Determination of exchangeable cations in soil extracts using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer

Application note

Agriculture

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Introduction

Accurate, routine testing of nutrients in soil samples is critical to understanding its potential fertility. Many of the nutrients that are vital to plants are exchangeable cations. These are ions loosely attached to and/or adsorbed onto clay particles and organic matter in soil that may become available to plants. Determination of these cations is of great interest for agronomic diagnostic and soil sustainability, enabling more accurate assessment and management of nutrient requirements [1, 2]. If the results indicate there is a nutrient imbalance, then this can be corrected for by the application of a suitably formulated fertilizer.

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This application note describes an analytical method for the determination of Ca, K, Mg, Mn and Na in soils using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). A chemical extraction with 1 M ammonium acetate is recommended (standard NF X 31-108) [1, 2, 3]. In this work, results obtained with MP-AES are compared to those obtained by other well-proven, validated techniques flame atomic absorption spectrometry (FAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES), and with inter-laboratory results to demonstrate the reliability and accuracy of MP-AES data.

Which measurement technique is right for you?

There are many factors to be taken into account when selecting the right analytical technique. In many cases several techniques will provide adequate detection range, so the technique of choice will depend on factors such as sample throughput requirements, ease-of-use, infrastructure required, and on-going operating costs. In the case of this application, it has been more common for smaller laboratories with low sample throughput requirements to use FAAS, while some larger laboratories (with higher sample throughput requirements) may use ICP-OES.

The 4100 MP-AES fits between FAAS and ICP-OES in many aspects such as detection power, dynamic range, and speed of analysis. For these key performance metrics, the MP-AES offers a unique alternative to both FAAS and ICP-OES.

There are also some clear differentiating benefits of the MP-AES technology over these more traditional options. By eliminating the need for on-going gas resupply, the MP-AES offers significantly reduced on-going operating costs over both FAAS and ICP-OES — and avoids flammable gases (required for FAAS), hence enhancing safety and allowing unattended, overnight operation. The reduced infrastructure required for MP-AES also makes it well-suited to remote sites where supply of gases can be difficult and/or expensive. These features make the MP-AES an attractive technique for many small to medium size agricultural laboratories, particularly those at remote locations, and for an

increasing number of laboratories requiring the lowest possible on-going operating costs.

Experimental

Instrumentation

The 4100 MP-AES revolutionizes the way analysts conduct multi-elemental analysis. Using a microwave plasma that is based on nitrogen, supplied from a compressed air supply and the Agilent 4107 Nitrogen Generator, the 4100 MP-AES does not require flammable or expensive gases such as acetylene, nitrous oxide or argon. This improves lab safety, results in a significant reduction in operating costs and allows installation in mobile labs or remote locations where gas supplies may not be available.

Additionally, the 4100 MP-AES has been designed to improve the analytical performance and productivity when compared with FAAS, with good sensitivity and detection limits down to sub ppb levels over a wide linear range.

Instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	OneNeb
Spray chamber	Glass cyclonic single-pass
Sample tubing	White-white
CsCl tubing	Orange-yellow
Waste tubing	Blue-blue
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Fast pump during sample uptake	Yes
Pump speed	15 rpm

The analysis of soil samples was also carried out by ICP-OES and FAAS. Conditions of analysis are as described in Table 2.

Table 2. Global conditions of analysis

Instrument	Dilution	Comments
Agilent 4100 MP-AES	On-line with CsCl 1.5%	OneNeb nebulizer
Agilent 280 FS AAS	SIPS 20. Dilution factor set by element	CsCl as modifier for Na and K, La/CsCl as modifier for Mg
Agilent 725 ICP-OES	No dilution	OneNeb nebulizer

Table 3. Calibration standards used for soil extraction analysis (mg/L)

	Ca	K	Mg	Mn	Na
Blank	0	0	0	0	0
Standard 1	100	5	5	1.0	0.5
Standard 2	200	10	10	2.0	1.0
Standard 3	300	15	15	3.0	2.0
Standard 4	600	30	30	6.0	4.0

Table 4. Agilent 4100 MP-AES wavelengths and calibration parameters selected for analysis

