample weight) (10^6 mcg/g)
NBS factor = 53.45 or 89.78 / ppm reading (ICP) of NBS standards
$MgCO_3$ found (%) =

NBS factor * [ppm reading (ICP)] * (flask volume) * dilution factor * 100/ (sample weight) (10^6 cg/g)
NBS factor = 43.99 / ppm reading (ICP) of NBS standards

Gypsum

% $CaSO_4$ = (%S) * (S conversion factor) * ((100 - %moisture)/(100))
or
% $CaSO_4$ = (%Ca) * (Ca conversion factor) * ((100 - %moisture)/(100))
Conversion factor (Ca --------> $CaSO_4$) = 3.3968
Conversion factor (S --------> $CaSO_4$) = 4.2465
NOTE: Conversion factor (SO_4 --------> S) = 27.424

EDTA TITRATION:

NOTE: A wet chemistry confirmation is used to confirm initial ICP setup or method integrity.

1. Pipet two 10 mL aliquot from the sample into two 250 mL beakers for the calcium and magnesium titration.
2. Add 100 mL of deionized water to each beaker.
3. 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 the beaker under a UV light source and titrate with the standardized EDTA solution while stirring.
4. The endpoint is when all the fluorescent color is completely gone.
5. For magnesium titration, add 7 mL of the $MgCO_3$ buffer solution and 10 drops of the Eriochrome black-T indicator. This should give a wine red color. Titrate with the EDTA solution, while stirring, to an endpoint of permanent pure blue color.
6. For EDTA titration: To standardize the EDTA solution for calcium and magnesium titration, take two 10 mL aliquots of the NBS 88B and NBS 1C standard from the

standard preparation and titrate it as described under sample analysis. The calcium titration gives the titer calcium value for a dolomite and limestone. Take two 10 mL aliquots of the NBS 88B from the calcium standard preparation again and titrate it as described under sample analysis for the magnesium titration. This gives the titer magnesium value (see EDTA titration analysis).

EDTA TITRATION ANALYSIS:

1. % $CaCO_3$ = (titer Ca) * (mL EDTA) * (200 mL/10 mL) * (100.09/40.08) * 100/ 500 mg = (titer Ca) * (mL EDTA) * 9.982
2. % $MgCO_3$ = (titer Mg) * [(mL EDTA for Ca + Mg) – (mL EDTA for Ca)] * (200 mL/10 mL) * (84.33/24.32) * 100/500 mg
   = (titer Mg) * (net mL of EDTA) * 13.870

CORRRECTION 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.

(100 - % moisture "as received") / (100 - % moisture "guaranteed") = W (correction factor)

% $CaCO_3$ * W = % $CaCO_3$ corrected for purpose of penalty assessment

% $MgCO_3$ * W = % $MgCO_3$ corrected for purpose of penalty assessment

APPROVAL:

Approved by: Leigh Humphreys **Date: 12/4/02**

Signature

Bureau Chief

Title

METHOD REVISION HISTORY:

Version	Date	Description	Author
Original	12/04/02	Original	Ging-Hoen Huang

REFERENCE:

AOAC 16th Edition, *Method 965.09 and 962.01*