

Microwave induced plasma optical emission spectrometry in agricultural analysis

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ABSTRACT

The article describes the use of the recently commercially available technique of microwave induced plasma optical emission spectrometry with plasma gas (nitrogen) generation for the determination of calcium, magnesium, phosphorus and potassium in Mehlich 3 extracts. The specifics of the analysis of the agricultural samples for soil fertility assessment mean there are often a great number of samples to analyse in laboratory (the daily throughput of 500 or more samples). The analytical procedures were adapted to special requirements by the use of the new multielemental instrumental techniques. The detection limits were 0.43; 0.86; 0.20 and 0.06 mg/L; the precision for real sample analysis: 4.6; 1.0; 1.8 and 1.0%; the mean accuracy 97; 92; 107 and 100% for P, Ca, Mg and K, respectively, the real throughput reached 100 samples per hour.

Keywords: spectrometric techniques; nutrients extraction; fertilization; macromineral composition

Soil, follow soil science glossary is: The unconsolidated mineral or organic material on the immediate surface of the Earth that serves as a natural medium for the growth of land plants. As soil fertility depends on physical, chemical and biological characteristics, the macromineral composition of soils is an important subject in agricultural studies (Tiessen 1994, Mäder 2002). All plants are characterized by certain nutrient requirements. Therefore, to maintain soil fertility, the used nutrients must be replaced by fertilizers.

Macrominerals consist of elements, which can exist in soil in different chemical forms: cations (Na, K, Ca, Mg), anions (e.g. P, C, Cl, N, S), or be built into organic molecules. Determination of four alkali and alkaline earth elements has been of vast importance to soil studies for over 50 years (David 1960). Although in the past there have been many approaches to colorimetric determination of Na (Arnold 1943), K (Takagi 1977), Mg (Pieters et al. 1948), and Ca (Peaslee 1964), the flame photometry used to be a leading method of determination of these elements in agrolaboratories, nowadays these techniques seem outdated. The rapid growth of

spectrometric techniques, like atomic absorption spectrometry (AAS), microwave induced plasma optical emission spectrometry (MIP-OES), inductively coupled plasma optical emission spectrometry (ICP-OES) have caused these older techniques to lose their primal significance in analytical chemistry.

MIP-OES, with its first analytical application in 1960s (Mavrodineanu 1964) and later commercialization of instruments (Jankowski 2001a) comes to increase significance in modern determination of elements. The application of the method for determination of: Na (Jankowski 2001b), K, Ca, Mg (Matusiewicz 2010), is based on laboratory-made analytical instruments. MIP-OES can easily compete with technique based on inductively coupled plasma source (ICP-OES), due to the possibility of using nitrogen (in opposition to more expensive Ar) as a plasma gas (Arai 2013) and may offer lower detection limits for Na and K (Jankowski 2001), which is especially important in this study.

The low cost of instrumentation and low running cost (nitrogen can be produced from air by nitrogen generator) are very attractive for routine use of MIP-OES instruments.

Prior to determining element content by MIP-OES technique, elements in soil need to be extracted into aqueous phase. Many different extraction methods were proposed in studies (McIntosh 1969, Rauret 1998), including extraction using EDTA as a chelating agent (Manouchehri et al. 2006). Mehlich-3 (M-3) is a widely used multi-element nutrient extractant effective on soils with a wide range of physical and chemical properties (Mehlich 1984). Comparison studies between different extractants have shown that M-3 can be adapted as a suitable extractant for routine soil analysis (Alva 1993). The Mehlich 3 solution (Wuenschel et al. 2015) is an agrochemical extractant used for determination of bioavailable P, Ca, Mg and K for soil fertility assessment in agriculture (with additional potential to determine content of some micronutrients). Extractability of phosphorus is improved by addition of ammonium fluoride and acetic acid. EDTA is added to improve extractability of microelements.

The specifics of the analysis of the agricultural samples for soil fertility assessment mean there is often a great number of samples to analyse per laboratory (the daily throughput of 500 or more samples). The analytical procedures should be adapted to special requirements e.g. by the use of the multielemental instrumental techniques. This article describes the use of the new commercially available technique of microwave induced plasma optical emission spectrometry with plasma gas (nitrogen) generation for determination of Ca, Mg, P and K in Mehlich's solution extracts.

