Application Note

Soil quality and fertilizer analysis

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Determination of Macro and Micronutrients in Fertilizers using MP-AES

Fast analysis of six elements in mineral and organo-mineral fertilizers

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Introduction

Fertilizers are used to amend the mineral content of soils. They are usually applied in pellet, powder, or liquid-form to promote plant growth, increase yields, and to improve the nutritional content of crops. While most fertilizers are applied directly to the soil, some can be sprayed on leaves. The classification of fertilizers as organic or inorganic, depends on the source of the raw materials rather than any differences in the nutrient content.

Most fertilizers contain the three primary macronutrients that play a structural role in plant development: nitrogen (N), phosphorus (P), and potassium (K). Fertilizers may also contain lower levels of the three secondary macronutrients, calcium (Ca), sulfur (S), magnesium (Mg), as well as trace minerals, such as boron (B), manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), molybdenum (Mo).

The quantitative determination of these elements in fertilizers is important for product quality control and regulatory requirements. Fertilizers that are produced or sold within the European Union (EU) must comply with the concentration limits set out in Reg. CE 2003/2003 (mineral products) (*1*). In addition, many EU member states have detailed, national rules and standards in place for non-harmonized fertilizers that do not apply to EC-fertilizers. Italy, for example, has regulations that relate to organic products (*2*).

In the US, the Environmental Protection Agency (EPA) sets standards and regulations for some types of fertilizer but States can adopt regulations that are more stringent and/or broader in scope than the Federal regulations (*3*). In China, fertilizers are subject to approval by the Ministry of Agriculture (MOA) in compliance with the Food Safety Law (*4*).

Elemental analysis of fertilizers is typically performed using flame atomic absorption spectroscopy (FAAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). More recently, Microwave Plasma Atomic Emission Spectroscopy (MP-AES) has been used for the analysis. MP-AES is a fast-sequential emission-based multi-element analytical technique that uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The gas can be supplied from a cryogenic cylinder (Dewar), tank, or via a gas generator using air supplied from an air compressor. N_2 eliminates the need for more expensive and hazardous gases such as acetylene, increasing lab safety and allowing unsupervised operation. Also, the N_2 plasma reaches around 5000 K, eliminating many of the chemical interferences that are common in FAAS.

In this study, six elements in two mineral fertilizers and an organo–mineral fertilizer were analyzed by MP-AES.

Results and Discussion

Standards and reagents

Analytical grade concentrated HNO_3 (65% w/w) and H_2O_2 (30% w/v) were used for digestion of the organo-mineral fertilizer. The calibration standards were prepared by diluting a 1000 mg/L multi element standard solution (Sigma Aldrich and Scharlab S.L.) in 1% HNO_3. Details of the concentration ranges are given in Table 4.

Samples and sample preparation

Two liquid inorganic fertilizers (sample A and sample B) were diluted 2000x with de-ionized (DI) water in 1% HNO_3.

The liquid organo-mineral fertilizer (sample C) was acid digested using a MARS 6 microwave digestion system (CEM, USA). Approximately 0.5 g of sample C was weighed directly into a 100 mL PTFE digestion vial, followed by 9 mL of HNO_3 and 1 mL of H_2O_2. The temperature was gradually increased to 200 °C over 20 minutes and held for a further 15 minutes to ensure complete digestion. Once cooled, the digested sample was diluted to a final volume of 50 mL with DI water, before a further dilution of 20x.

The typical concentrations of elements present in the three fertilizers are shown in Table 1.

Table 1. Typical concentration (mg/L) of elements present in the samples before dilution.

	K_2O	CaO	MgO	B	Mn	Mo
Inorganic fertilizer, sample A	200,000	-	-	1,000	1,000	100
Inorganic fertilizer, sample B	-	100,000	50,000	-	-	-
Organic fertilizer, sample C	60,000	-	-	-	-	-

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES fitted with a double-pass cyclonic spray chamber and a OneNeb nebulizer. N_2 gas was supplied from a tank. The MP Expert software allows automatic background correction (Auto), improving precision and accuracy. The software also performs the optimization of nebulizer flow to accelerate method development. All wavelengths were selected in the software library according to the sensitivity that was required.

Method operating parameters for the fertilizer sample analysis are listed in Tables 2 and 3.

Table 2. MP-AES operating conditions.

Parameter	Setting/setup
Nebulizer	OneNeb inert nebulizer
Spray chamber	Double-pass cyclonic
Sample introduction	Manual
Pump speed	15 rpm
Number of replicates	3
Sample uptake delay	15 s
Stabilization time	15 s
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Table 3. Element wavelengths and nebulizer flow rate.

Element	Wavelength (nm)	Nebulizer flow (L/min)
Mn	403.076	1
Mo	379.825	1
Mg	518.360	0.8
B	249.772	0.45
Ca	643.907	1
K	769.897	0.75

Results and Discussion

Calibration

All wavelengths were selected to provide the widest dynamic range, avoiding the need to dilute the samples for reanalysis. Each element was calibrated using a three-point calibration. All calibration curves showed good linearity across the concentration range, as indicated by the correlation coefficients given in Table 4.

