APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Meeting the Challenges of Soil Analysis with the Avio 200 ICP-OES

Introduction

Micronutrients contained within soil are the building blocks for the crops we eat, process, or feed to livestock. These micronutrients provide the core for proper growth and development of plants which are then consumed and passed up the food chain to eventually reach each of us. As such, the balance of micronutrients in soil is of global importance to growers, producers and consumers. Every soil varies in its basic elemental makeup depending on the local geology and whether the soil has been amended with fertilizers or other additions throughout its use. Without direct elemental analysis, there is no way to confidently understand the condition of the soil and make adjustments to the soil or to efficiently select the crop to be grown in the soil.

The analysis of soils for elemental contents presents challenges during the sample preparation step. A common method for preparing a soil sample for inorganic elemental analysis involves digesting the soil sample in an acid that is heated to near-boiling to extract the elements for analysis. When using open vessels in heating blocks, this extraction method typically takes four hours or more to complete. The sample must then be centrifuged or filtered to remove solid particles prior to analysis. The use of a microwave digestion system can speed this up significantly by completing the acid digestion in less than 50 minutes. In addition, if desired, the microwave digestion system can deliver complete sample digestion with the use of appropriate acids, thereby providing an analysis of the total elemental content instead of only the extractable concentrations.

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Inductively coupled plasma optical emission spectroscopy (ICP-OES) is generally favored in a multi-element analytical environment with detection capabilities appropriate for the quantification of micronutrients as demonstrated in this application. Flame atomic absorption (AA) systems, which provide cost savings, simplicity, and single-element analytical speed, can be an attractive alternative[1]. However, measuring multiple elements by Flame AA requires each sample to be analyzed individually for each element, which can eliminate the speed advantage of Flame AA for multi-element analysis.

This work will focus on the analysis of micronutrients in a selection of soil samples using a PerkinElmer Avio™ 200 ICP Optical Emission Spectrometer.

Experimental

Samples and Sample Preparation

Soils vary greatly from region to region and can be vastly different even within a single large plot of land. To represent some of this variance, soil samples were taken from residential back yards and garden plots and also from commercial farms and pastures. The garden plot samples are interesting in that they represented well-tended and highly amended soils and also have a high ratio of industrially composted "bagged" soil, as commonly available at home and garden stores. All soil samples represented healthy areas in current production and did not show any signs of depletion or disease prior to collection. To confirm the accuracy of the methodology, two certified reference materials were used: Soil Solution A and Soil Solution B (High Purity Standards™, Charleston, South Carolina, USA). Both of these samples were analyzed directly, without dilution.

A micronutrient extraction method was selected for sample preparation as this represents the most commonly used method for the analysis of soil samples. A mixture of hydrochloric acid and nitric acid was used for the extraction and, as expected, residue remained for every sample after digestion. Soil samples were prepared for analysis by closed-vessel microwave-assisted digestion using a PerkinElmer Titan MPS microwave digestion system. The digestion method, sample parameters, and reagents used are listed in Tables 1 and 2. Samples were weighed and placed into Titan MPS 75 mL Standard Pressure Digestion Vessels, and then the reagents and any sample spikes were added. The samples and reagents then sat open in the vessels for 10 minutes, which allows any early reactions to occur safely. After this time, the vessels were closed and placed into the Titan MPS system for heating and digestion. When the digestion had finished, the samples were transferred out of the digestion vessels by triple-rinsing with deionized (DI) water into sample vials and then diluted to the final volume. After dilution, the samples were set aside to allow the suspended particles to settle out of solution. This can also be achieved more rapidly by centrifuging the samples for around 10 minutes.

Table 1. Titan MPS Digestion Method.

Step	Temp (°C)	Pressure Limit (bar)	Ramp Time (min)	Hold Time (min)	Power Limit (%)
1	150	35	5	5	80
2	195	35	2	20	100
3	50	35	1	15	0

Table 2. Digestion Information.

