Application Note

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Determination of Multiple Elements in Fertilizers using the Agilent 4210 MP-AES

Meeting Brazilian regulations with the accurate analysis of 17 elements in commercial fertilizers

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Introduction

Fertilizers are widely used to increase crop yield by supplying essential minerals to plants. Several authors (*1–5*) have described the importance of fertilizers to the agribusiness sector to achieve high crop productivity. It is important to understand and assess the composition of the raw materials used to manufacture a fertilizer, to ensure its effectiveness for a specific soil and/or plant. Mineral fertilizers are obtained by processing natural minerals that contain high levels of P, K, Ca, Mn, and other elements that are essential to plant-growth. However, the final product may also contain elements that are potentially harmful to plants and humans, such as As, Cd, Cr, Hg, and Pb. These elements can migrate away from the crops to underground waters, contaminating the environmental, or remain on edible plants. To regulate the production of fertilizers, the Brazilian Ministry of Agriculture, Livestock and Supply (MAPA) issued Ordinance n. 27, altered by Normative Instruction n. 7 in May 2016 (*6*).

The maximum permitted concentrations for heavy metals specified in the regulations depend on the fertilizer's composition and intended use.

The determination of elements in fertilizers is typically done using Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). These are well documented and reliable techniques, but AAS uses hazardous gases and AAS-techniques typically measure one element at a time. The concentrations of potentially harmful elements that are commonly observed in fertilizers are below ICP-OES's limits of quantitation, so there is need for extra sensitivity. More recently, Microwave Plasma-Atomic Emission Spectrometry (MP-AES) has been used for the analysis of these elements (*3, 5*). MP-AES combines the multi-element characteristics of ICP-OES with the ease-of-use of FAAS. Since it is an atomic emission technique, there is no need for expensive consumables such as hollow cathode lamps or continuous sources.
The Agilent 4210 MP-AES uses nitrogen to generate the plasma, which can be obtained from air using the Agilent 4107 Nitrogen Generator. Since the instrument "runs on air", the cost-of-ownership is lower than other techniques.

Measuring the elemental content of fertilizers that contain organic matter can be challenging using atomic spectroscopy, but MP-AES has been used successfully to determine multiple elements in fertilizers (*1*). Sample preparation is crucial, and the preparation method used depends on the elements to be measured.

In this study, five fertilizers with different compositions were acid-digested and analyzed in a single run using the Agilent 4210 MP-AES. The element list included. Al, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, V, and Zn. The method was in accordance with Ordinance n. 27 from the Brazilian Ministry of Agriculture, Livestock and Supply to verify the composition of commercial fertilizers. The determination of As and Hg in fertilizers using the 4210 MP-AES is described elsewhere (*3, 5*).

Experimental

Instrumentation

All measurements were performed using an Agilent 4210 MP-AES fitted with a double-pass cyclonic spray chamber and a OneNeb Series 2 nebulizer. N_2 was supplied using an Agilent 4107 Nitrogen Generator. All wavelengths were selected from the MP Expert software library, according to the sensitivity that was required. MP-AES operating conditions are shown in Table 2.

Table 2. MP-AES operating conditions.

Parameter	Setting
Replicates	3
Background correction	Auto (except Mo and Cd: off-peak right)
Read time (s)	3 (except Cd, 10 s, and Pb, 5 s)
Viewing position	0
Nebulizer flow (L/min)	0.5
Pump speed (rpm)	12
Uptake time (s)	15
Stabilization time (s)	15
Calibration fit	Linear
Sample tubing	Orange/green
Drain tubing	Blue/blue
Spraychamber	Double-pass
Nebulizer	OneNeb Series 2, with nitrogen humidifier
Total run time (min)	4

Reagents and standards

Agilent 1,000 mg/L single element stock standards of Al, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, V, and Zn were mixed to a final solution containing 10% (v/v) of HCl (Merck, São Paulo, Brazil) and Type 1 water (Sartorius, Göttingen, Germany). The concentration ranges included: 0.2 to 1.0 mg/L for Cd, Co, Mo, and Ni; 1 to 5 mg/L for Al, Cr, Mg, Mn, V, and Zn; 2 to 10 mg/L for B, Ca, Cu, Fe, and Pb; 5 to 25 mg/L for K, and 5 to 50 mg/L for P.

