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Comparison of MP AES and ICP-MS for analysis of principal and selected trace elements in nitric acid digests of sunflower (*Helianthus annuus*)

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ABSTRACT

The use of nitrogen as plasma gas for microwave plasma atomic emission spectroscopy (MP AES) is an interesting development in analytical science since the running cost can be significantly reduced in comparison to the inductively coupled argon plasma. Here, we evaluate the performance of the Agilent 4100 MP AES instrument for the analysis of principal metals (Ca, K, Mg, and Na), lithogenic metals (Al, Fe, and Mn) and selected trace metals (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn) in nitric acid plant digests. The digests were prepared by microwave-assisted dissolution of dry plant material from sunflower (*Helianthus annuus*) in concentrated nitric acid. Comparisons are made with analysis of the same solutions with ICP-MS (Agilent 7500cx) using the octopole reaction system (ORS) in the collision mode for As, Fe, and V.

The limits of detection were usually in the low μg L^{-1} range and all principal and lithogenic metals were successfully determined with the MP AES and provided almost identical results with the ICP-MS. The same applies for the selected trace metals except for As, Co and Mo where the concentrations were below the detection limit with the MP AES. For successful analysis we recommend that (i) only atom lines are used, (ii) ionization is minimized (e.g. addition of $CsNO_3$) and (iii) the use of internal standards should be considered to resolve spectral interferences.

1. Introduction

Although the micro-plasma has been available for a couple of decades very few commercially available analytical instruments have explored its possibilities [9,11,6,13,18,24,3,4,22,15–17]. Today, the most common multi-element techniques for metal analysis in a wide variety of matrices rely on the inductively coupled argon plasma, in combination with either optical emission (OES) or mass detectors (MS). Therefore, the properties of the argon plasma and its applicability are well known [8,5,21,19,20]. The use of a micro-plasma that runs on nitrogen is definitely of interest for many fields of analytical chemistry since the operating cost is significantly lower for instruments that use argon as plasma gas. Supplying the nitrogen gas from a generator instead of bottles or liquid storing systems can cut the analytical cost even more. Recently, Agilent Technologies released the MP 4100 instrument which uses a nitrogen micro-plasma and atomic emission detector. The instrument has successfully been applied for the quantification of principal and several trace metals in animal feed [12]. However, very less scientific information on the performance of the technology is available for other matrices and elements although some application notes are available from the manufacturer [1].

The nitrogen micro-plasma has different properties than the more common inductively coupled argon plasma [23,2,5,14] that must be considered when designing the analysis. The most important features are of course the lower “temperature” of the nitrogen MP and its different redox properties. Since the operating “temperature” is somewhere around 7000 °C it is likely that most elements are not fully ionized and it is also likely that the thermal decomposition of the sample is less efficient than in the argon plasma. It is therefore likely that the sample matrix influences the ratio of excitation to ionization for a particular element. Hence, ion lines might not be the best choice for analysis. This is not necessarily a problem since the majority of elements have atom lines that are sufficiently free from spectral interference and with enough intensity to allow for measurements in the low μg L^{-1} range, for some, in the high ng L^{-1} range [10,7,21]. It is then a matter of controlling ionization, which would be of particular importance for easily ionized elements.

Instead of optimizing for the production of ions the strategy for measurements with the MP AES would be to optimize conditions

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for the excitation of atoms. For most systems with ICP this can be achieved by controlling the effect of the radio frequency in combination with the flow rate of the gas. In the MP 4100 these parameters are not possible to change. Instead chemical control can be used to assure that easily ionized elements will form excited species. One such technique is the addition of an ionization suppression element to the samples.

As for many other techniques where signals in the UV/vis region are of interest it is necessary to quantify the impact of the background on the analytical signal. In the software to the MP 4100 there are four different models for this: (i) automatic; (ii) off peak left; (iii) off peak right; (iv) off peak right+left and (v) and Fast Linear Interference Correction (FLIC). The operator can choose the appropriate method for the actual wavelength in relation to the sample matrix. An alternative approach is the use of matrix matched calibration solutions or standard addition. Although these methods usually provide data with high quality they are expensive to use because of cost for labour and chemicals. It is therefore attractive to use the built in features of the instrument.

In optical ICP it is sometimes beneficial to use internal standard (IS) elements in order to correct for matrix interferences, such as differences in ionization efficiency. Theoretically, the same applies to MP AES unless addition of the IS element in itself alters the production of excited atoms. Since the efficiency of the MP would be lower than that for the ICP this possibility should be examined for each kind of matrix.

