Determination of available nutrients in soil using the Agilent 4200 MP-AES

Application note

Agriculture

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Introduction

Multielement testing of soil samples provides valuable understanding of its yield potential. Essential elements are divided into macronutrients (required in larger quantities because of their structural roles in the plant) and micronutrients (required in smaller quantities because they tend to be involved in regulatory roles in the plant).

Primary macronutrients, such as potassium (K) are most often in short supply in soils, requiring replenishment in the form of applied fertilizer. Deficiencies of secondary macronutrients, such as calcium (Ca) and magnesium (Mg) are less commonly encountered. Micronutrients include iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), and boron (B). The presence of any of the essential elements in excessive amounts may result in toxic effects.

Accurate and timely analysis of soil samples is vital so action can be taken to improve the soil's fertility if a nutrient imbalance is present or if there is a risk of environmental pollution due to excess elemental concentrations.

Depending on the group of nutrients of interest, different extraction methods and analytical procedures are required. Generally, determination of nutrient elements in soil samples is carried out by Flame Atomic Absorption Spectroscopy (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). However, with laboratory budgets under increasing pressure and a desire for simplified workflow, improved ease of use and improved safety, Microwave Plasma–Atomic Emission Spectrometer (MP-AES) is gaining attention from soil testing facilities, particularly those looking to transition from FAAS to another technique.

Agilent's 4200 MP-AES is suited to the multielement analysis of samples with high dissolved solids content, such as soil. It offers improved performance when compared to FAAS, with lower detection limits, particularly for boron in this application, and a wider working analytical range. The MP-AES uses nitrogen, that can be easily generated from air, making it attractive to facilities that have difficulty in sourcing gases or are under pressure to improve safety or reduce costs. Eliminating expensive and hazardous gases such as acetylene from the lab also allows the instrument to be operated unattended, even in remote locations. The simplicity of the instrumentation and Agilent's user-friendly MP Expert software facilitates instrument setup, method development and data interpretation with minimal training.

This application note describes three sample preparation procedures for the estimation of exchangeable cations and available micronutrients, including boron, using the Agilent 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES with nitrogen plasma gas supplied via an Agilent 4107 Nitrogen Generator. The generator alleviated the need and expense of sourcing analytical grade gases. The sample introduction system comprised a double-pass cyclonic spray chamber and the OneNeb nebulizer. An Agilent SPS 3 autosampler was used to deliver samples to the instrument, allowing unattended operation of the system. The instrument operated in a fast sequential mode and featured a Peltier-cooled CCD detector. Background and spectral interferences could be simutaneously corrected easily and accurately using the MP Expert software. Method parameters are given in Table 1.

Table 1. Agilent 4200 MP-AES method parameters

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	35 seconds
Rinse time	30 seconds
Stabilization time	15 seconds
Fast Pump during uptake and rinse	On (80 rpm)
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Samples

Soil samples and standard solutions were provided by The International Crops Research Institute for the Semi-Arid-Tropics (ICRISAT), India.

Sample preparation methods

Different sample preparation methods were required, depending on the target suite of elements. DTPA extraction was used for the analysis of micronutrients (Fe, Cu, Zn and Mn) in soils. The determination of exchangeable cations (macro nutrients, Na, K, Ca and Mg) required extraction with 1M ammonium acetate. For the determination of B, extraction with calcium chloride ($CaCl_2$) is typically used.

Method 1: DTPA extraction for available Cu, Fe, Mn and Zn

Preparation of extraction solution: the extractant comprised diethylenetriaminepentaacetic acid (DTPA) 0.005M, 0.01M $CaCl_2.2H_2O$ and 0.1M triethanolamine (TEA). The first step was to add 1.967 g DTPA and 13.3 mL TEA to 400 mL distilled water in a 500 mL flask.

In a separate 1 L flask, 1.47 g $CaCl_2.2H_2O$ was dissolved in 500 mL of distilled water. This solution was then mixed with the DTPA/TEA mixture. The pH was adjusted to 7.3 using 1M HCl before the volume was made up to 1 L with distilled water.

Extraction procedure: 10 g of soil sample was weighed into a polyethylene shaking bottle and 20 mL of DTPA reagent was added. After shaking for 120 minutes, the sample was filtered through a Whatman number 42 filter paper.

Working standards: 1, 2, 3, 4 and 5 ppm of Cu and Zn standards; 5, 10, 15, 20 and 25 ppm of Fe and Mn standards were prepared in the DTPA reagent.

Method 2: 1M ammonium acetate extraction for cation exchangeable elements: Na, K, Ca and Mg

Preparation of extraction solution: 1M ammonium acetate solution was prepared by dissolving 77.09 g of ammonium acetate in 1 L of distilled water. The pH was adjusted to 7.0 using HCl.