Sample preparation

Five different types of fertilizer were bought in a local store in São Paulo, Brazil (Figure 1). A Multiwave GO (Anton Paar, Graz, Austria) closed vessel microwave-assisted digestion system was used to prepare the samples. Each fertilizer was prepared in triplicate by adding 5.0 mL of HCl and 5.0 mL of Type I water to 0.25 g of ground sample. The mixture was left to react for five minutes before closing the PTFE vessel and applying the sample digestion procedure outlined in Table 1. After cooling, the solution was transferred to a 50 mL volumetric flask and made up to volume with Type 1 water. The initial dilution factor was 200x, and this solution was used to make further dilutions as needed.

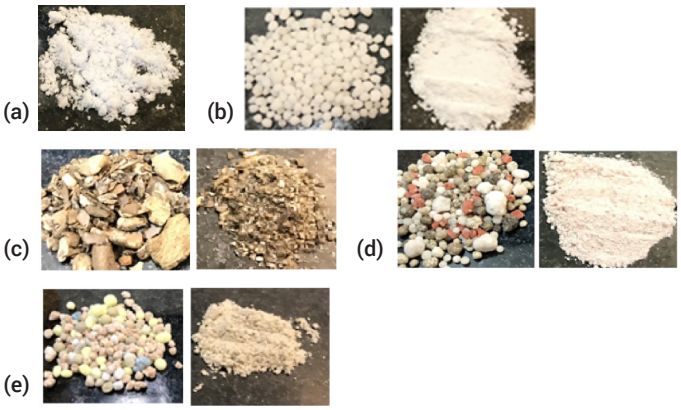

Figure 1. Fertilizer samples before and after grinding: a: urea (already ground), b: foliage fertilizer, c: organic fertilizer, d: NPK fertilizer, and e: mineral fertilizer.

The Standard Reference Material (SRM) 695 - Trace elements in multinutrient fertilizer (National Institute of Standards and Technology, Department of Commerce, USA) was also prepared in triplicate. It was used to check the accuracy of the method and to validate the sample preparation procedure. Seven blanks of HCl 10% (v/v) were prepared using the same preparation procedure as for the samples.

Table 1. Microwave-assisted digestion program.

Step	Ramp Time (min)	Temperature (°C)	Hold Time (min)
1	10	100	2
2	10	150	10
3	10	170	5

Results and discussion

Calibration linearity

Each element was calibrated using a six-point calibration. All calibration curves showed good linearity across the concentration range, as indicated by the correlation coefficients (R > 0.999) given in Table 3. Representative calibration curves for P 213.618 nm, Cd 228.802 nm, Al 396.152 nm, and K 769.897 nm are shown in Figure 2.