Here, we present some results on the performance of the MP 4100 when it was used for the determination of principal metals (Ca, K, Mg, and Na) in nitric acid digests of sunflower biomass. This matrix is quite complex and several kinds of interferences can be expected. The study also encompasses a selection of lithogenic metals (Al, Fe, and Mn), trace metals (Ba, Cd, Co, Cr, Cu, Ni, Pb, Sr, V, and Zn) and one metalloid (As). The results are compared with the analysis of the same sample solutions with ICP-MS (Agilent 7500cx) operated with the octopole reaction system (ORS) for elements with severe interferences such as As, Fe and V. The comparison also includes a diluted multi-element certified calibration solution as an example of a less complex nitric acid matrix.

2. Materials and methods

2.1. Chemicals

A central water purification unit produced the 18.2 MΩ water that was used throughout in this study to prepare all solutions. The metal concentrations in the water are monitored weekly by clean room procedures using ICP-MS. High purity nitric acid for digestion and preparation of all 1% nitric acid solutions was produced by sub-boil distillation of analytical grade acid in a class 10–100 clean room. The quality of the individual batches is measured with ICP-MS and is typically better than the specification for “ultra-pure” nitric acid.

Calibration solutions for the ICP-MS were prepared volumetrically by dilution of the Merck VI multi-element calibration solution with 1% nitric acid. The accuracy of the stock solution is 5% according to the manufacturer. The calibration range was from 10 ng L^{-1} to 100 μg L^{-1} except for Fe, Zn and As where it was from 100 ng L^{-1} to 1000 μg L^{-1} and Ca where it was from 1 μg L^{-1} to 10,000 μg L^{-1}. For calibration of the MP, 1.00 g L^{-1} single element solutions (CertiPure, Merck) were used to prepare mixed calibration standards in the range 0.01–10.0 mg L^{-1} for all elements. For estimation of detection limits the lowest concentration was 0.0002 mg L^{-1}. The analytical signals from both instruments were evaluated with their original software, i.e. Mass Hunter (Agilent Technologies) for ICP-MS and MP Expert (Agilent Technologies) for MP AES.

The ionization suppression stock solution was prepared from $CsNO_3$ salt (99.8%, Alfa Aesar) by dissolving the appropriate amount in 1% nitric acid. The working concentrations were then diluted with 1% nitric acid to desired concentration. The internal standard mix of La, Lu and Y was prepared from single element solutions (Inorganic Ventures Inc.) to give a final concentration of 1.0 mg L^{-1} in the samples.

2.2. Samples and sample preparation

The test solutions consisted of four nitric acid digests of dry sunflower biomass. The identity of the samples was retained and identical solutions were brought to the instruments. In addition, a control solution that consisted of diluted Merck VI multi-element standard solution was used for comparison since it is a defined solution with a simple and light nitric acid matrix in comparison with the digests.

2.2.1. Preparation of the sunflower samples

The plant experiment is a part of studies on interactions between plants, mycorrhiza and silver nanoparticles. The sunflowers (*Helianthus annuus*) were cultivated from seeds that had germinated on moist filter paper in Petri dishes. After two weeks the seedlings were transferred to pots containing 1 kg of a pasteurized sand and clay mixture (3:1 v/v) with an addition of 50 g L^{-1} rock phosphate. Each pot had three seedlings. All pots were kept in a growth chamber at 23 °C with 12 h of light and 12 h of darkness. The pots were watered twice a week. After the seedlings had been transferred, the pots were inoculated with a mixture of *Glomus intraradices* propagules (50 propagules g^{-1} substrate).

After three months of growth the plants were harvested and dried. Then the biomass was ground and homogenized with an agate mortar and pestle. Then digestion was made by microwave assisted dissolution using a CEM MarsV microwave system. In this procedure, 0.1 g of the biomass was mixed with 10 ml concentrated nitric acid in the system specific Teflon tubes. The digestion lasted for a total of 60 min in two different steps. In the first step the power was set to 300 W and the maximum temperature of 180 °C was reached after 30 min. In the second step the temperature was maintained at 180 °C for another 30 min, with a power of 1200 W. During the digestion the maximum allowable pressure was set to 250 PSI. After cooling for 30 min the digests were transferred to 50 ml test tubes (Sarstedt) and diluted to 50 ml with 18.2 MΩ water.

