FERTILIZER METHODS

Chapter

SECONDARY/MICRONUTRIENT ANALYSIS

Subject

Zinc – Soluble ~ AA

SCOPE: This is an automated analytical procedure for the determination of soluble zinc in mixed or pure material fertilizers. Some examples of soluble zinc sources used in fertilizers are: zinc (II) sulfates, chlorides, nitrates and sucrates.

PRINCIPLE:

Samples are extracted in a pH 6.0 buffer solution, brought to volume with deionized water and shaken. After appropriate dilution, samples are analyzed by atomic absorption (A.A.) spectroscopy. By measuring the amount of light absorbed (at the specific wavelength), a quantitative determination of the amount of zinc present can be made. The pH 6.0 buffer is a composite of a 0.24M Bis (hydroxymethyl)-2,2',2"-nitrilotriethanol ($C_8H_{19}NO_5$) and hydrochloric acid (HCl). Zinc oxides (ZnO) are slightly soluble (10-13%) at this pH level but do not generally give a positive bias. This extraction solution insures that all of the soluble zinc sources are fully recoverable. There is no significant loss of soluble zinc due to the presence of soluble phosphates during the extraction process. The most probable reaction between the soluble micronutrient and the phosphate salt is a recombination reaction which forms a stable (reciprocal) salt pair. This reaction proceeds in an irreversible manner to near completion in which the salt pair is of much lower solubility than the original compounds.

$MeSO_4 + (NH_4)_2HPO_4 \text{ ----> } MeNH_4PO_4 + NH_4HSO_4$
(DAP)

$MeSO_4 + (NH_4)_4P_2O_7 \text{ ----> } Me(NH_4)_2P_2O_7 + (NH_4)_2SO_4$
Ammonium Polyphosphate
(pyrophosphates)

($Me = Mn^{+2}, Cu^{+2}, Fe^{+2}, Zn^{+2}$)

This particular reaction has been documented in Lehr (1972), where he listed a number of such reactions that may take place during the manufacture or storage of fertilizers. Many reactions require only water which is attracted to the hygroscopic fertilizer ingredients. Logic tells us that if a reaction can happen in a bulk product, it can happen when the materials are put into solution for analysis. This must be avoided during analytical procedures.

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:

- Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrometer with associated hardware and software (or equivalent)
- Balance, (accuracy to 0.001 g)
- Hamilton Digital Diluter or equivalent pipets
- Volumetric flasks (Class A 200 mL, 500 mL and 1 L)
- Acid fume hood
- Plastic funnel
- Culture tubes (16 x 125 mm, or equivalent)
- Vortex shaker
- Filter paper (Whatman 113V grade or better)
- pH meter, (accuracy to 0.01 pH units)

REAGENTS & CHEMICALS:

- Deionized (D.I.) water q.s.
- 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.**

  1:1 Hydrochloric acid/water (v/v) solution

  Hydrochloric acid, conc. 250 mL

  Deionized water q.s.

  Add 250 mL conc. hydrochloric acid to approximately 200 mL deionized water in 500 mL volumetric flask, bring to volume with D.I. water and mix well.
- Sodium hydroxide (NaOH) NF/FCC grade or equivalent - **Caution: Avoid breathing vapors and skin contact. Use in a fume hood and wear protective equipment.**

  1:1 Sodium hydroxide/water (w/w) solution

  Sodium Hydroxide, pellets 250 g

  Deionized water q.s.

  Add 250 g sodium hydroxide pellets to approximately 200 mL deionized water in 500 mL volumetric flask, bring to volume with D.I. water and mix well.

- Certified Buffer Solutions, pH 4 - used for pH meter calibration
- Certified Buffer Solutions, pH 7 - used for pH meter calibration
- Disodium EDTA ($Na_2C_{10}H_{14}O_8N_2 \bullet 2H_2O$) Certified A.C.S. grade or equivalent

  10% (w/v) disodium EDTA ($Na_2C_{10}H_{14}O_8N_2 \bullet 2H_2O$) Extraction Solution: Dissolve 100 g of disodium EDTA into 900 - 950 mL of hot deionized water. Bring volume to 1 L with D.I. water and mix well.
- Bis (hydroxymethyl)-2,2',2"-nitrilotriethanol ($C_8H_{19}NO_5$)- 99+%

  0.24M Bis (hydroxymethyl)-2,2',2"-nitrilotriethanol ($C_8H_{19}NO_5$)- Extraction Solution: Dissolve 50 g of Bis(hydroxymethyl)-2,2',2"-nitrilotriethanol in 700 mL of deionized water. Add 4 mL of concentrated HCl and mix well. Calibrate pH meter. Verify final pH of buffer solution (5.95-6). Adjust final pH to 6.0 by adding 1:1 HCl or 1:1 NaOH if needed. Bring solution to 1 L with D.I. water and mix well. For 20 L of solution, add exactly 250 mL of concentrated HCl to1200-1500 mL of deionized water, dissolve 1,000 g of buffer in 100 g increments to solution. Transfer each 100 g increment to 20 L container and mix well till dissolved. Calibrate pH meter. Verify final pH of buffer solution (5.95-6). Adjust final pH to 6.0 with 1:1 HCl or 1:1 NaOH if needed. Bring solution to 20 L with deionized water and mix well.
- Stock standards (Comply with UL ISO 9001 Quality Assurance System)

  A. Copper stock standard - 1000 ppm Cu in 2% Nitric or Hydrochloric acid

  B. Iron stock standard - 1000 ppm Fe in 2% Nitric or Hydrochloric acid

  C. Manganese stock standard – 1000 ppm Mn in 2% Nitric or Hydrochloric acid

  D. Zinc stock standard – 1000 ppm Zn in 2% Nitric or Hydrochloric acid

  E. Custom Laboratory Internal Standard – 2000 ppm (Ca, Cu, Fe, Mg, Mn, Zn), 500 ppm Mo in 5% Hydrochloric acid
- Calibration standard 4

  Copper stock standard 5.0 mL

  Iron stock standard 5.0 mL

  Manganese stock standard 5.0 mL

  Zinc stock standard 5.0 mL

  Hydrochloric acid, conc. 20.0 mL

  Deionized water q.s.