MATERIAL AND METHODS

Instrumentation and reagents. The nitrogen (with on-line nitrogen generator) microwave induced plasma optical emission spectrometer MP-AED 4100 (Agilent, USA) set up in a multi-elemental mode was used. The spectrometer was equipped with the Czerny-Turner monochromator with 600 mm focal length with fixed entrance slit, holographic diffraction grating with 2400 lines/mm (wavelength range 178–780 nm) and CCD detector (532 × 128 pixels) directly cooled to 0°C using a thermoelectric Peltier device. The microwave excitation assembly was an air-cooled magnetron operating at 2450 MHz (fixed plasma power of 1 kW, vertically-oriented plasma with end-on or

axial viewing). The plasma gas flow (nitrogen) was fixed at 20 L/min and the auxiliary gas flow was fixed at 1.5 L/min. The spray chamber, plastic One-Neb nebuliser and quartz plasma torch (Agilent, USA) were used. The operating parameters: viewing position and nebuliser pressure were optimised for each element respectively and discussed in the text.

As the reference analytical method the inductively coupled plasma optical emission spectrometer Agilent 5100 ICP-OES (Agilent, USA) was used. The common conditions were used: radio frequency (RF) power 1.2 kW, nebulizer gas flow 0.7 L/min, auxiliary gas flow 1.0 L/min, plasma gas flow 12.0 L/min, charge coupled device (CCD) temperature –40°C. The determination of phosphorus was provided at 213.618 nm; calcium 616.217 nm; magnesium 279.553 nm and potassium 766.491 nm, respectively.

Only reagents of analytical purity and deionised water produced in a Milli-Q device (Millipore, USA) were used. For MIP-OES analysis the commercial standards 1.00 g/L (Merck, Germany) after appropriate dilution were used. For sample preparation the Mehlich-3 solution: 0.2 mol/L CH_3COOH ; 0.25 mol/L NH_4NO_3 ; 0.015 mol/L NH_4F ; 0.013 mol/L HNO_3 ; 0.001 mol/L EDTA (all chemicals obtained from Merck, Germany) was used.

Sample preparation and extraction. The soil samples were acquired from farmers (the samples origin was the agricultural areas) for the soil fertility assessment and were dried in the laboratory drier at 40°C, sieved through a 2.0 mm sieve to remove bigger rocks and organic matter and homogenized by grinding according the international standard ISO 11464, 2006. 5.00 g of sample was extracted by 50.0 mL of Mehlich's solution (extraction 1:10 m/V) over the course of 5 min at the ambient temperature with continuous shaking. Next, the sample was filtered by paper filter and stored before analysis not longer than one day in the darkness.

RESULTS AND DISCUSSION

Analytical procedure. The most important condition for the analysis of agricultural samples is a big number of samples to analyse per laboratory (500 or more samples each day). This is the reason that the analytical procedure of calcium, magnesium, phosphorus and potassium determination

in Mehlich's solution extract should be different to the standard analytical procedure used e.g. for geochemical studies (Niedzielski et al. 2015). Given the sufficiently high quality of the results (according to the quality management system based on ISO 17025), the analysis should be shortened to obtain the high laboratory throughput. The parameters of the MIP-OES analysis were optimised to obtain the maximal speed of analysis.

Optimisation of instrumental conditions. In MIP-OES technique the following parameters should be optimised for each element determined: the nebuliser gas pressure (nebuliser pressure) and the plasma observation position (viewing position). The results of the signal measurement at different conditions (SRBR – signal to root background ratio) are put together in Figure 1a (nebuliser pressure) and Figure 1b (viewing position). To compare the results the signal to root background ratio data were normalised to the highest signal value. The nebuliser gas pressure (changes of conditions of aerosol production, especially of drops dimension and aerosol density) essentially affected the increase of analytical signal for potassium and magnesium, whereas for phosphorus and calcium the changes of the analytical signal were slight. Additionally, the highest emission was recorded in the central part of plasma for all elements determined.