Element	Wavelength (nm)	Read time (s)	Nebulizer pressure (kPa)	Background correction
Ca	430.253	3	240	Auto
K	769.897	3	240	Auto
Mg	383.829	3	240	Auto
Mn	403.076	3	240	Auto
Na	588.995	3	240	Auto

Material

Soil samples were provided (air-dried and sieved <2 mm) by the French inter-laboratory comparisons organization BIPEA (Inter-professional Bureau of Study and Analysis, France). All samples have been recently analyzed in proficiency testing, so that the reference values and standard deviations for CaO, K_2O, MgO and Na_2O concentrations in ammonium acetate were known. Note: manganese was not included in the testing scheme but has been included in this investigation.

The reference numbers of the soil samples used were 403, 418, 421 and 423.

Sample preparation

As described in the standard NF X 31-108, 1 M ammonium acetate adjusted to pH 7, was used as extractant. The total concentration of dissolved salt was 77 g/L.

For each soil, 50 mL of 1 M ammonium acetate was added to 2.5 g of soil. The mixture was shaken by rotation in a room at 20 °C ±2 °C over 1 hour. After extraction, the samples were filtered using a filter paper and the clear solutions were analyzed immediately.

Standard preparation

Four multi-element standard solutions were prepared in 1 M ammonium acetate. Table 3 provides details of the calibration concentration range for each analyte. Single element stock solutions from Merck Germany were used. Table 4 displays selected wavelengths and calibration parameters used for analysis.

Cesium chloride was used as an ionization buffer. This was added on-line via a 'Y' piece to avoid manual spiking of standards and samples.

Results

Calibration

The calibration curves for Ca, K, Mg, Mn and Na on the MP-AES are displayed in Figure 1. Results show good linearity. This highlights the better linear dynamic range achieved with the 4100 MP-AES as compared to FAAS. Less sample dilutions are then needed when using MP-AES avoiding sample contamination and enhancing productivity.

Sample analysis

The accuracy of the results obtained by MP-AES was evaluated by two methods: i) comparison of the MP-AES results with results obtained with another analytical technique (FAAS and/or ICP-OES) and ii) calculation of z-scores for the MP-AES results with data from the inter-laboratory test (reference results and corresponding standard deviations).
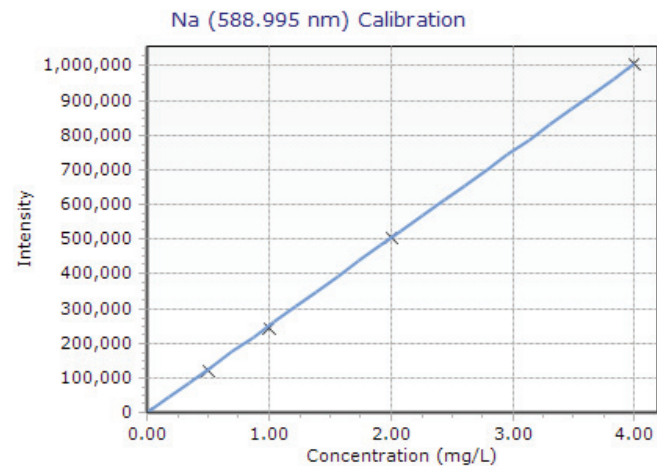
Ca (430.253 nm) Calibration
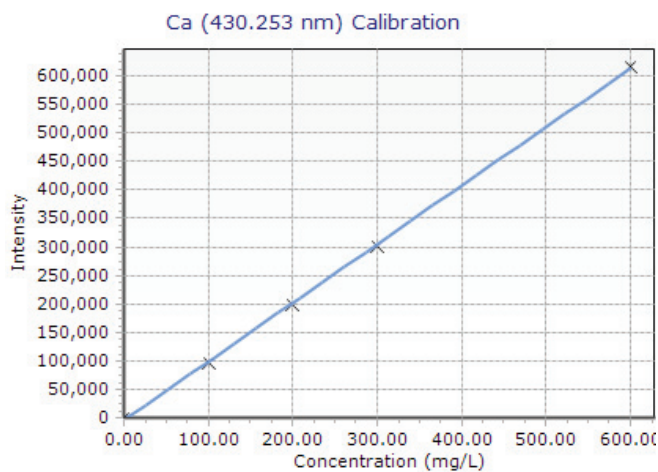
Intensity = 1029.74 * Concentration - 4133.88
Correlation coefficient: 0.99991