2.3. Instrumental

The MP 4100 was equipped with a concentric nebulizer (Meinhard, TR-30-K1) and a double pass cyclonic spray chamber. The pump speed during analysis was kept at 10 rpm and the sample introduction tygon tube diameter was 0.89 mm. The analytical cycle consisted of 30 s rinsing with 1% nitric acid followed by 25 s of sample uptake (pump speed 40 rpm) and then 20 s of equilibration before the reading at preselected integration times (pump speeds 10 rpm). An ionization suppression solution of 1.25 g L^{-1} $CsNO_3$ in 1% nitric acid was added automatically by connecting a 0.19 mm tygon tubing to the sample line by a Y-piece. The IS elements were La, Lu and Y at 1 mg L^{-1} each and they were added manually to each solution. Wavelength calibration was made at the beginning of each working day. Both the viewing angle and the nebulizer pressure were optimized before each analytical sequence by the software. The selected elements and the corresponding wavelengths are given in Table 1. The integration time was set to 3 s for principal elements and 5 s for the traces. Unless otherwise stated the automatic background correction mode available in the

Table 1
Wavelengths and isotopes used in the study, recommended wavelengths for the sunflower matrix is given in italics.

Element	MP AES Wavelength (nm)	ICP-MS Isotope
Al	394.401; 396.152	27
As	193.695; 234.984	75 (ORS[a])
Ba	455.403; 614.171	137
Be	234.861	9
Ca	393.366; 422.673	43
Cd	226.502; 228.802	111
Co	340.512; 345.351	59
Cr	357.868; 425.433	53
Cu	324.754; 327.395	63
Fe	259.940; 371.993	56 (ORS[a])
K	766.491; 769.897	39
La (IS[b])	394.910	n.m.[c]
Lu (IS[b])	261.542	n.m.[c]
Mg	285.213; 383.829	24
Mn	403.076; 403.307	55
Mo	379.825; 386.410	95
Na	588.995; 589.592	23
Ni	341.476; 352.454	60
Pb	368.346; 405.781	206+207+208
Sr	407.771; 460.733	88
Y (IS[b])	371.029	n.m.[c]
V	309.311; 437.923	51
Zn	213.857; 481.053	66

[a] ORS=octopole reaction system.
[b] IS=internal standard.
[c] n.m.=not measured.

software was used. An Agilent SPS-3 autosampler was used throughout the study.

The Agilent 7500cx ICP-MS was equipped with a MicoMist nebulizer and a Scott double pass spray chamber operating at 2 °C. The analytical cycle consisted of rinsing with 18.2 MΩ water (sample probe rinse, 30 s, 24 rpm), 18.2 MΩ water(sample line rinse, 20 s, 24 rpm), 1% nitric acid (30 s, 24 rpm), sample uptake (60 s, 24 rpm), stabilization (20 s, 6 rpm) and reading (6 rpm). A 1.02 mm (I.D.) tygon tubing was used. The internal standard consisted of ^{103}Rh that was added manually to all solutions to give a concentration of 10 μg L^{-1}. The ORS was operated in collision mode for the quantification of As, Fe and V. For these elements the cell conditions were set to a flow of He at 5 ml min^{-1} with octopole RF and Bias parameters at 180 V and −20 V, respectively.

2.4. Experimental design and data evaluation

After digestion and adjustment of volumes 10 mL of each solution was transferred to an individual 15 ml polypropylene test tube (Sarstedt). These aliquots were then used to prepare the appropriate dilutions for analysis with 1% nitric acid. For MP AES the analyses were made on the concentrated sample or a 20 time dilution. The lower detection limits of ICP-MS required dilutions of 100 and 1000 times. Finally, the internal standard elements were added from the mix as 100 μL of the stock solution per 10 mL of sample.

The impact of the ionization suppressor concentration was evaluated on a separate solution from sample 2. In this experiment the pump speed was kept constant at 10 rpm and the ionization suppressor was added in a (0.19 mm I.D.) tygon tubing to the sample (0.89 mm I.D.) line via the Y-piece. The concentration of the $CsNO_3$ solution was varied from 0.25 g L^{-1} to 5 g L^{-1}. The reference in this experiment consisted of 1% nitric acid. All instrument signals were processed with the original software of the system, i.e. Mass Hunter and MP expert from Agilent Technologies for ICP-MS and MP AES, respectively.

3. Results and discussion

3.1. Ionization suppression

In MP AES measurements the signals for Na and K increased when adding $CsNO_3$ up to a certain level, thereafter they decreased. This was taken as evidence that the plasma became overloaded. The lowest concentration that gave maximum signals would represent the impact of the matrix on the ionization of those elements. The upper limit, however, would also reflect the total capacity of the plasma, i.e. the total element amount that is possible to atomize and excite in a reproducible manner. In the studied matrices addition of $CsNO_3$ in the range of 1–2.5 g L^{-1} would be suitable for the determination of Na and K with the selected combination of tubings and pump speed. The amount of $CsNO_3$ was first optimized by manual addition before using the Y-piece. The performance of the latter was evaluated by measuring the variation of the signals from the elements in the IS solution as a measure on the stability of the delivery. In the time frame of a sample reading 3–90 s the relative standard deviation (n=20) varied from 0.5% to 2% whereas it reached 4.3% during an 8 h working day. This was concluded insufficient for the delivery of IS but within the tolerable variation for the ionization suppressor.