Parameter	Volume
Reagents Used	6 mL of HCl (37%) and 3 mL of HNO_3 (70%)
Initial Sample Weight	1 g
Final Solution Weight (after dilution)	50 g

Instrumental Conditions

All analyses were performed on an Avio 200 ICP Optical Emission Spectrometer equipped with a PerkinElmer S10 Autosampler. The elements of interest and instrument conditions for the analysis of the soil samples are outlined in Tables 3 and 4. A Meinhard® glass nebulizer was used with the standard baffled cyclonic spray chamber and a reduced sample uptake rate of 0.80 mL/min. When combined with the online flow of the internal standard, the total liquid flow rate for the nebulizer was 1 mL/min of solution. External calibration standards were created from stock standards and were diluted with DI water and trace-metal-grade hydrochloric and nitric acid to the final elemental concentrations listed in Table 5. The final acid concentration of the standards was approximately 10% of the acid blend to match the relatively high concentration of acid in the digested and diluted samples.

Table 3. Avio 200 ICP-OES Instrumental Parameters.

Parameter	Value
Nebulizer	Meinhard® Glass Type K1 (Part No. N0777707)
Spray Chamber	Glass Cyclonic Baffled (Part No. N0791352)
Sample Uptake Rate (mL/min)	0.80
RF Power (Watts)	1500
Nebulizer Gas (L/min)	0.70
Auxiliary Gas (L/min)	0.2
Plasma Gas (L/min)	8

Table 4. Method Parameters.

Element	Wavelength (nm)	Plasma View	Integration Range (sec)
Al	308.215	Radial	0.1-2
Ba	233.527	Axial	0.1-5
Ca	317.993	Radial	0.1-2
Co	228.616	Axial	0.1-5
Cu	327.393	Axial	0.1-5
Fe	238.204	Radial	0.1-2
K	766.490	Radial	0.1-2
Mg	285.213	Radial	0.1-2
Mn	257.610	Radial	0.1-2
Na	589.592	Radial	0.1-2
Ni	231.604	Axial	0.1-5
P	178.221	Axial	0.1-5
S	181.975	Axial	0.1-5
V	292.464	Axial	0.1-5
Zn	206.200	Axial	0.1-5
Y (int std)	371.029	Radial	0.1-5
Y (int std)	371.029	Axial	0.1-5

Table 5. Calibration Standards.

Element	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	Std 5 (mg/L)
Al			25	100	500
Ba	1	10	25		
Ca			25	100	500
Co	1	10	25		
Cu	1	10	25		
Fe			25	100	500
K			25	100	500
Mg			25	100	500
Mn	1	10	25		
Na		10	25	100	
Ni	1	10	25		
P		10	25	100	
S		10	25	100	
V	1	10	25		
Zn	1	10	25		

Analysis was performed using standard 2-point background correction with no other spectral correction formulas. Yttrium was included as an internal standard for all elements analyzed using an axial or radial plasma view where appropriate.

Leveraging PerkinElmer's proven track record of ICP performance, the Avio 200 spectrometer benefits from a number of unique capabilities as well. The patented Flat Plate™ plasma technology delivers a robust plasma with zero maintenance and requires no cooling while using nearly half the argon plasma gas of helical load-coil systems. The entire sample introduction system and torch assembly are packaged into a single cassette that is simple to use and maintain. The Avio's Dual View capability allows automated axial or radial viewing, and teamed with its outstanding optical resolution, delivers a large linear dynamic range and exceptional stability and detection limits. All instrument control, sample analysis, and data processing were done through PerkinElmer's Syngistix™ software.

Results and Discussion

Calibration results are shown in Table 6. The excellent correlation for the calibration standards demonstrates the accuracy and precision of the Avio 200 ICP-OES. The independent calibration verification (ICV) recoveries ensure that the calibration is valid, and that the creation of the standards is accurate.

Table 6. Calibration Results.