Mn (403.076 nm) Calibration
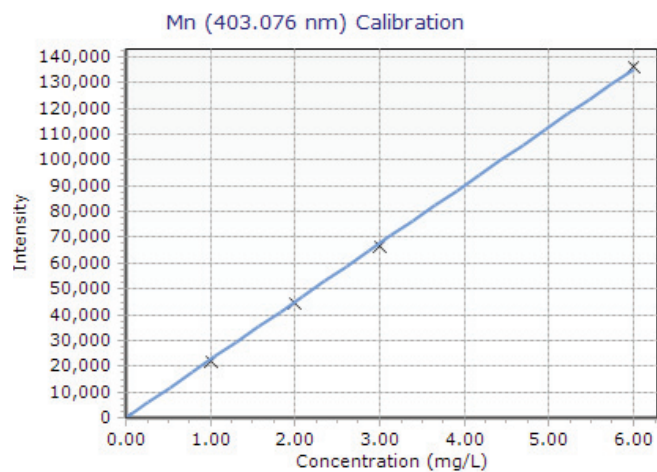
Intensity = 22559.16 * Concentration + 0.01
Correlation coefficient: 0.99992

K (769.897 nm) Calibration
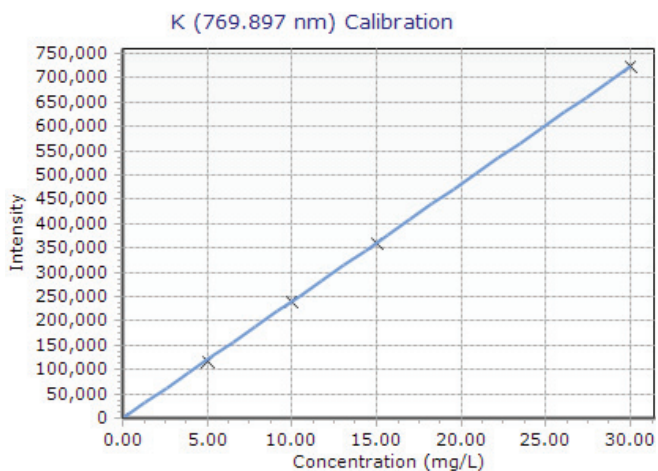
Intensity = 24098.63 * Concentration + 0.01
Correlation coefficient: 1.00000

Na (588.995 nm) Calibration

Intensity = 251417.80 * Concentration - 0.01
Correlation coefficient: 0.99994

Mg (383.829 nm) Calibration
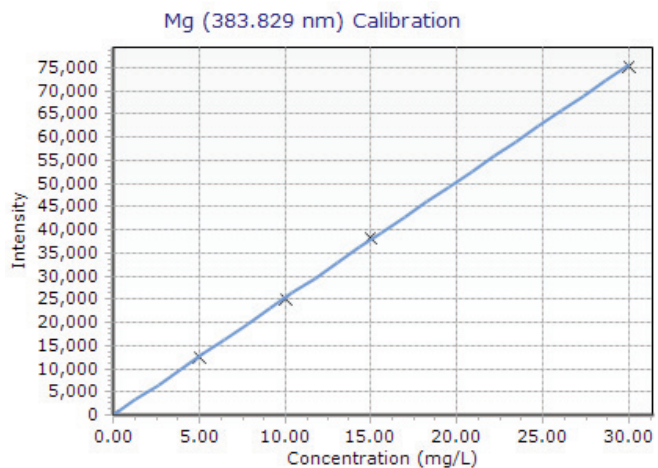
Intensity = 2519.46 * Concentration + 0.97
Correlation coefficient: 0.99997