At high $CsNO_3$ concentrations the signals were lowered also for elements that are less sensitive to ionization. This is another indication that the capacity of the plasma was exceeded. Hence, the concentration of the ionization suppressor should be optimized for both the lower and upper tolerable concentrations. A lowered response was found when the sample delivery rate exceeded the capacity of the plasma. Hence, the resulting combination of the diameter of tubings, pump speed and concentration of the ion suppressor solution is a compromise for this particular kind of matrix.

3.2. Principal metals

3.2.1. Sodium and potassium

There was a large impact on the signal intensities as a function of $CsNO_3$ concentration that is taken as evidence for the impact of the matrix on the ionization of these elements. Without any $CsNO_3$ the intensity of the atom lines increased with increasing total element concentration in the calibration solutions, a typical behaviour when ionization is suppressed by elements in the solution. The optimum concentration of $CsNO_3$ was found to be in the range 1.0–2.5 g L^{-1}. A $CsNO_3$ concentration of 1.25 g L^{-1} was chosen as a compromise between the quantification of these elements and the excitation suppression for elements that might occur at high concentrations of $CsNO_3$. Without any ionization suppression there was a non-linear response at this concentration interval, as evidenced by non-linear calibration functions having a better fit to the data. It is also clear from the analysis of the Merck VI solutions where 0.65 mg L^{-1} sodium and 0.82 mg L^{-1} potassium was reported in the absence of $CsNO_3$ while the expected concentrations were 0.100 mg L^{-1} for both elements. With 1.25 g L^{-1} $CsNO_3$ the reported concentrations for sodium and potassium were 0.103 mg L^{-1} and 0.098 mg L^{-1} respectively.

The calibration functions for the MP AES measurements were linear (r^2 0.9999) for both elements and at all selected wavelengths in the presence of 1.25 g L^{-1} $CsNO_3$. For sodium the signal intensities of the 5 mg L^{-1} standard were 1,200,000 counts and 610,000 counts for the 588.595 nm and 589.592 nm lines, respectively. The corresponding values for potassium at 5 mg L^{-1} were 364,000 counts and 194,000 counts at 766.491 nm and 769.892 nm,

Table 2
Concentrations (mg L^{-1}) and relative standard deviation ($n=3$) for principal and lithogenic metals in plant digests and the Merck VI multi-element standard solution (0.100 mg L^{-1} Na, K, Mg, Al, Mn, V, Cr, Co, Ni, Cu, Mo, Mo, Cd, Ba, Pb; 1.00 mg L^{-1} Zn, Fe, As and 10.0 mg L^{-1} Ca).

Sample	**Na**				**K**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.109	0.97	0.100	1.16	148.0	1.29	141.1	0.12
2	0.150	1.87	0.158	0.68	137.3	0.74	127.6	0.38
3	0.298	1.92	0.305	0.27	152.8	0.31	147.2	0.27
4	0.071	0.21	0.103	0.66	153.7	0.15	154.9	0.9
Merck VI			0.103	0.22			0.098	0.44

Sample	**Ca**				**Mg**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	98.28	0.465	98.78	0.51	11.71	1.36	11.72	0.20
2	83.81	1.755	82.92	0.53	6.764	0.69	6.360	0.65
3	101.8	0.629	102.0	0.54	11.97	0.21	11.18	0.56
4	75.32	0.926	74.98	0.38	7.741	0.14	7.500	0.89
Merck VI			9.98	0.08			0.102	0.72

Sample	**Al**				**Mn**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.062	0.21	0.062	10.04	0.251	0.680	0.256	0.08
2	0.045	1.08	0.041	13.34	0.296	0.017	0.301	0.66
3	0.074	0.78	0.076	5.62	0.136	0.438	0.137	0.64
4	0.045	5.27	0.043	6.33	0.143	1.020	0.147	0.34
Merck VI			0.102	5.66			0.101	0.28

Sample	**Fe**			
	ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)
1	0.255	0.64	0.251	0.58
2	0.284	0.50	0.279	0.18
3	0.272	0.59	0.270	0.44
4	0.259	0.55	0.253	0.25
Merck VI			0.998	0.19

