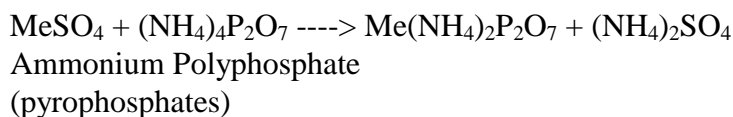
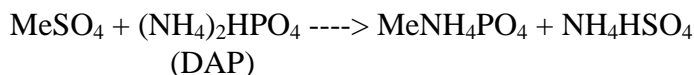


FERTILIZER METHODS	FM-831	
	Chapter	
	SECONDARY/MICRONUTRIENT ANALYSIS	
	Subject	
	Copper – Soluble ~ AA	

SCOPE: This is an automated analytical procedure for the determination of soluble copper in mixed or pure material fertilizers. Some examples of soluble copper sources used in fertilizers are: copper (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 copper present can be made. The pH 6.0 buffer is a composite of a 0.24M 2,2Bis (hydroxymethyl)-2,2',2"-nitrilotriethanol (C₈H₁₉NO₅) and hydrochloric acid (HCl). Copper oxides (CuO) are slightly soluble (4-5%) at pH 6.0. This low solubility of copper oxides is not enough to give a positive bias. This extraction solution insures that all of the soluble copper sources are fully recoverable. There is no significant loss of soluble copper 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.



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:

- Atomic Absorption Spectrometer with associated hardware and software (or equivalent)
- Balance (accuracy to 0.0001 g)
- Digital Diluter or equivalent pipets (Class A)
- Acid fume hood
- Volumetric flasks (Class A 200 mL, 500 mL and 1 L)
- Plastic funnel
- Culture tubes (16 x 125 mm or equivalent)
- Vortex shaker
- Filter column, 40 to 50 micro meter or equivalent
- pH meter (accuracy to 0.01 pH units)

REAGENTS & CHEMICALS:

- Deionized (D.I.) water
- 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

D.I. water

Add 250 mL conc. hydrochloric acid to approximately 200 mL D.I. water in 500 mL volumetric flask, bring to volume with D.I. water and mix well.

- Sodium hydroxide (NaOH) Certified A.C.S. 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/v) solution

Sodium hydroxide, pellets 250 g

D.I. water

Add 250 g sodium hydroxide pellets to approximately 200 mL D.I. 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 Ethylenediamine Tetraacetate EDTA ($\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$) Certified A.C.S. grade or equivalent
 10% (w/v) disodium EDTA ($\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$) Extraction Solution: Dissolve 100 g of disodium EDTA into 900 - 950 mL of hot D.I. water. Bring to volume of 1 L with D.I. water and mix well.
- 2,2Bis (hydroxymethyl)-2,2',2''-nitrilotriethanol ($\text{C}_8\text{H}_{19}\text{NO}_5$)- 99+%
 0.24M 2,2Bis (hydroxymethyl)-2,2',2''-nitrilotriethanol ($\text{C}_8\text{H}_{19}\text{NO}_5$)- Extraction Solution: Dissolve 50 g of Bis(hydroxymethyl)-2,2',2''-nitrilotriethanol in 700 mL of D.I. 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.
 - The volume of extraction solution may be adjusted to meet the number of samples.
- Stock standards
 - 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	20.0	mL
Iron stock standard	20.0	mL
Manganese stock standard	20.0	mL
Zinc stock standard	5.0	mL
Hydrochloric acid, conc.	20.0	mL
D.I. water		

To a Liter flask containing 500 mL of D.I. water pipet 20 mL of HCl, pipet 20 mL each of copper, iron, and manganese and pipet 5 mL zinc stock standard solutions into the 1000 mL flask, bring to volume with D.I. water and mix well.
- Calibration standard 3

Copper stock standard	10.0	mL
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Iron stock standard	10.0	mL
Manganese stock standard	10.0	mL
Zinc stock standard	3.0	mL
Hydrochloric acid, conc.	20.0	mL
D.I. water		

To a Liter flask containing 500 mL of D.I. water pipet 20 mL of HCl, pipet 10 mL each of copper, iron, and manganese and pipet 3 mL zinc stock standard solution into the 1000 mL flask, bring to volume with D.I. water and mix well.

- Calibration standard 2

Copper stock standard	5.0	mL
Iron stock standard	5.0	mL
Manganese stock standard	5.0	mL
Zinc stock standard	1.0	mL
Hydrochloric acid, conc.	20.0	mL
D.I. water		

To a Liter flask containing 500 mL of D.I. water pipet 20 mL of HCl, pipet 5 mL each of copper, iron, and manganese and pipet 1 mL zinc stock standard solutions into the 1000 mL flask, bring to volume with D.I. water and mix well.

- Calibration standard 1

Copper stock standard	0.5	mL
Iron stock standard	0.5	mL
Manganese stock standard	0.5	mL
Zinc stock standard	0.5	mL
Hydrochloric acid, conc.	20.0	mL
D.I. water		

To a Liter flask containing 500 mL of D.I. water pipet 20 mL of HCl, pipet 0.5 mL each of copper, iron, manganese and zinc stock standard solutions into the 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 filter column 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 D.I. water and shake vigorously for 30 seconds.
3. Sample extracts may be allowed to sit overnight before analyzing.
4. **Deficient samples**, always verify Total copper 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.
5. **Deficient liquid samples containing ammonium polyphosphate** as a phosphate source must be extracted in a 10% disodium EDTA solution due to the strong complexing characteristics of ammonium polyphosphate for copper. The disodium EDTA extraction solution solubilizes the copper because it has a stronger chelating affinity for copper than the strongly complexing ammonium polyphosphate. 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 disodium EDTA buffer with the extracted sample.

**SAMPLE
ANALYSIS:**

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

Dilution Chart

% G	DILUTION
0.01 – 0.30	No dilution
0.31 – 1.50	1/5
1.51 – 2.50	1/10
2.51 – 3.00	1/25
3.01 – 6.00	1/50
> 6.00	1/100

2. A custom internal standard is weighed and analyzed with each set (Cu = .20%) to check the precision and accuracy of the method and the AA.
2. 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 copper set.
- 2.
- 2.

3. AA spectrometer parameters used in Cu analysis:

ELEMENT	BURNER HEAD ALIGNMENT	WAVELENGTH (nm)	SLIT WIDTH (nm)	ACETYLENE FLOW (L/min)	OXIDANT FLOW (L/min)
Cu	Straight	324.8	0.7	1.7	4.0

4. Use D.I. water for blanks in the standardization of the instrument.

SYSTEM START-UP:

See **FSFL-SOP-508: Operation of PE Flame AAanlyst 100.**

QA/QC:

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

CALCULATION:

% Soluble Cu found = [Cu ppm (AA)] (flask volume) (dilution factor) * 100 / (sample weight) (10⁶ mcg/g)

APPROVAL:

Approved by:



Date: 12/28/09

Signature

Bureau Chief

Title

METHOD REVISION HISTORY:

Version	Date	Description	Author
Original	6/15/98	Replaces M-112	J. Corry
Revised	9/23/09		Jack Andreu

REFERENCE:

AOAC 16th Edition, Method 965.05
FSFL SOP-508