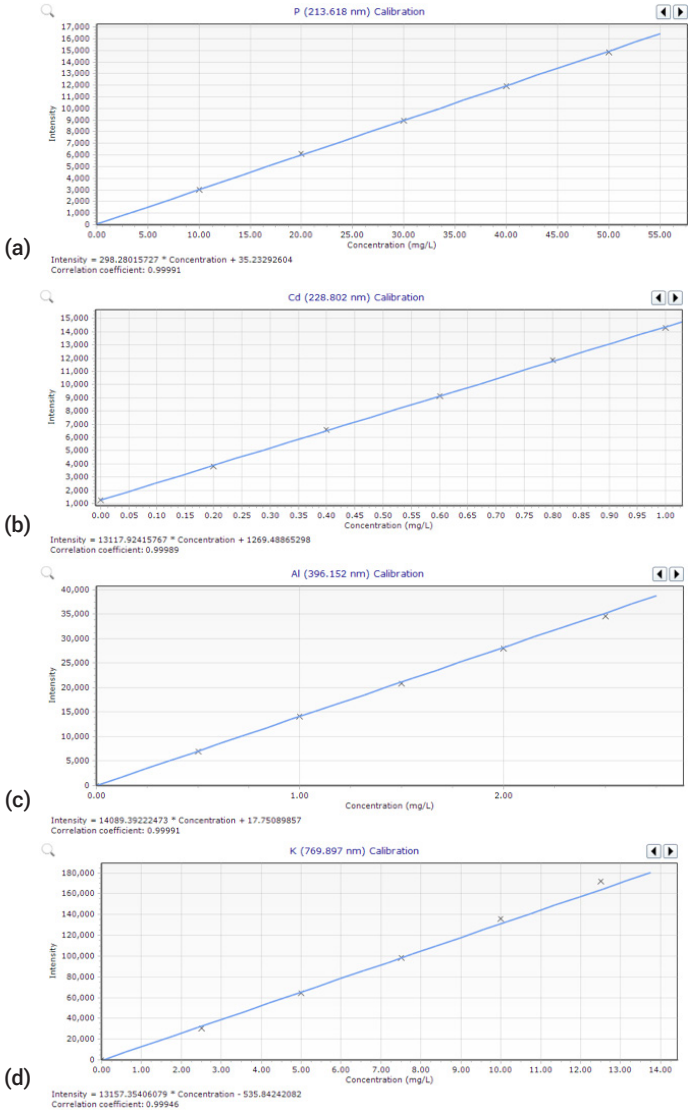

Figure 2. Calibration curves for (a) P 213.618 nm, (b) Cd 228.802 nm, (c) Al 396.152 nm, and (d) K 769.897 nm.

Excellent figures of merit were obtained for all 17 elements measured by MP-AES, as shown in Table 3. The limits of quantitation (LOQs) were calculated using 10 times the standard deviation of readings from seven blanks and multiplying the result by the initial dilution factor (200x). All LOQs exceeded the requirements specified in Ordinance n.27, showing the sensitivity of MP-AES is sufficient for the analysis. If data is required for fewer analytes, the analysis time can be reduced. Sample throughput can be improved using productivity accessories such as the Agilent SPS 4 autosampler and Advanced Valve System (AVS 4). The AVS 4 also reduces the matrix load on the sample

introduction system, which is useful if large numbers of samples are being analyzed. Less sensitive wavelengths were used for high concentration elements, such as Ca, K and Mg, while the most sensitive emission wavelengths were used for less sensitive or low concentration elements, such as Cd, Pb, and P. This approach allowed all elements to be determined in the same run. By eliminating the need to make successive dilutions, productivity is improved and potential errors from contamination due to multiple dilutions are avoided. No significant spectral interferences on the SRM and samples were observed when comparing the spectra from the standards and samples.

Table 3. Linearity and limits of quantitation for 17 elements analyzed by MP-AES.

Element	Wavelength (nm)	Correlation Coefficient	LOQ (mg/kg)	Normative Instruction SDA n.27 (mg/kg)[a]
Al	396.152	0.9999	0.8	-
B	249.772	0.9998	18	-
Ca	616.217	0.9996	4.1	-
Cd	228.802	0.9999	2.1	3.00
Co	350.228	0.9999	6.5	-
Cr	425.433	0.9997	0.3	200
Cu	324.754	0.9999	3.9	-
Fe	371.993	0.9997	4.6	-
K	769.897	0.9995	4.8	-
Mg	383.230	0.9998	81	-
Mn	403.076	0.9998	0.9	-
Mo	386.410	0.9998	2.3	-
Ni	341.476	0.9999	6.4	70
P	213.618	0.9999	684	-
Pb	405.781	0.9998	10	100
V	437.923	0.9998	1.1	-
Zn	213.857	0.9995	12	-

[a]Lowest regulated limit.

Long-term stability test

A fertilizer SRM solution was analyzed about 100 times, which equates to approximately 7 hours. Figure 3 shows excellent stability for P, Zn, Cu, Fe, Mg, Al, Mn, Cr, V, Ca, and K with %RSDs below 2.4%. This excellent precision means that the 4210 MP-AES can run throughout a typical working day, without the need to recalibrate.

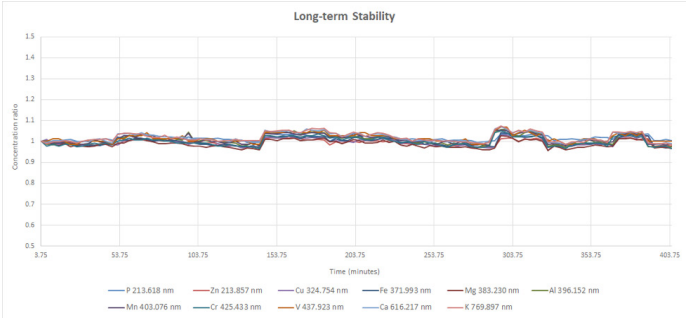

Figure 3. Long-term stability test results for the continuous measurement of multiple elements in a diluted fertilizer SRM sample over seven hours.