  Pipet 5.0 mL each of copper, iron, manganese and zinc stock standard solutions into 1000 mL flask, bring to volume with D.I. water and mix well.
- Calibration standard 3

  Copper stock standard 3.0 mL

Iron stock standard 3.0 mL

Manganese stock standard 3.0 mL

Zinc stock standard 3.0 mL

Hydrochloric acid, conc. 20.0 mL

Deionized water q.s.

Pipet 3.0 mL each of copper, iron, manganese and zinc stock standard solution into 1000 mL flask, bring to volume with D.I. water and mix well.

- Calibration standard 2

Copper stock standard 1.0 mL

Iron stock standard 1.0 mL

Manganese stock standard 1.0 mL

Zinc stock standard 1.0 mL

Hydrochloric acid, conc. 20.0 mL

Deionized water q.s.

Pipet 1.0 mL each of copper, iron, manganese and zinc stock standard solutions into 1000 mL flask, bring to volume with D.I. water and mix well.

- Calibration standard 1

Copper stock standard .5 mL

Iron stock standard .5 mL

Manganese stock standard .5 mL

Zinc stock standard .5 mL

Hydrochloric acid, conc. 20.0 mL

Deionized water q.s.

Pipet 0.5 mL each of copper, iron, manganese and zinc stock standard solutions into 1000 mL flask, bring to volume with D.I. water and mix well.

SAMPLE HANDLING:

For samples containing "free-floating" particles filter a portion of the sample into a culture tube using Whatman 113V grade filter paper or better).

SAMPLE PREPARATION:

1. Weigh 0.5 g sample into 200 mL volumetric flask containing 100 mL of the pH 6.0 buffer extraction solution when the guarantee is less than 5%. Weigh 0.3 g when the guarantee is greater than 5%. **For pure materials,** weigh 0.3- 0.5 g of sample into 1 L volumetric flask containing 500 mL of pH 6 buffer Bis-extraction solution.
2. Bring the sample to volume with deionized water and shake vigorously for

30 seconds.

3. **Deficient samples**, always verify total zinc by FDACS Fertilizer Method FM-822. Verify pH of extraction solution and pH of extracted sample solution. pH value for sample solution should be pH 6.0 + or - 0.2.
4. **Deficient liquid samples containing polyammonium phosphate** as a phosphate source, must be extracted in a 10% EDTA solution due to the strong complexing characteristics of polyammonium phosphate for zinc. The EDTA extraction solution solubilizes the zinc because it has a stronger chelating affinity for zinc than the strongly complexing polyammonium phosphate. Reprepare the sample starting with step #1, except, buffer with 100 mL of 10% disodium EDTA instead of pH 6 buffer Bis-extraction solution. Follow steps 2-4. Analyze a blank of the EDTA buffer extraction solution with the extracted sample.

SAMPLE ANALYSIS:

1. **Zinc sample must be analyzed within 1 hour of weighing into buffer solution. The solubility of zinc oxides increases with time under these pH conditions.**

DO NOT ANALYZE IF TIMEFRAME IS EXCEEDED

2. Make appropriate dilution using dilution chart, analyze on AA.

Dilution Chart

%G	DILUTION
.01 -.10	No dilution
.11 - 1.5	1/10
>1.5	1/50

3. A custom internal standard is weighed and analyzed with each set (Zn = .20%) to check the precision and accuracy of the diluter and the AA. Weigh 0.5 g of the custom internal standard into a 200 mL volumetric flask containing 100 mL of pH 6 Bis-buffer solution, with each soluble zinc set.
4. AA spectrometer parameters used in Zn analysis:

ELEMENT	BURNER HEAD ALIGNMENT	WAVELENGTH (nm)	SLIT WIDTH (nm)	ACETYLENE FLOW (L/min)	OXIDANT FLOW (L/min)
Zn	Straight	213.9	0.7	1.6	12.5

5. Use Deionized water for blanks in the standardization of the instrument.
6. Analyze Bis-extraction solution as a buffer blank with each soluble zinc set. (100 mL of pH 6.0 buffer Bis-extraction solution/ 100 mL of deionized water).

SYSTEM START-UP: See standard operating procedures for all elements by Perkin-Elmer AAnalyst 100.

QA/QC:

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

CALCULATION:

% Soluble Zn found = [Zn ppm (AA)] (flask volume) (dilution factor) * 100 / (sample weight) (10^6 mcg/g)

APPROVAL:

Approved by: Leigh Humphreys **Date: 1/3/03**

Signature

Bureau Chief

Title

METHOD REVISION HISTORY:

Version	Date	Description	Author
Original	6/15/98	Replaces M-114	J. Corry
Revised	1/3/03		G. H. Huang

REFERENCE:

None