

<b>FERTILIZER METHODS</b>	<b>FM-820</b>	
	Chapter	
	SECONDARY/MICRONUTRIENT ANALYSIS	
	Subject	
	Secondary/Micronutrient Elements-AA	

**SCOPE:** This is an automated analytical procedure for the determination of total micronutrients (**Aluminum Calcium, Cobalt, Copper, Iron, Manganese, Molybdenum, and Zinc**) in mixed or pure material fertilizer samples by Atomic Absorption Spectrophotometry.

**PRINCIPLE:** Atomic Absorption Spectrometric determination of total micronutrient in fertilizer is achieved by measuring the amount of light emitted by the analyte as it is aspirated into a flame. A quantitative determination of the amount of analyte present can be made at the specific wavelength emitted by each analyte. Fertilizer samples are prepared by digesting the sample with 20 mL of Certified A.C.S. grade concentrated hydrochloric acid for 30 minutes. The solution is brought to volume, filtered, diluted and analyzed.

**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:**

- Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrometer (or equivalent)
- Hamilton Digital Diluter (optional) or equivalent pipets
- Volumetric flasks (Class A) 100 mL, 200 mL, 500 mL and 1 L
- Plastic funnel
- Culture tubes (16 x 125 mm, or equivalent)
- Vortex shaker
- Seraclear Filters (Westco) or equivalent filter paper

**REAGENTS & CHEMICALS:**

1. Deionized (D.I.) water
2. Ammonium chloride (Certified A.C.S.) grade or equivalent

3. Hydrochloric acid (HCl) (Certified A.C.S.) grade or equivalent
4. Potassium chloride (Certified A.C.S.) grade or equivalent
5. 20% (w/v) ammonium chloride solution:

Weigh 200 g of  $\text{NH}_4\text{Cl}$  (99.5%) into a 1 L volumetric flask. Bring to volume with D.I. water.

6. 1% (w/v) potassium chloride solution:

Weigh 1 g of  $\text{KCl}$  (99%) into a 100 mL volumetric flask. Bring to volume with D.I. water.

7. Aluminum, Calcium, Cobalt, Copper, Iron, Manganese, Molybdenum, and Zinc standard (1000 ppm - Certified)

A) Secondary Mixed Standard:

Pipet 20 mL of the 1000 ppm Mn stock standard, 20 mL of the 1000 ppm Cu stock standard, 20 mL of the 1000 ppm Fe stock standard and 5 mL of the 1000 ppm Zn stock standard into a 1 L volumetric flask. Add 20 mL of concentrated HCl to flask and bring to volume with D.I. water. The final concentration of this standard is: 20 ppm Mn, 20 ppm Cu, 20 ppm Fe and 5 ppm Zn with 2% HCl. This is a calibration standard for the AA.

B) Molybdenum Standard:

Pipet 5 mL of the 1000 ppm Mo stock standard into a 1 L volumetric flask and bring to volume with D.I. water. This makes a 5 ppm Mo standard. Pipet 50 mL of the 5 ppm Mo standard into a 500 mL volumetric flask and add 50 mL of the 20%  $\text{NH}_4\text{Cl}$  solution. Bring to volume with D.I. water and mix thoroughly. This makes a 0.5 ppm Mo standard with 2%  $\text{NH}_4\text{Cl}$  solution. This is the calibration standard for the AA spectrometer instrument.

C) Cobalt Standard:

Pipet 5 mL of the 1000 ppm Co stock standard solution into a 1 L volumetric flask and bring to volume with D.I. water. This makes a 5 ppm Co standard. Pipet 25 mL of the 5 ppm Co standard into a 50 mL volumetric flask and add 1 mL of concentrated HCl. Bring to volume with D.I. water and mix thoroughly. This makes a 2.5 ppm Co standard with 2% HCl. This is the calibration standard for the AA spectrometer instrument.

D) Aluminum Standard:

Pipet 5 mL of the 1000 ppm Al stock standard into a 100 mL volumetric flask. Add 10 mL of the 1%  $\text{KCl}$  solution and bring to volume with deionized  $\text{H}_2\text{O}$ . Mix thoroughly. This gives a 50 ppm Al standard with 0.1%  $\text{KCl}$ . This is the calibration standard for the AA spectrometer instrument.

