Method to Determine Water-Soluble Secondary and Micronutrients in Fertilizer:

A Progress Report

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2019 Method's Forum Suggested *Action Items*

1. *Scope – Secondary and nutritive metals*
2. *Draft a definition – What water soluble means?*
3. *Look up AOAC References –*
4. *Survey AAPFCO OP for current list of micro definitions for ones that might claim water solubility*
5. *Look at how state laws address soluble (micros/secondary) – ask Joe Slater (and Ed-TFI survey)*

2019 Method's Forum Suggested *Action Items*….Cont.

6. *Look at water solubility (to deactivate phosphorous and sulfur)*
7. *Look at anions that might react with extracted metals*
8. *Locate Magruder data and determine methods being used for soluble metals*
9. *Examine source materials for micros and secondary to look at solubilities*
10. *Separate defined materials with potential solubility claims*

2019 Method's Forum Suggested *Action Items*….Cont.

11. Get list of material manufacturers to contact regarding solubility

12. Look at sample/solvent ratio

13. Look at how does end farmer get benefit…Label correctness with regard to effectiveness…product must have shown correlation

14. Compile list of researchers (SME) doing work in this area

Justification:

1. Total concentration of secondary and micro nutrients analysis does not adequately address the plant-available-nutrient pool.

2. Water-soluble Zn has been found to be the best predictor of Plant available Zn

3. Plant availability of other nutrients, for example P, is best predicted by neutral solution extraction

4. Soil nutrients are best extracted with solutions that dissolve the plant available fraction

Goal

Develop a method for extraction and simultaneous analysis of water-soluble:

Ca, Mg, B, Co, Cu, Fe, Mn, Mo, Ni, and Zn.

AOAC Official methods for water-soluble secondary or micronutrients

Nutrient	Year	Method #	Extraction	Detection
Boron	1949	949.03	2.5 g in 125 mL boiling water	pH titration
Boron	2006	982.01	2 g in 50 mL boiling water, dilute to 100 mL	Spectrophotometry
Chlorine	1928	928.02	2.5 g washed with 250 mL boiling water	Ag titration
Magnesium	1966	937.02	1 g in 350 mL boiling water	Gravimetric, Volumetric, or EDTA titration
Manganese	1974	972.03	1 g in 20 mL H2O then wash with 230 mL H2O	

Proposed Procedure

1. Prepare fertilizer according to AOAC 929.02
2. Weigh ca. 1 g fertlizer and transfer to 250 mL beaker
3. Add 50 mL of deionized water to the beaker
4. Boil gently for 10 minutes
5. Let beakers cool
6. Prepare 100 mL volumetric flask with 5 mL of 10% (v/v) HCl
7. Filter the extract into 10% HCl to prevent precipitation

Proposed Procedure Cont..

8. Filter beaker contents through Whatman No. 40 filter paper or equivalent into the 100 mL volumetric flask.

9. Rinse all beaker content with hot, boiled water.

10. Rinse solids on filter paper with hot, boiled water until vol. in flask is ~ 80 mL.

11. Add 2.5 mL concentrated HCl and 9 mL of concentration HNO_3 to the volumetric flask.

12. Dilute volumetric flasks to volume with deionized water

13. Transfer to plastic bottle immediately.

14. Analyze solutions on ICP-OES using calibration standards prepared as in AOAC 2017.02 for Mo, Ni, Co (Group A analytes) and Ca, Mg, Fe, Cu, Mn, Zn (Group B analytes) and Boron.

Proposed ICP Conditions

Factor	Setting
Power	1.45 kW
Plasma Flow	19.5 L/Min
Auxiliary Flow	2.25 L/min
Nebulizer Flow	0.9 L/Min
Nebulizer Type	SeaSpary/Concentric
Spray Chamber	Cyclonic/Double Pass
Sample Tube	Red/Red
Internal Std Pump Tube	Black/Black
Read Time	16 Seconds
Stabilization Delay	19 Seconds
Rinse Time	300 Seconds
Total Sample Analysis Time	

Experimental Design

Phase I intra-laboratory studies

1. Objective: Conduct independent single lab validation (SLV) trials to determine ruggedness, LOD, LOQ, repeatability, and reproducibility.

2. About 3 to 5 laboratories will be chosen to conduct SLV - AOAC OMA Appendix K.

3. About 8 samples (with acid and water soluble data) from the Magruder program will be used in the study.

Phase I Statistical Analysis:

1. Ruggedness will be evaluated on the following parameters
    - Sample wt (0.5, 1, and 2 g)
    - Boiling times (5, 10, and 20 minutes)
    - Wavelength used in ICP analysis

2. 8 samples x2/lab and 2 blanks. Variability of the duplicates will be used to assess repeatability.

3. Each set of 18 samples will be tested on 4 different days to assess reproducibility

4. Data will be analyzed for:
    - Repeatability, between-day variability,
    - Reproducibility according to ISO 5725-2.
    - The variances will be evaluated based on the Horwitz equation.

5. Method LOD and LOQ will be determined from the results of blanks in each set.

6. Evaluate best method details for moving forward with Phase II interlaboratory study.

Proposed Magruder Samples

		Acid-soluble (%)								Water-soluble (%)						
ID	Sample description	Ca	Mg	Fe	Cu	Mn	Zn	Mo	B	Mg	Fe	Cu	Mn	Zn	Mo	B
160711	12-12-12+micros			0.5	0.1	0.4	2	0.025	0.1							
170411	15-15-15+micros		1.2	1.6	0.5	1	1	0.005	0.08	0.9	1	0.3	0.6	0.6	0.003	0.08
180111	Sec & Micro	18					1.5		0.5					1.5		
180711	High micros				1	5	20		1							
181111	17-6-18 and micros		1.2				0.1		0.2							
181211	11-11-21 and micros		1.5	0.1	0.05	0.25	0.05	0.002	0.05	1						
190211	14-14-14+micros		1	1	0.06	0.16	0.13	0.005	0.2	1	0.5	0.03	0.1	0.1	0.005	0.1
190711	High micros	2	1.7	1	1	1.5	2		1.5							

Phase II inter-laboratory studies

Objective:

a. Evaluate repeatability - between-lab variability,

a. Evaluate reproducibility for the method in an inter-laboratory study.

Experimental Design

1. Samples from the Magruder program and other sources will be used
   At least 5 samples will be ground to a fine powder according to AOAC 929.02 and homogenized.

2. Homogeneity will be tested using AOAC 2017.02.

3. At least 8 laboratories will be tapped to collaborate

4. Sample Preparation:

   a. Samples will be prepared to deliver to the participating labs by spreading out powdered fertilizer in a thin layer
   b. Sampling approximately 10 increments of fertilizer for each analytical sample will be highly encouraged.

5. Laboratories will perform the test in duplicate on analytical samples provided to them.

Statistical Analysis:

a. Parameters of trueness and precision will be determined by ISO 5725-2

b. Horwitz values according to AOAC OMA Appendix D.