Figure 1. Typical MP-AES calibration curves for Ca, Mn, K, Na and Mg

Comparison of MP-AES with ICP-OES and/or FAAS

Figures 2 to 6 show for all cations an excellent agreement between the 4100 MP-AES results and those from other spectrometric techniques. The correlation of the analytical results between the different techniques was made and linear regressions are observed: coefficients of determination are $0.995 < R^2 < 0.999$ and the slopes are between 0.969 and 1.043 (Table 5).
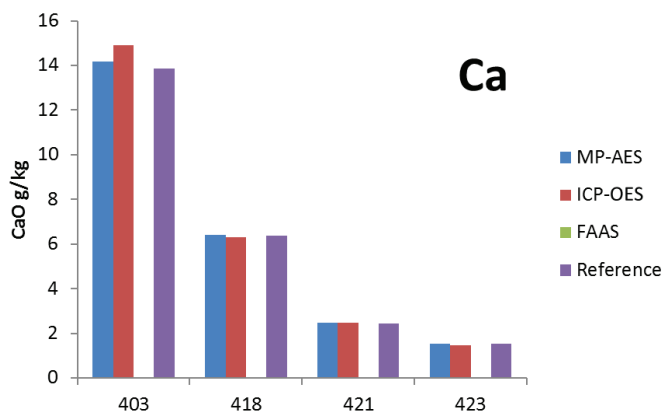

Figure 2. Reference results and Ca concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined)
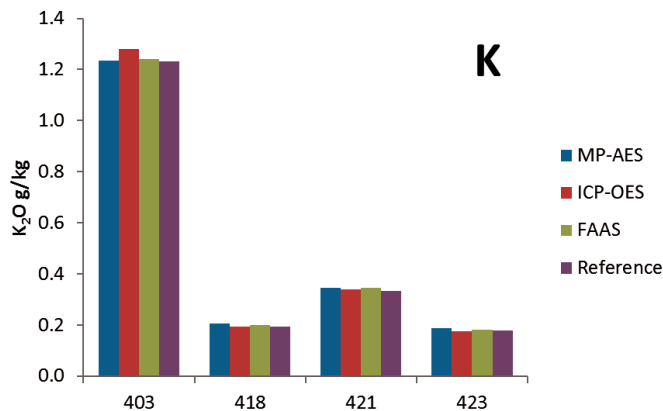

Figure 3. Reference results and K concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS
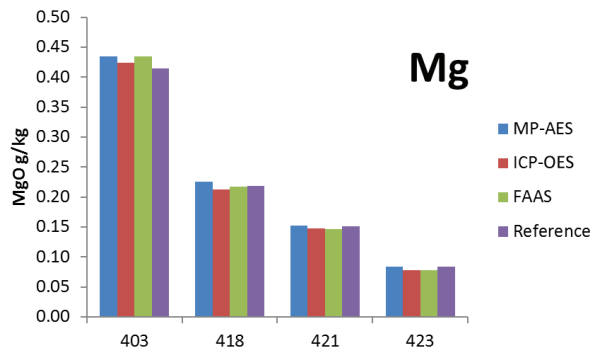

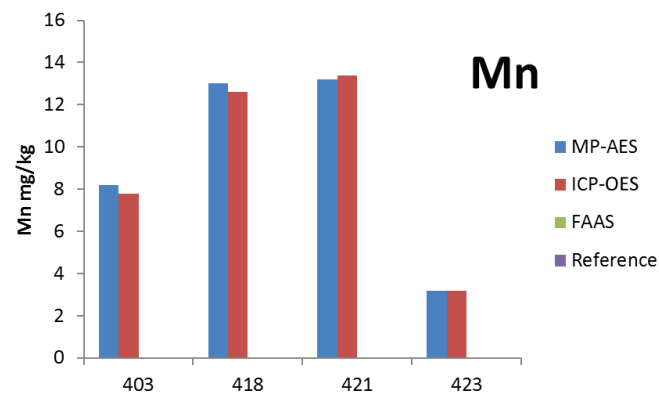**Figure 4.** Reference results and Mg concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