Extraction procedure: 25 mL of 1M ammonium acetate solution was added to 5.00 g of sample in a polyethylene shaking bottle. After shaking for 30 minutes, the sample was filtered through a Whatman Grade 1 filter paper.

Working standards: 1, 2, 5, 10, 20, 40, 60, 80 and 100 ppm of Na, K, Ca and Mg standards were prepared in 1M ammonium acetate solution.

Method 3: $CaCl_2$ hot water extraction for available B

Extraction solution: 1.47 g of 0.01M $CaCl_2$ was dissolved in approximately 900 mL of distilled water. The solution volume was adjusted to 1000 mL with distilled water.

Extraction procedure: 25 g of air-dried 2 mm sieved soil samples were weighed into a 250 mL boron-free digestion tube. 50 mL 0.01M $CaCl_2$ solution was added to the tube. A block digester was heated to 120 °C. The digestion tubes were transferred to the block digester for 15 minutes. The tubes were then removed from the digester and allowed to cool to room temperature before filtering through a Whatman Grade 42 filter paper.

Working standards: 0.25, 0.5, 0.75 and 1 ppm B standards were prepared in 0.01M $CaCl_2$ solution.

Wavelength selection and calibration range

Details of wavelength selection and calibration range of the standard solutions are given in Table 2. Continuous wavelength coverage allows lines to be chosen that have appropriate sensitivity for the concentration range, and that avoid spectral interferences. As the working range of the 4200 MP-AES far exceeds that of FAAS (by up to 20x in some instances), only one dilution of the sample was required to measure the complete set of elements. This large linear dynamic range means that less sample dilutions are needed which improves productivity and avoids the risk of sample contamination.

The calibration fit for all wavelengths used was linear.

Table 2. Wavelength and working calibration concentration range

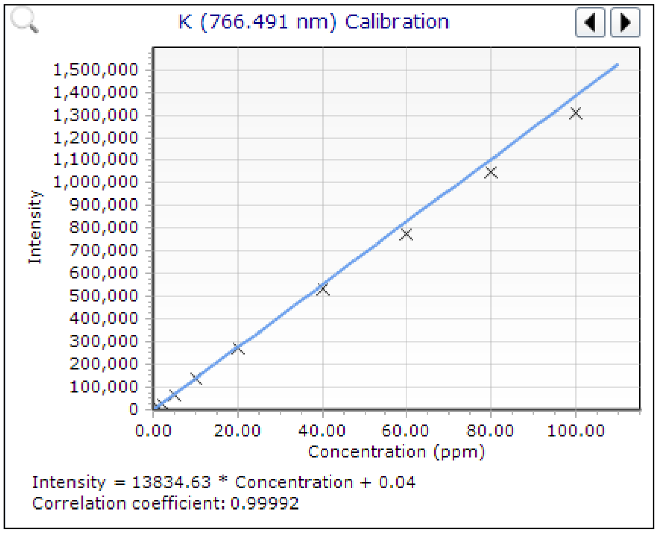
Element and wavelength (nm)	Calibration range (ppm)
Cu 324.754	1—5
Fe 259.940	5—25
Mn 257.610	5—25
Zn 213.857	1—5
Na 568.820	2—100
K 766.491	1—100
Ca 616.217	20—100
Mg 518.360	1—100
B 249.772	0.25—1.0

Results and discussion

Calibration

The calibration curves for the macronutrients Na, K, Mg and Ca in ammonium chloride, the micronutrients Cu, Mn, Fe and Zn, in DTPA, and B in the $CaCl_2$ solution showed good linearity across the concentration range. MP-AES has an increased linear dynamic range compared to FAAS and a good example of this is the calibration curve for K, shown in Figure 1. On the MP-AES, a calibration up to 100 ppm was performed with good linearity, far exceeding the working range for K on FAAS. This greatly simplifies the workflow by eliminating the need for multiple sample dilutions, or measuring K or Na in emission instead of absorption.

Figure 2 shows the calibration curve for B, which was calibrated up to 1 ppm. The ability to determine B on the MP-AES means that all elements can be determined on one instrument and can eliminate other processes required to determine the entire suite of elements.



Intensity = 13834.63 * Concentration + 0.04
Correlation coefficient: 0.99992

Figure 1. Calibration curve for K obtained on the 4200 MP-AES. The working range far exceeds that of FAAS.