The sequential analysis was performed automatically with the appropriate (optimised) changes of operating parameters: viewing position and nebulizer pressure while the nebulizer pressure indicates (automatically by spectrometer software)

the sequence of analysis (the elements determination was grouped from the lowest to the highest value of the nebuliser pressure, in this case: P, Ca, Mg, and K).

For high differences of the analytical wavelengths: 769.897 nm for K, 616.217 nm for Ca, 383.829 nm for Mg follow previous work (Niedzielski et al. 2015) and 213.618 nm for P (follow manufacturer of the spectrometer) the monochromator adjusting is the most time-consuming step of the analysis. Additionally, the emission at analytical wavelength of phosphorus (213.618 nm) and potassium (766.491 nm or 769.897 nm) was essentially higher than at the alternative wavelengths (the relative emission factor 56 824 for K at 766.491 nm or 110 084 for K at 769.897 nm versus 164 for K at 344.738 nm, and 547 for P at 213.618 nm versus 131 for P at 764.934 nm). To find the maximal efficiency of the monochromator (adjusting for calcium and magnesium determination) the alternative wavelengths 616.217 nm (Ca) and 517.268 nm (Mg) were used. The final sequence of the analysis was: P (213.618 nm), Ca (616.217 nm), Mg (517.268 nm), K (766.491 nm) with more than a 50% of time consumption saving.

Analytical performance of the method. Optimised analytical methodology was characterised following the ISO 17025 criteria. The following parameters were defined (follow the previous work Niedzielski et al. 2015): detection limits (defined as 3sigma criteria, where sigma is a standard deviation of a series of 6 replications of a blank) and limits of quantification (6 sigma criteria) for extractant and for soil sample extracts,

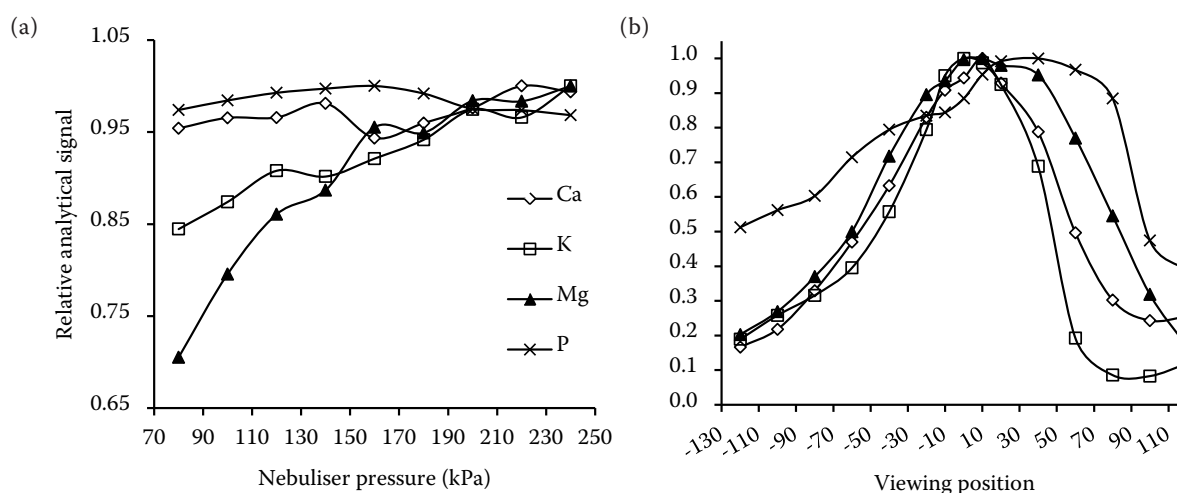


Figure 1. The changes of analytical signal with (a) the nebuliser pressure changes and (b) viewing position changes (viewing position in dimensionless manufacturer units)

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Table 1. The analytical condition for MIP-OES analysis and analytical figures of merit ($n = 6$)