Element	Correlation Coefficient	ICV (% Recovery)
Al	0.99999	97
Ba	0.99999	98
Ca	0.99998	101
Co	0.99993	96
Cu	0.99988	96
Fe	0.99999	100
K	0.99992	97
Mg	0.99991	108
Mn	0.99999	102
Na	0.99985	96
Ni	0.99998	97
P	0.99986	98
S	0.99985	98
V	0.99995	99
Zn	0.99990	98

To verify the accuracy of the methodology, two certified reference material soil solutions were measured, with the results shown in Table 7. All concentrations are within 15% of the certified values for both samples, validating the accuracy of the method. The total sample-to-sample analysis time is less than five minutes for the measurement of these 15 elements and internal standards. By comparison, a typical Flame AA instrument would take over 30 minutes to sequentially analyze the same list of elements, not including the required extra calibration time.

With the analytical methodology validated, the collected soil samples were prepared and analyzed. Using the Titan MPS digestion system, the samples were simply and quickly prepared for analysis, a major time saving over the typical process of open-vessel digestion. The results from the analysis of the soil samples are shown in Figure 1 and demonstrate the value of quantitative analysis in characterizing the samples. Some soils varied by as much as a factor of 10X in the concentration of specific elements, but otherwise showed surprising consistency. Since all the samples were taken from a relatively small geographic area, this is not entirely unexpected.

Table 7. Analysis of Soil Reference Solutions.

Element	Soil Solution A			Soil Solution B		
	Certified (mg/L)	Experimental (mg/L)	% Recovery	Certified (mg/L)	Experimental (mg/L)	% Recovery
Al	500	459	92	700	662	95
Ba	5	4.75	95	7.00	6.94	99
Ca	350	343	98	125	126	101
Co	---	0.027	---	0.100	0.087	87
Cu	0.300	0.289	96	3.00	3.01	100
Fe	200	201	101	350	356	102
K	200	196	98	210	210	100
Mg	70	73	104	80.0	82.6	103
Mn	0.100	0.110	110	100	95.2	95
Na	70.0	63.8	91	100	92.5	92
Ni	0.300	0.287	96	0.20	0.20	100
P	---	6.72	---	---	6.76	---
S	---	1.86	---	---	2.03	---
V	0.100	0.096	96	0.800	0.772	97
Zn	1.00	1.02	102	70.0	68.9	98