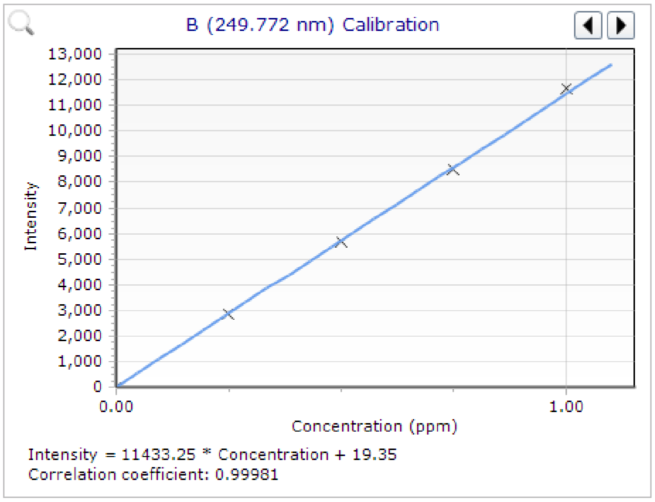


Figure 2. Calibration curve for B on the MP-AES.

Sample analysis

The results obtained by MP-AES were compared to values obtained via FAAS or ICP-OES. Tables 3, 4 and 5 show good agreement between the 4200 MP-AES results and those from other spectrometric techniques. All concentration results are shown in the original sample.

	B	
Wavelength (nm)	249.772	249.772
Technique	MP-AES	ICP-OES
	Final conc. µg/g	
SSTD-Trail 1	1.2	1.3
SSTD-Trail 2	1.3	1.2
SSTD-Trail 3	1.2	1.3
Av, µg/g	1.3	1.3
Std dev.	0.04	0.05

The results for the macronutrient elements Na, K, Mg and Ca in ammonium acetate demonstrate the capability of the MP-AES to determine elements across a wide range of concentrations in a single measurement, with Ca being determined at approximately 10000 ppm at the same time as Na at approximately 50 ppm; an analysis that would require multiple dilutions and elements measured in absorption and emission on FAAS.

Table 3. MP-AES results for Cu, Fe, Mn & Zn in DTPA extraction of soil, compared to FAAS

	Cu		**Fe**		**Mn**		**Zn**	
Wavelength (nm)	324.754	324.7	259.94	372	257.61	280.1	213.857	213.9
Technique	MP-AES	FAAS	MP-AES	FAAS	MP-AES	FAAS	MP-AES	FAAS
	Measured conc. µg/g							
SSTD-Trail 1	1.44	1.42	7.76	8.44	24.26	26.22	0.64	0.62
SSTD-Trail 2	1.46	1.45	7.96	8.24	24.40	25.96	0.64	0.64
SSTD-Trail 3	1.44	1.42	8.08	8.64	23.70	26.50	0.62	0.58
Av, µg/g	1.45	1.43	7.93	8.44	24.12	26.23	0.63	0.61
Std dev.	0.01	0.02	0.16	0.20	0.37	0.27	0.01	0.03

Table 4. MP-AES results of Na, K, Ca & Mg in 1M ammonium acetate extraction of soil compared to FAAS

	Na		**K**		**Ca**		**Mg**	
Wavelength (nm)	568.82	589.592	766.491	766.491	616.217	317.933	518.36	285.213
Technique	MP-AES	FAAS	MP-AES	FAAS	MP-AES	FAAS	MP-AES	FAAS
	Final conc. µg/g							
SSTD-Trail 1	53.1	52.4	206.9	202.0	9701.7	9426.1	845.4	941.8
SSTD-Trail 2	53.1	52.1	218.9	215.2	9988.4	9835.2	848.1	934.7
SSTD-Trail 3	52.6	56.5	214.5	220.3	9941.4	9427.6	845.1	928.1
Av, µg/g	52.9	53.7	213.5	212.5	9877.2	9563.0	846.2	934.9
Std dev.	0.32	2.46	6.04	9.44	153.78	235.76	1.65	6.85

Table 5. MP-AES results of boron in $CaCl_2$ extraction of soil, compared to ICP-OES

Conclusions

The Agilent 4200 MP-AES was used successfully for the analysis of exchangeable cations and available micronutrients in soil samples prepared using three extraction methods.

Elements that are difficult to analyze by FAAS such as B were also successfully determined in the study. The results for all elements show good agreement with values obtained by FAAS and ICP-OES.

The workflow to determine the complete set of elements in also simplified, compared to FAAS, with easier sample preparation, no need to change lamps or switch between absorption and emission measurement, and all elements determined in one sample analysis.

The nitrogen for the microwave plasma source was obtained from air using a nitrogen generator. The Agilent 4107 Nitrogen Generator is a highly efficient device that greatly reduces running costs compared to an FAAS or ICP-OES that rely on a constant supply of analytical grade gases.

Eliminating the hazardous gases associated with FAAS also improves lab safety, and leads to productivity gains through unattended operation.

With improved sensitivity, linear dynamic range, and detection limits compared to FAAS, the Agilent 4200 MP-AES is the ideal FAAS replacement.

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Published May 10, 2015
Publication number: 5991-5675EN

Agilent Technologies