		P	Ca	Mg	K
Wavelength	nm	213.618	616.217	517.268	766.491
Viewing position		60	10	10	0
Nebuliser pressure	kPa	160	220	240	240
Replicates		3	3	3	3
Read time		1	1	1	1
Uptake time	s	5	5	5	5
Uptake pump speed	rpm	75	75	75	75
Stabilisation time	s	5	5	5	5
Pump speed	rpm	15	15	15	15
Background correction		auto	auto	auto	auto
Detection limit	mg/L	0.43	0.86	0.20	0.06
Determination limit		0.86	1.7	0.40	0.12
Detection limit	mg/kg	4.3	8.6	2.0	0.6
Determination limit		8.6	17	4.0	1.2
RSD for standard 10 mg/L		4.9	5.2	1.9	1.1
RSD for standard 20 mg/L		2.8	3.2	1.6	0.6
RSD for real sample	%	4.6	1.0	1.8	1.0
Recovery for standard 10 mg/L		105.9	104.1	113.7	110.1
Recovery for standard 20 mg/L		105.9	114.1	95.8	118.2

the instrumental precision of determinations for standards and real samples (Table 1). The same conditions were obtained for maximum sensitivity and the lowest limit of detection with minimum matrix effect and, additionally, no interferences were recorded for Mehlich's solution matrix of standards compared with water based standard

solutions. For all analysis water based standards were used. The obtained values of parameters characterising the analytical method showed a real possibility to apply MIP-OES technique in the determinations of elements content in the Mehlich's extracts of environmental samples. The calibration range was the highest range of linear-

Table 2. The traceability studies based on the inter-laboratory analysis

	Sample A				Sample B			
	P	Ca	Mg	K	P	Ca	Mg	K
IntLab (mg/kg)	180 ± 17	7344 ± 833	257 ± 17	177 ± 11	133 ± 10	6956 ± 691	241 ± 26	149 ± 11
MIP-OES 1	168 ± 8	6772 ± 345	261 ± 7	163 ± 4	137 ± 4	6387 ± 293	270 ± 7	157 ± 5
MIP-OES 2	162 ± 7	6586 ± 311	257 ± 7	171 ± 5	136 ± 4	6527 ± 321	269 ± 6	160 ± 5
Recovery (%)								
MIP-OES 1	93 ± 4	92 ± 5	102 ± 3	92 ± 2	103 ± 3	92 ± 4	112 ± 3	105 ± 3
MIP-OES 2	90 ± 4	90 ± 4	100 ± 3	97 ± 3	102 ± 3	94 ± 5	112 ± 2	107 ± 3

IntLab – results obtained in inter-laboratory comparison (9 laboratories); MIP-OES – results obtained by MIP-OES technique in two independent analysis ± standard error

Table 3. The comparison of the results obtained by MIP-OES techniques and received from commercial accredited laboratory (ComLab)

Sample	MIP-OES				ComLab			
	P	Ca	Mg	K	P	Ca	Mg	K
(mg/kg)								
1	109	802	153	200	91	–	170	211
2	96	57	31	67	44	–	79	75
3	168	1440	64	180	147	–	85	194
4	68	5470	261	163	137	7340	232	146
5	129	413	83	150	108	–	101	168
6	137	5890	280	197	181	7160	250	176
7	113	669	141	238	98	–	163	251
8	104	1230	64	96	78	–	68	101
9	116	102	18	61	77	–	25	70
10	109	582	102	202	105	–	112	214
Recovery (%)	P	Ca	Mg	K				
1	119.2	–	90.1	94.8				
2	218.6	–	39.2	89.9				
3	113.9	–	75.8	93.0				
4	49.9	74.6	112.6	111.5				
5	119.4	–	81.8	89.4				
6	75.5	82.2	111.8	111.7				
7	115.3	–	86.2	95.0				
8	133.3	–	93.4	95.4				
9	150.9	–	72.0	87.0				
10	103.8	–	90.7	94.3				
Min	49.9	74.6	39.2	87.0				
Median	117.3	78.4	88.1	94.6				
Max	218.6	82.2	112.6	111.7				

P values are approximate only because of the spectrophotometric determination (content of PO_4) and cannot be directly compared with MCP or ICP determination (total P)

ity of calibration curves. For some samples – not numerous – manual dissolving have to be used.