Figure 5. Mn concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined and no reference results available)
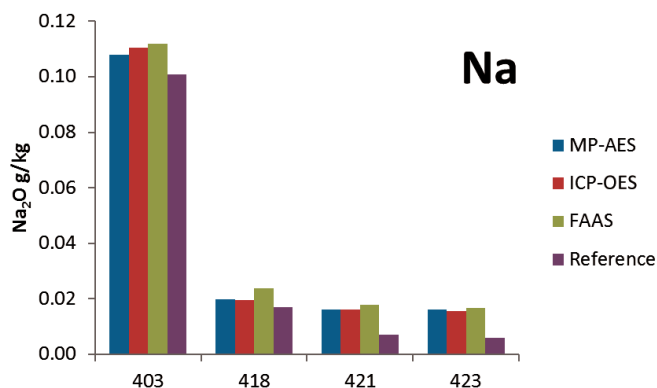

Figure 6. Reference results and Na concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

Table 5. Coefficients of determination (R^2) and slope of linear regressions between MP-AES results and ICP-OES or FAAS (nd = not determined)

	MP-AES vs FAAS		MP-AES vs ICP-OES	
	R²	slope	R²	slope
Ca	nd	nd	0.998	1.038
K	0.999	1.003	0.998	1.029
Mg	0.998	0.988	0.999	0.969
Mn	nd	nd	0.995	0.986
Na	0.998	1.043	0.999	1.022

Compared to the FAAS, the 4100 MP-AES has significant analytical advantages which offer throughput benefits and limit contamination.

- It is a multi-element method.

- There is no need for any manual predilution of the samples with specific conditions for each element (different modifiers and dilution factors), because of a high linear dynamic range and on-line dilution.

- It avoids technical problems like burner blockage in FAAS, despite of a high level of dissolved salt.

Determination of z-scores

For all analytical data obtained with the 4100 MP-AES, a z-score is calculated according to the formula:

z-score = $(X - X_{mean})/SD$

where:
X = the measured concentration obtained on the 4100 MP-AES

X_{mean} = the mean calculated concentration from the inter-laboratory data

SD = the standard deviation calculated from the inter-laboratory data.

The z-scores calculated from MP-AES results are shown in Table 6. All z-scores are <2 for Ca, K and Mg confirming the accuracy of the 4100 MP-AES analytical data. For Na, z-scores are <2 for soil 403 (0.97) and soil 418 (0.98) but are >3 for soil 421 (4.59) and soil 423 (3.39). As observed previously, the MP-AES results are in good agreement with those obtained by FAAS and ICP-OES (Figure 6 and Table 5). The concentration of Na is overestimated for all techniques and the high z-scores are not related to an analytical bias but to the

soil extraction procedure. The source of contamination of soil extracts with Na is well known and is assigned to the manual manipulation of the filter paper. To avoid this contamination, it is recommended to centrifuge rather than filter the soil extracts.

Table 6. z-scores calculated with MP-AES results. nd = not determined (no available inter-laboratory data).

	Soil 403	Soil 418	Soil 421	Soil 423
Ca	0.49	0.04	0.37	0.08
K	0.04	0.79	0.92	1.03
Mg	0.93	0.58	0.13	-0.10
Mn	nd	nd	nd	nd
Na	0.97	0.98	4.59	3.39

Conclusion

The analysis of exchangeable cations in 1 M ammonium acetate extracted soil samples was conducted using the innovative microwave plasma, the 4100 MP-AES. The results show good agreement with values from inter-laboratory tests and with results obtained by well-proven techniques such as FAAS and ICP-OES. This confirms the suitability of the 4100 MP-AES to this application.

Furthermore, MP-AES offers a number of advantages compared to more traditional well proven techniques:

- Enhanced productivity — with safe, reliable, unattended multi-element analysis, the sample throughput of MP-AES is more than twice that of conventional FAAS systems.

- High-performance — the magnetically-excited microwave plasma source provides improved sensitivity, linear dynamic range, and detection limits compared to FAAS.

- MP-AES eliminates the need for costly consumables such as hollow cathode lamps and deuterium lamps for background correction, while avoiding burner blockage.

- The cost of ownership associated with MP-AES is low by avoiding the need for on-going supply of flammable or expensive gases such as acetylene, nitrous oxide and argon.

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