Table 4. Concentration range of calibration standards and calibration correlation coefficient.

Element	Standard concentration range (mg/L)	Linear correlation coefficient
Mn	0.4, 1, 2	0.99989
Mo	0.05, 0.5, 1.5	0.99899
Mg	10, 25, 50	0.99988
B	0.4, 1, 2	0.99975
Ca	20, 50, 200	0.99989
K	20, 100, 200	0.99902

The calibration curve for Mn 403.076 nm (Figure 1) is a typical example, showing excellent linearity across the calibration range, up to 2 ppm. Figure 2 shows the calibration curve for Mg 518.360 nm, which was calibrated up to 50 ppm. The ability to measure major and trace elements in a single run increases the productivity of the method.

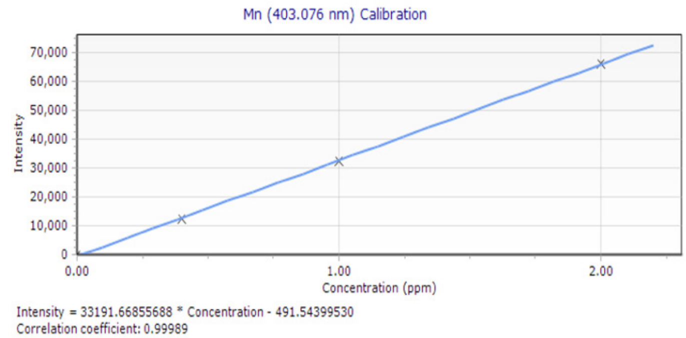

Figure 1. MP-AES calibration curve for manganese.

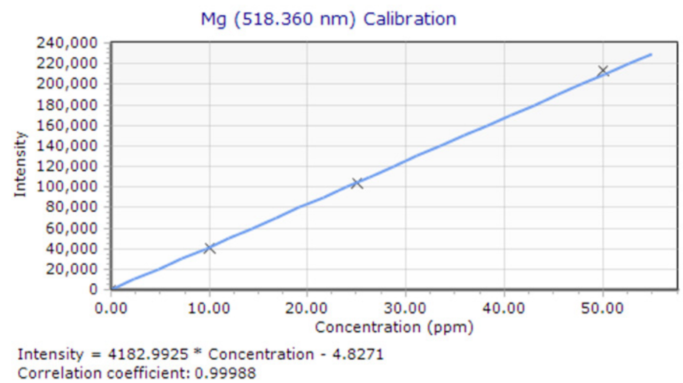

Figure 2. MP-AES calibration curve for magnesium.

Spike recovery test

Quantitative results for elements measured in three different fertilizers by MP-AES are shown in Table 5. To check the accuracy of the method, each sample was spiked as detailed in Table 5. The measured concentrations and recovery results of the elements in the fertilizer samples are shown in Table 5. Recoveries for all elements were within ±10% of the spike level, demonstrating the accuracy of the method. The results show that the 4200 or 4210 MP-AES can accurately measure macro and micronutrients in fertilizers across a wide linear range.

Table 5. Quantitative results and spiked recovery data for elements in fertilizers.

Sample C				
Element and wavelength (nm)	Measured value % (w/v)	Spike conc (mg/L)	Δ Measured Conc (mg/L)	Recovery (%)
K 769.897 nm	7.42	10	9.88	98

Sample B				
Element and wavelength (nm)	Measured value % (w/v)	Spike conc (mg/L)	Δ Measured Conc (mg/L)	Recovery (%)
Ca 393.366 nm	14.67	5	4.91	98
Mg 518.360 nm	8.56	5	4.81	96

Sample A				
Element and wavelength (nm)	Measured value % (w/v)	Spike conc (mg/L)	Δ Measured Conc (mg/L)	Recovery (%)
K 769.897 nm	28.60	10	10.89	109
B 249.772 nm	0.12	1	0.987	99
Mn 403.076 nm	0.17	0.1	0.108	108
Mo 379.825 nm	0.017	0.1	0.102	102

Conclusions

The study demonstrates the analytical performance of the Agilent 4200 or 4210 MP-AES for the routine analysis of macro and micronutrients content in mineral fertilizers and organo-mineral fertilizer-digests. Following simple dilution of the inorganic fertilizers or microwave digestion of the organic samples, all elements were analyzed in a single run, without any matrix modifier. The excellent recoveries demonstrate the ability of the MP-AES to determine K, Ca, Mg, B, Mn, and Mo in fertilizers.

MP-AES outperforms conventional FAAS in terms of detection limits, linear range, and speed of analysis. It also eliminates the need for hazardous gases, multiple sample preparation steps, and lamp changes. In addition to analytical performance and lab-safety advantages, MP-AES is more productive, flexible, and cost–effective over the long term than FAAS.

References

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Verified for Agilent
4210 MP-AES

Results presented in this document were obtained using the 4200 instrument, but performance is also verified for the 4210 MP-AES

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