Due to the lack of standard reference material for Mehlich's extraction the traceability studies were provided using two methods. The first was recovery studies by two level standard additions (final added level in solution as 10 mg/L and 20 mg/L) to real samples (Table 1). The mean recovery was found as 106; 109; 105 and 114% for P;

Ca; Mg and K, respectively. The second method was the comparison of the results obtained by MIP-OES technique with the results obtained for the same samples during inter-laboratory comparisons (atomic absorption or flame emission spectrometry for metals and spectrophotometric method for phosphorus, Table 2). The interlaboratory studies were provided for the solid samples that were sent to participants and the whole analytical procedure

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Table 4. The results of P, Ca, K and Mg determination (mg/kg) in different soil samples by the two independent analytical techniques: MIP-OES and ICP-OES

Sample	P		Ca		Mg		K	
	MIP	ICP	MIP	ICP	MIP	ICP	MIP	ICP
1	105	104	1106	1183	113	128	89	92
2	95	95	4654	4446	160	149	176	164
3	108	107	6584	6457	269	232	257	246
4	97	88	4611	4513	139	133	185	179
5	118	119	4200	4120	130	115	219	222
6	133	147	1997	1831	158	162	132	130
7	106	105	1600	1631	131	136	157	146
8	144	159	1400	1335	90	101	121	118
9	137	161	1769	1733	171	175	133	127
10	90	86	2262	2084	184	182	135	126
11	74	61	2054	1970	152	154	103	97
12	55	50	2238	2077	144	142	77	69
13	57	52	5357	4743	322	297	113	96
14	123	120	3477	3151	128	124	152	140
15	159	172	1051	1010	77	92	203	206
16	99	93	4203	3798	155	142	152	132
17	90	82	4045	3670	158	145	161	139
18	118	114	2017	1874	137	140	157	146
19	85	74	6004	5824	279	267	117	99
20	92	88	6194	5967	201	200	140	118
21	118	122	5986	5589	263	233	176	154
22	108	109	3568	3295	120	118	182	159
23	151	169	1085	1025	61	72	145	140
24	71	62	16580	15876	155	143	113	109
25	63	50	19780	17650	185	179	84	80
26	117	122	1513	1420	117	134	187	176
27	121	125	1325	1168	89	109	104	90
28	98	88	1448	1275	148	161	138	118
29	113	116	1599	1421	176	189	154	142
30	102	103	1455	1197	111	122	108	93

was provided. The lack of the ideal homogeneity of the samples produced higher inter-laboratory recovery range. The recovery results in the range

90–112% (the mean accuracy 97; 92; 107 and 100% for P, Ca, Mg and K, respectively) were very good and allowed the use of the optimised procedure for real samples analysis.

Environmental samples analysis. Ten samples were analysed using the proposed analytical procedure. The results were compared with the results obtained by the certified commercial laboratory (Table 3). Although the median values for recovery were good (78–117%), the isolated results were different from the results obtained in a commercial laboratory. The difference was probably caused by the non-homogenous character of the examined soil samples. Additionally, the series of 30 analyses using two independent techniques: MIP-OES and ICP-OES have been provided (Table 4). Based on *T*-test the statistically significant lack of the differences of results has been found ($P > 0.05$ for hypothesis of statistically significant differences of the results). The difference of the results obtained by MIP-OES and ICP-OES was in the level 0.2–21% for phosphorus (mean difference 6.9%); 1.9–18% for calcium (mean 6.8%); 0.3–22% for magnesium (mean 7.9%) and 1.4–16% for potassium (mean 8.0%). Despite the differences, all of the results have been acceptable for soil fertility assessment. The real throughput reached 100 samples per hour and was excellent compared to non-multielemental procedures.

In conclusion, the efficient agricultural production needs to be supported by different tools, e.g. the fertility assessment. The soil analysis should be provided with the use of efficient techniques, especially multielemental plasma based spectroscopic techniques such ICP-OES and ICP-MS or a recently commercially available technique of MIP-OES. Connecting the high sample throughput with the low cost of using the MIP-OES technique seems to be a very good option in agricultural analysis of soil fertility.

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