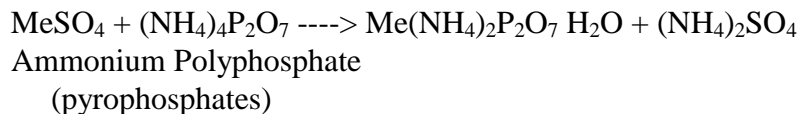
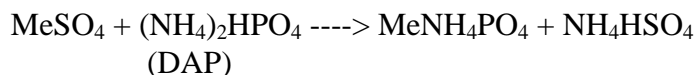


<b>FERTILIZER METHODS</b>	<b>FM-830</b>	
	Chapter	
	SECONDARY/MICRONUTRIENT ANALYSIS	
	Subject	
	Manganese – Soluble ~ AA	

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

**PRINCIPLE:** Samples are extracted in a pH 5.0 buffer (potassium hydrogen phthalate), brought to volume with deionized water and shaken. After appropriate dilution, samples are analyzed by atomic absorption spectroscopy (A.A.). By measuring the amount of light absorbed (at the specific wavelength), a quantitative determination of the amount of manganese present can be made. Manganese oxides are slightly soluble (1-1.5%) at pH 5.0. This low solubility of manganese oxides is not enough to give a positive bias. In samples containing high phosphate (%P<sub>2</sub>O<sub>5</sub> Guar = 10 or greater), and the source is monoammonium, diammonium or polyammonium phosphate, the soluble manganese can be precipitated as manganese ammonium phosphate. This is significant at a pH above 5.20, especially if the sample extracts are allowed to sit overnight. 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:**

- Certified Buffer Solution, pH 4 – used for pH meter calibration.
- Certified Buffer Solution, pH 7 – used for pH meter calibration.
- Deionized (D.I.) water
- 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.**

1N Sodium Hydroxide solution

Sodium Hydroxide, pellets 8 g

D.I. water

Add 8 g of sodium hydroxide pellets to approximately 100 mL D.I. water in 200 mL volumetric flask. Cool to room temperature. Bring to volume with D.I. water and mix well.

- Potassium Hydrogen Phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) Buffer Certified A.C.S. grade or equivalent

- Potassium Hydrogen Phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) Buffer Extraction Solution (0.05M)

Make 1 L by dissolving 10 g ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) in 800 mL of D.I. water.

Adjust pH to 5.0 by adding 20 mL of 1N NaOH and bring to volume with D.I. water. Mix well. This buffer material is stable under normal temperature and pressure.

- Disodium Etythylenediamine tetraacetate (Disodium 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 ( $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ ) Buffer 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.
- Stock standards
  - A. Copper stock standard - 1000 ppm Cu in 2% Nitric acid
  - B. Iron stock standard - 1000 ppm Fe in 2% Nitric acid
  - C. Manganese stock standard – 1000 ppm Mn in 2% Nitric acid
  - D. Zinc stock standard – 1000 ppm Zn in 5% Nitric 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

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
Iron stock standard	10.0	mL
Manganese stock standard	10.0	mL
Zinc stock standard	3.0	mL
Hydrochloric acid, conc.	20.0	mL

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

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

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 conical centrifuge tube using filter column or better

### SAMPLE

#### PREPARATION:

1. Weigh 0.5 g of sample into 200 mL volumetric flask containing 100 mL of the pH 5.0 potassium hydrogen phthalate 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 5.0 potassium hydrogen phthalate buffer solution.
2. Bring to volume with D.I. water and shake vigorously for 30 seconds.
3. Samples must be analyzed on the same day as extracted by buffer.
4. **Deficient samples**, always verify total manganese by FDACS Fertilizer Method FM-822. Verify pH of extraction solution and pH of sample. If pH

of sample is greater than 5.20, weigh a smaller amount (about 0.3 g) or add an additional 50 mL of buffer to sample and re-analyze. **Always check the final pH of the solution.**

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 manganese. The disodium EDTA extraction solution solubilizes the manganese because it has a stronger chelating affinity for manganese than the strongly complexing ammonium polyphosphate. Prepare the sample starting with step #1 except buffer with 100 mL of 10% disodium EDTA instead of pH 5.0 potassium hydrogen phthalate buffer. Follow steps 2-4. Analyze a blank of the disodium EDTA buffer extraction solution with the extracted sample.

**SAMPLE ANALYSIS:**

1. Use dilution chart below as a guideline and 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 (Mn = .20%) to check the precision and accuracy of the method and the A.A. Weigh 0.5 g of the custom internal standard into a 200 mL volumetric flask containing 100 mL of potassium hydrogen phthalate buffer solution, with each soluble manganese set.
3. AA spectrometer parameters used in Mn analysis:

ELEMENT	BURNER HEAD ALIGNMENT	WAVELENGTH (nm)	SLIT WIDTH (nm)	ACETYLENE FLOW (L/min)	OXIDANT FLOW (L/min)
Mn	Straight	279.5	0.2	3.0	10.0

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 better.

**CALCULATIONS:**

$$\% \text{ Soluble Mn found} = [\text{Mn ppm (AA)}] (\text{flask volume}) (\text{dilution factor}) * 100 / (\text{sample weight}) (10^6 \text{ mcg/g})$$

**APPROVAL:**

Approved by:

Date: 12/28/09

Signature

Bureau Chief

Title

**METHOD REVISION HISTORY:**

Version	Date	Description	Author
Original	6/15/98	Replaces M-111	J. Corry
Revised	09/23/09		Jack Andreu

**REFERENCE:**

*AOAC 16<sup>th</sup> Edition, Method 972.03*  
*FSFL SOP-508*