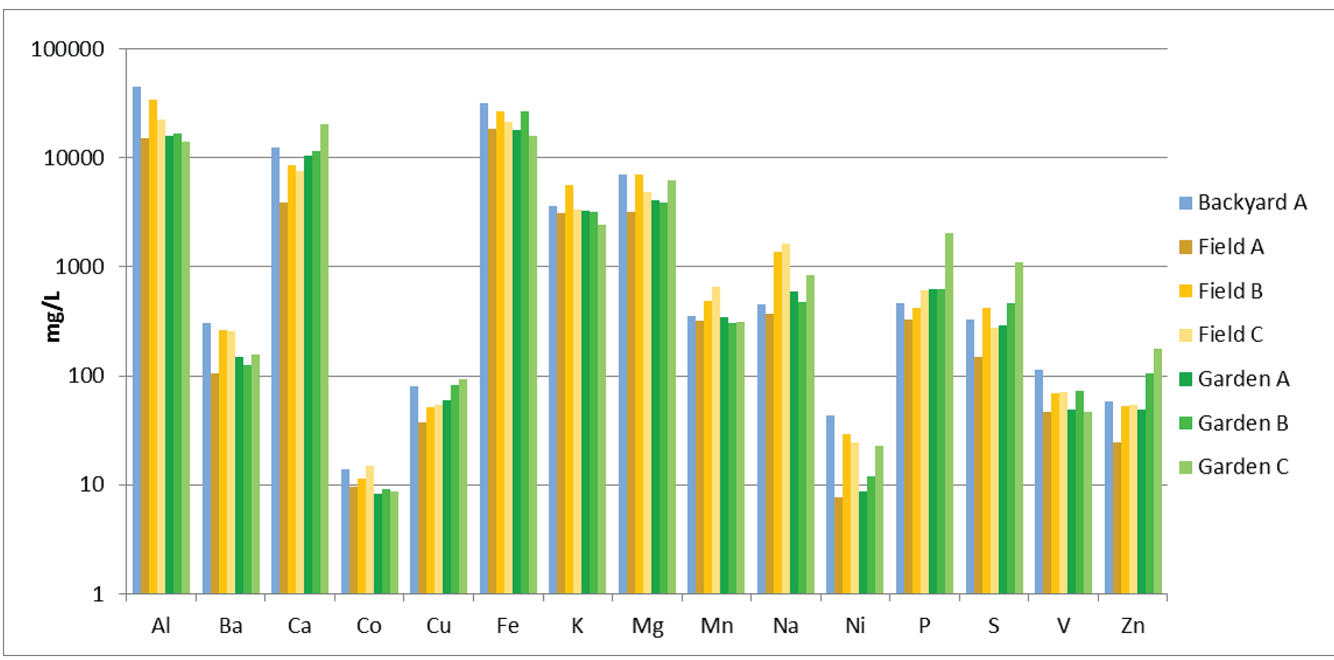

Figure 1. Results from analyses of soil samples (logarithmic scale).

With a large dynamic range and the Dual View capability of the Avio 200 ICP-OES, it was not necessary to make multiple sample dilutions for elements at high and low relative concentrations, which meant that every element could be measured in a single analysis at a single sample dilution. This resulted in increased productivity and higher sample throughput. Calibration curves covering the appropriate concentration range for each element, along with the use of calibration check solutions, ICVs, and sample spikes ensured accurate analysis.

To assess any remaining matrix effects from the various soil samples after digestion, all samples were spiked prior to digestion with all elements at the levels shown in Table 8. The resulting spike recoveries appear in Figure 2 and show that all recoveries are within 10% of their true values. Effective digestion via the Titan MPS system eliminated the need for per-sample matrix matching or the use of a method of standard addition for accurate analysis. In all cases, the spike concentrations were selected to try to match or approach the expected concentration of the elemental concentration in the samples. This ensures that the spike signal is meaningful in relation to the sample signal for the purposes of analytical evaluation.

Table 8. Pre-Digestion Spike Levels (all units in mg/L).

Element	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	V	Zn
Conc.	5000	500	5000	50	100	5000	5000	5000	500	500	50	500	400	50	50