8. Secondary Internal Standard: This is a certified secondary standard consisting

of 2000 ppm of manganese, copper, iron and zinc. This standard is preserved in 1%(v/v) HCl. The standard is ordered through AccuStandard, Inc. This standard is weighed with each analytical set.

**SAMPLE  
HANDLING:**

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 seraclear filter. For molybdenum analyses, interferences can be controlled by the addition of 2% ammonium chloride to samples and standards. For aluminum analyses, ionization can be controlled by the addition of an alkali salt (0.1% Potassium Chloride) to sample and standards.

**SAMPLE  
PREPARATION:**

1. Weigh 1 g of sample into a 200 mL volumetric flask. For guarantees over 5%, weigh 0.3 - 0.5 g.
2. Add approximately 20 mL of concentrated HCl to each sample and digest sample for 30 minutes (**do not allow sample to go dry**). Add approximately 15 mL of 1:1 HCl/ D.I. water to sample if it is close to dryness. Samples for **molybdenum analysis**, add 20 mLs of the 20% ammonium chloride solution to sample extracts along with the concentrated hydrochloric acid as described in the above statement. Samples for **aluminum analysis**, add 20 mLs of the 1% potassium chloride solution to sample extracts along with the concentrated hydrochloric acid as described in the above statement.
3. Allow samples to cool to room temperature, bring to volume with D.I. water and shake.
4. An internal standard is weighed with each set (Mn - 0.20%, Cu - 0.20%, Fe - 0.20%, Zn - 0.20%) to check the method and dilution steps. Take same weight as described above in Step 1.

**SAMPLE  
ANALYSIS:**

Make appropriate dilutions and analyze on AA.

Dilutions are as follows:

**DILUTIONS**

ELEMENT	% G	DILUTIONS
Mn, Cu, Al, Mo, Co	.01 - .40%	No dilution
	.41 - 2.00%	1/5 dilution
	2.00 - 4.00%	1/10 dilution
	4.00 - 15.00%	1/50 dilution
Fe	0 - 4.00%	1/10 dilution
	4.0 - 15.00%	1/50 dilution
Zn	0 - 0.05%	No dilution
	.06 - 1.00%	1/10 dilution
	1.00 - 5.00%	1/50 dilution

The atomic absorption spectrometer parameters are as follows:

ELEMENT	SLIT WIDTH (nm)	READ DELAY (SEC)	WAVELENGTH (nm)	FUEL FLOW liters/min	OXIDANT FLOW liters/min
Al	0.7	1.0	309.3	5.3	11.0
Ca	0.7	3.0	422.7	1.6	14.0
Cu	0.7	3.0	324.8	1.2	11.0
Co	0.2	3.0	240.7	1.6	12.8
Fe	0.2	3.0	248.3	1.3	9.0
Mg	0.7	3.0	285.1	1.2	14.2
Mn	0.2	3.0	279.5	1.5	12.5
Mo	0.7	4.0	313.3	5.3	11.0
Zn	0.7	5.0	213.9	1.6	12.5

**NOTE:** Ca, Cu, Co, Fe, Mg, Mn, Zn analysis use acetylene/air for fuel/oxidant.

**NOTE:** Al, Mo analyses use acetylene/nitrous oxide for fuel/oxidant.

**NOTE:** All of the elements above, except for Ca, use a straight burner head alignment.

**NOTE:** Ca analysis - use the 30° burner head alignment.

**NOTE:** Expected cv (coefficient of variation) should be less than 5%.

**CALCULATIONS:**

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

**APPROVAL:**

Approved by: Leigh Humphreys Date: 5/12/03  
 Signature

Bureau Chief  
 Title

**METHOD REVISION HISTORY:**

Version	Date	Description	Author
Original	6/12/98	Replaces S-111	J. Corry
Revised	4/8/02		G. H. Huang
Revised	5/8/03		L. Humphreys

**REFERENCE:**

AOAC 16<sup>th</sup> Edition, *Method 965.09*