

<b>FERTILIZER METHODS</b>	<b>FM-841</b>	
	Chapter	
	SECONDARY/MICRONUTRIENT ANALYSIS	
	Subject	
	Chelated Secondary/Micronutrient Elements ~ AA	

**SCOPE:** This is an analytical procedure for the determination of chelated metals [manganese (Mn), copper (Cu), iron (Fe), zinc (Zn)] in mixed fertilizers.

**PRINCIPLE:** In this method, samples are weighed into a sodium acetate buffer solution designed to give an acidic pH range between 3 and 4. An acidic extraction solution is specified to compensate for the basic condition brought about when large amounts of dolomite or limestone are used as fillers. This acidic extraction prevents iron chelates from undergoing irreversible ligand exchange reactions with copper, manganese, zinc and other metal ions and forming of insoluble iron salts. Ferric (Fe<sup>+3</sup>) iron forms insoluble salts at pH > 3 if no complexing agent is present. The chelated metal is determined by atomic absorption spectroscopy analysis.

**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:**

- Balance, accuracy to 0.001 g
- pH meter, scale graduated in 0.01 pH units
- Digital diluter (optional) or equivalent pipets
- Vortex shaker
- Acid fume hood
- Air compressor
- Auto sampler
- Atomic Absorption Spectrometer with associated hardware and software (or equivalent)
- Flask, 200 mL volumetric (class “A”)
- Beaker, 300 mL
- Nalgene container, 20 liter
- Stopper, for 200 mL volumetric flask
- Disposable culture tube (16 x 125 mm)

- Disposable centrifuge tube (50 mL)
- Glass funnel
- Screen columns

### REAGENTS & CHEMICALS:

- Deionized (D.I.) H<sub>2</sub>O
- Sodium acetate
- Glacial acetic acid **Caution: Strong acid. Avoid breathing vapors and skin contact. Use in a fume hood and wear protective equipment**
- Chelate buffer (extraction solution): Dissolve 1 g of sodium acetate and 25 mL of glacial acetic acid in 700 mL of D.I. H<sub>2</sub>O and bring to a final volume of 1 L with D.I. H<sub>2</sub>O.
- Commercial bleach
- Diammonium phosphate solution: Dissolve 5 g of diammonium phosphate in 300 mL of D.I. H<sub>2</sub>O and bring to a final volume of 500 mL with D.I. H<sub>2</sub>O.
- Sodium hypochlorite solution: Add 2 mL of commercial bleach to 50 mL of D.I. H<sub>2</sub>O and bring to a final volume of 100 mL with D.I. H<sub>2</sub>O.
- 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 Standards:

- Calibration standard 4
 

Iron stock standard	20.0	mL
Hydrochloric acid	20.0	mL

Deionized water (D.I.)  
Pipet 20.0 mL of iron stock standard solution and 20 mL concentrated HCl into 1000 mL flask, bring to volume and mix well.
- Calibration standard 3
 

Iron stock standard	10.0	mL
Hydrochloric acid	20.0	mL

Deionized water (D.I.)  
Pipet 10.0 mL of iron stock standard solution and 20 mL concentrated HCl into 1000 mL flask, bring to volume and mix well.
- Calibration standard 2

Iron stock standard 5.0 mL

Hydrochloric acid 20.0 mL

Deionized water (D.I.)

Pipet 5.0 mL of iron stock standard solution and 20 mL concentrated HCl into 1000 mL flask, bring to volume and mix well.

- Calibration standard 1

Iron stock standard 0.5 mL

Hydrochloric acid 20.0 mL

Deionized water (D.I.)

Pipet 0.5 mL of iron stock standard solution and 20 mL concentrated HCl into 1000 mL flask, bring to volume and mix well.

- 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**

#### SAMPLE HANDLING:

Fertilizers containing chelated materials should be analyzed as soon as possible upon receipt. In samples containing non-chelated ferrous sulfates, the addition of the hypochlorite and ammonium phosphate reagents oxidizes ferrous iron to ferric iron which readily forms insoluble precipitates. These reagents are necessary only when soluble ferrous salts are present. Higher concentrations of sodium hypochlorite or longer reaction times may result in some loss of chelated iron.

#### SAMPLE PREPARATION:

1. Weigh 1 g of sample into a 200 mL volumetric flask containing 100 mL of extraction buffer.
2. After weighing sample, bring to volume with D.I. H<sub>2</sub>O.
3. Shake flask for a minimum of 30 seconds and then filter through screen column
4. Collect filtrate in culture tube (approximately 10 mL)
5. Make appropriate dilution and analyze on AA.
6. Analyze the filtrate as soon as possible after preparing sample in buffer solution (within 30 minutes).

#### NOTE:

1. For excessively high chelate samples (% Found is 3X > % Guar), weigh sample into buffer solution and add 15 mL of hypochlorite solution and 15 mL of diammonium phosphate solution to sample. Weigh sample in a 200 mL volumetric flask with same required sample weight.

2. Bring to volume with D.I. H<sub>2</sub>O and shake for 30 seconds. Allow samples to sit for 5-10 minutes, to insure precipitation reaction goes to completion.
3. Repeat steps (4-6) under sample preparation.

**SAMPLE  
ANALYSIS:**

1. For samples containing a considerable amount of "free-floating" particles in the flask, filter a portion of the sample in a culture tube using a screen column
2. Make appropriate dilutions and analyze on AA.
3. The atomic absorption spectrometer parameters are as follows:

ELEMENT	SLIT WIDTH (nm)	READ TIME (sec)	WAVELENGTH (nm)	FUEL FLOW liters/min	OXIDANT FLOW liters/min
Cu	0.7	3.0	324.8	1.2	11.0
Fe	0.2	3.0	248.3	1.3	9.0
Mn	0.2	3.0	279.5	1.5	12.5
Zn	0.7	5.0	213.9	1.6	12.5

4. All the elements above use acetylene/air for fuel/oxidant gases and have a straight burner head alignment.
5. Blanks for instrument calibration should contain 50% chelate buffer solution / D.I. H<sub>2</sub>O.

**QA/QC:**

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

**CALCULATIONS:**

$$\%Chelated\ metal = \frac{(ppm\ found\ (AA)\ reading)(FlaskVolume)}{sample\ weight(g) \times 10^6\ mcg/g} \times dilution \times 100$$

**APPROVAL:**

Approved by: Weldon Collier Date: 12/18/2008  
 Signature  
Bureau Chief  
 Title

**METHOD REVISION HISTORY:**

<b>Version</b>	<b>Date</b>	<b>Description</b>	<b>Author</b>
Original	11/12/01	Original	G. H. Huang
Revised	12/18/08		Carl Huang

**REFERENCE:**AOAC 16<sup>th</sup> Edition, Method 983.03