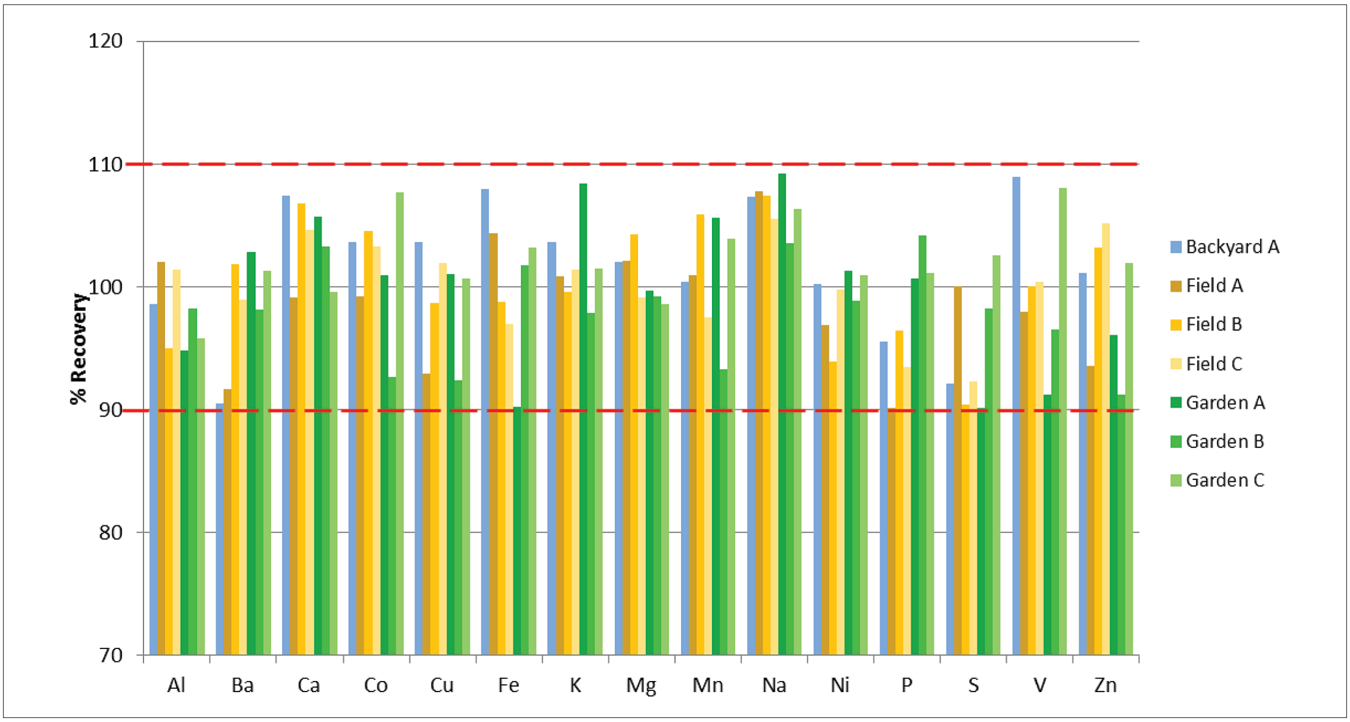

Figure 2. Spike recoveries in soil samples (% Recovery).

The analytical results and spike recoveries for the samples, as well as confirmation of method accuracy in the measurement of CRMs, demonstrate an efficient method for the preparation and analysis of soil samples using a Titan MPS digestion system for sample preparation along with an Avio 200 ICP-OES for final sample analysis.

Conclusion

This work has demonstrated the ability of the Avio 200 ICP-OES to reliably and effectively analyze a variety of soil samples for an array of elements over a wide range of concentrations. With its extended capabilities, the Avio 200 ICP-OES provides greater multi-element sample throughput when compared to Flame AA, while allowing analysis of elements which are typically challenging for Flame AA (such as phosphorus and sulfur).

Using the Titan MPS microwave digestion system simplified sample preparation while greatly increasing throughput and productivity for the laboratory when compared to hot plate or hot block digestions. The ability to completely digest the samples, if needed, is a capability unmatched by open-vessel digestion.

The use of the Titan MPS system for sample preparation and the Avio 200 ICP-OES for analysis is an ideal combination for fast, simple, and accurate analyses of micronutrients in soil.

Reference

1. Spivey, Nick, "Analysis of Micronutrients in Fruit Juice Using FAST Flame Sample Automation for Increased Sample Throughput", Application Note, PerkinElmer, 2015.

Consumables Used

Avio 200 ICP-OES	
Component	**Part Number**
Red/Red PVC Pump Tubing (drain)	09908585
Black/Black PVC Pump Tubing (sample)	09908587
Orange/Green PVC Pump Tubing (internal standard)	N0777110
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
Instrument Calibration Standard 2	N9301721 (125 mL)
Instrument Calibration Verification Standard	N9303953 (125 mL)
Pure-Grade Phosphorus Standard (10,000 mg/L)	N9303788 (125 mL) N9300139 (500 mL)
Pure-Grade Sulfur Standard (1000 mg/L)	N9303796 (125 mL) N9300154 (500 mL)
Pure-Grade Yttrium Standard (10,000 mg/L)	N9303810 (125 mL) N9300167 (500 mL)

Titan MPS Digestion System	
Component	**Part Number**
Consumables Kit for Standard 75 mL Digestion Vessels	N3132000
Rupture Disks for Standard 75 mL Digestion Vessels (25 pieces)	N3132001
Pressure Seal for Standard 75 mL Digestion Vessels (10 pieces)	N3132002
End cap Plug for Gas Containment Manifold	N3134004
Single Lip Seal Forming Tool for Standard 75 mL Digestion Vessels	N3132015
8-Position Lip Seal Forming Tool for Standard 75 mL Digestion Vessels	N3132014

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