SRM recovery

The accuracy of the method was evaluated by analyzing the NIST 695 fertilizer SRM. The recovery results for all analytes reported in Table 4 ranged from 89 to 116% with precision (RSD %) lower than 10% (n = 3), as shown in Table 5. The results demonstrate the ability of the 4210 MP-AES to accurately determine all elements at required levels in fertilizer samples.

Table 4. NIST 695 - Trace elements in multinutrient fertilizer SRM results and recoveries based on certified or reference values. n=3.

Element	Reference Value (mg/kg)	Measured Concentration (mg/kg)	Recovery (%)
Al	6,100	6,724 ± 704	110
B	1,110	1,107 ± 102	100
Ca	22,600	21,338 ± 541	94
Cd	16.9 (12.4 – 23.2)*	16.9 ± 0.3	100
Co	65.3 (27.4 – 65.7)*	75.9 ± 0.4	116
Cr	244 (136 – 192)*	239 ± 1.8	98
Cu	1,225	1,246 ± 112	102
Fe	39,900	38,842 ± 777	97
K	116,500	107,849 ± 2.734	93
Mg	17,900	18,086 ± 369	101
Mn	3,050	3,076 ± 63	101
Mo	20.0 (10.2 – 16.8)*	17.7 ± 0.1	89
Ni	135 (85 – 131)*	125 ± 0.8	93
P	72,000	70,830 ± 5.018	98
Pb	273 (231 – 281)*	266 ± 2.0	97
V	122	110 ± 0.9	90
Zn	3,250	3,332 ± 278	103

**Concentration range provided in the NIST 695 Certificate of Analysis addendum, page 5 (7). The data was obtained using a more routine method of microwave digestion with concentrated nitric acid, followed by ICP-OES detection.*

Quantitative analysis of fertilizers

Five commercial fertilizers were analyzed using the 4210 MP-AES. The quantitative concentrations for Cd, Cr, Ni, and Pb were all below the regulatory limits specified in the Normative Instruction SDA n. 27, as shown in Table 5.

The results in Table 5 for K and P are given as compound concentrations. The measured concentrations were multiplied by 1.20458 and 2.29136, respectively, then converted to %. This was done automatically using the custom column calculation provided in the MP Expert software.

Table 5. Analysis of five fertilizers of different compositions using the Agilent 4210 MP-AES.

Element	Sample A (mg/kg)	Sample B (mg/kg)	Sample C (mg/kg)	Sample D (mg/kg)	Sample E (mg/kg)
Al	<0.8	<0.8	3,575 ± 121	6,531 ± 649	682 ± 49
B	<18	3,984 ± 262	35,017 ± 3.330	<18	219 ± 12
Ca	43 ± 3.7	1,268 ± 3.4	41,993 ± 3.,275	9,082 ± 719	123,707 ± 5,919
Cd	<2.1	<2.1	<2.1	<2.1	<2.1
Co	<6.5	<6.5	19 ± 1.4	<6.5	12 ± 0.4
Cr	<0.3	0.4 ± 0.01	<0.3	<0.3	<0.3
Cu	<3.9	4.1 ± 0.5	43 ± 1.9	26 ± 0.8	305 ± 30
Fe	<4.6	28 ± 2.2	2,716 ± 65	3,611 ± 343	7,102 ± 315
K_2O	0.03%	12.3%	11.7%	1.1%	13.3%
Mg	253 ± 20	224 ± 11	3,756 ± 316	4,133 ± 711	8,256 ± 187
Mn	<0.9	4.1 ± 0.3	344 ± 17	126 ± 9.2	858 ± 48
Mo	<2.3	<2.3	22 ± 1.3	<2.3	4.4 ± 0.3
Ni	<6.4	<6.4	<6.4	50 ± 4.3	13 ± 1.2
P_2O_5	<0.1%	19.3%	5%	0.8%	10%
Pb	<10	13 ± 0.4	29 ± 1.1	15 ± 0.1	<10
V	1.2 ± 0.2	1.3 ± 0.1	<1.1	<1.1	<1.1
Zn	14 ± 1.3	1,444 ± 102	212 ± 27	96 ± 2.9	621 ± 46

The concentration of nutrients on fertilizer-labels represents the manufacturer's guarantee for minimum percentage of nutrients in the product. The results in Table 6 compare the manufacturer's guaranteed nutrient concentrations with measured concentrations obtained using MP-AES.
Some of the MP-AES results are below the labeled values, e.g. Zn and B in sample B and K_2O in sample C. The lower results could be due to sample inhomogeneity. However, higher concentrations of K_2O and P_2O_5 were reported for MP-AES in samples B and E. Depending on the raw materials used for production, normally minerals, variations in the final composition of K_2O and P_2O_5 do arise. Manufacturers should strictly control the elemental content of raw materials and take a mass balance approach to the final composition of fertilizers.

Table 6. Guaranteed nutrient concentrations for three fertilizers and MP-AES analysis results. No guaranteed concentration information was supplied for samples A and D.

Fertilizer Sample	B	C	E
Concentration stated on product label	15% P_2O_5 0.2% Zn 0.7% B 10% K_2O	5% P_2O_5 15% K_2O	10% P_2O_5 10% K_2O
4210 MP-AES measured concentration	19.3% P_2O_5 0.14% Zn 0.4% B 12.3% K_2O	5.0% P_2O_5 11.7% K_2O	11.7% P_2O_5 13.3% K_2O

Conclusion

A simple and complete method for the determination of 17 elements in fertilizers using the Agilent 4210 MP-AES has been developed and evaluated. The 4210 MP-AES provides excellent analytical performance for the application, as indicated by the LOQs, long-term stability, and SRM recovery test.

Since MP-AES uses a nitrogen-based plasma, it eliminates the need for the expensive and hazardous gases required by FAAS. MP-AES therefore represents a safer, low-cost alternative to FAAS for the determination of nutrients and contaminants in fertilizers.

The 4210 MP-AES achieved excellent linearity for all elements across a wide linear dynamic range, outperforming the linear range of FAAS. It also offers greater sensitivity than FAAS, as shown by the LOQs for all elements, including B, P, and Al, which are difficult to analyze using a flame-based instrument. The results also complied with the lowest limits stated in the Brazilian SDA n.27 regulations for Cd, Cr, Ni, and Pb.

The accuracy of the method was evaluated by analysis of the NIST 695 fertilizer SRM. Recoveries for most elements were within ± 10% of the certified values.

This study and previous studies reported in the literature show that MP-AES can be considered as an alternative analytical technique to AA and ICP-OES for the analysis of fertilizer samples.

References

1. V. Pelizzaro, A. Pensato, A. Carcano, M. Costedoat, Determination of Macro and Micronutrients in Fertilizers using MP-AES, Agilent publication, 5994-0566EN
2. W. Li, P. Simmons, D. Shrader, T. J. Herrman, S. Y. Dai, Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper, iron, manganese and zinc in animal feed and fertilizer; *Talanta* 112, **2013**, 43–48.
3. A. F. Lima, M. C. Da Costa, D. C. Ferreira, E. M. Richter, R.A.A. Munoz, Fast ultrasound-assisted treatment of inorganic fertilizers for mercury determination by atomic absorption spectrometry and microwave-induced plasma spectrometry with the aid of the cold-vapor technique, *Microchem* J. 118, **2014**, 40–44.
4. A. F. Lima, F.F. Lima, E. M. Richter, R.A.A. Munoz, Combination of sonication and heating for metal extraction from inorganic fertilizers prior to microwave-induced plasma spectrometry determination, *Applied Acoustics*, article in press.
5. R. C. Machado, C.D.B. Amaral, J. A. Nóbrega, A.R.A. Nogueira, Multielemental Determination of As, Bi, Ge, Sb and Sn in Agricultural Samples Using Hydride Generation Coupled to Microwave-Induced Plasma Optical Emission Spectrometry, *J. Agric. Food Chem.* **2017**, 65, 4839-4842.
6. Ordinance n. 27, Brazilian Ministry of Agriculture, Livestock and Supply, May 2016, http://www.agricultura.gov.br/assuntos/insumos-agropecuarios/insumos-agricolas/fertilizantes/legislacao/in-sda-27-de-05-06-2006-alterada-pela-in-sda-07-de-12-4-16-republicada-em-2-5-16.pdf (accessed March 2019)
7. Certificate of Analysis, Standard Reference Material 695 Trace Elements in Multi-Nutrient Fertilizer, https://www-s.nist.gov/srmors/view_detail.cfm?srm=695 (accessed March 2019)

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