Sample	**V**				**Cr**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.0003	6.11	0	55.1	0.0028	4.87	0.003	22.16
2	0.0003	0.29	0	100	0.0013	25.35	0.002	33.85
3	0.0004	1.69	0.001	49.4	0.0025	16.54	0.003	17.05
4	0.0002	12.8	0	100	0.0014	4.28	0.001	27.15
Merck VI			0.096	0.76			0.099	0.61

Table 2 (*continued*)

Sample	**Na**				**K**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
Sample	**Co**				**Ni**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.0012	3.64	b.d.[a]		0.0123	1.06	0.011	0.59
2	0.0011	3.33	b.d.[a]		0.0120	1.68	0.011	4.18
3	0.0028	3.76	b.d.[a]		0.0231	2.21	0.021	3.13
4	0.0015	1.87	b.d.[a]		0.0089	1.75	0.009	9.77
Merck VI			0.103	2.28			0.101	1.56
Sample	**Cu**				**Zn**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.0707	0.73	0.071	0.1	0.4088	0.18	0.407	0.89
2	0.0602	1.10	0.061	0.25	0.2487	0.01	0.248	0.63
3	0.0473	0.63	0.048	0.92	0.2692	0.24	0.271	1.53
4	0.0263	0.09	0.026	0.54	0.1987	1.77	0.196	1.11
Merck VI			0.099	0.91			0.998	0.42
Sample	**As**				**Mo**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.0003	0.12	b.d.[a]		0.0097	1.06	b.d.[a]	
2	0.0002	26.8	b.d.[a]		0.0084	1.68	b.d.[a]	
3	0.0001	176	b.d.[a]		0.0044	2.21	b.d.[a]	
4	0.0001	195	b.d.[a]		0.0052	1.75	b.d.[a]	
Merck VI			0.995	0.68			0.098	0.97
Sample	**Cd**				**Ba**			
	ICP-MS		MP-AES		ICP-MS		MP-AES	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
1	0.0043	3.83	0.0043	35.3	0.0367	0.44	0.038	0.34
2	0.0063	0.20	0.0066	2.87	0.0600	2.02	0.06	0.66
3	0.0048	4.90	0.0049	4.25	0.0449	1.06	0.043	0.28
4	0.0046	5.86	0.0045	40.0	0.0477	0.84	0.045	1.02
Merck VI			0.099	1.44			0.101	0.39
Sample	**Pb**							
	ICP-MS		MP-AES					
	Mean	RSD (%)	Mean	RSD (%)				
1	c[b]	0.42	0.156	0.92				

respectively. The two most sensitive wavelengths were selected for the comparison since they gave slightly less variation between the replicate readings when analyzing the digests. In the digest the quantitatively most important interferences would be for sodium the molybdenum atom line at 588.831 nm and for potassium a very limited impact from lanthanum 766.434 nm atom line.

Without ionization suppression there was an underestimation of sodium and potassium in the digests, when comparing with ICP-MS (Table 2). The error was lower than that for the Merck VI solution and for most samples in the range of 10–25%, most likely because a higher ionic content in the digests lowered the ionization. In the presence of $CsNO_3$ at 1.25 g L^{-1} there was a good agreement between the techniques (Table 2). For sodium there was, however, a slight overestimation of the concentrations with the MP AES. It is not clear if this is related to differences caused by the preparation of the calibration solutions or if it is only related to the techniques. A similar tendency is present for potassium but in this case there is an underestimation why it seems likely that the preparation of the calibration solutions caused the differences.

The use of IS was insufficient to fully correct the ionization interferences for these elements in the digests. When only the IS elements were used for signal correction there was an underestimation of the concentrations with about 10%. Evidently, the slightly different matrix compositions in the digests were sufficient to induce differences in the production of excited atoms to be uncompensated by the IS. When the ionization suppressor was used in combination with IS correction the precision increased from 3% to 8% for potassium and sodium. The reason is unclear since the complete element compositions of the matrices were not determined but it seems that ionization interferences are best dealt with an ionization suppressor. In addition, remaining interferences can be improved by the use of IS. With such a combination it is clear that the MP AES measurements correspond well to ICP-MS.

3.2.2. Magnesium and calcium

In emission spectroscopy calcium has a number of atom lines as well as ion lines with different sensitivities and interferences while there is usually one suitable wavelength available. Here, we choose to include the most sensitive line at 393.366 nm, which is an ion line, i.e. whether the $CsNO_3$ will control the ionization. For comparison the most sensitive atom line at 422.673 nm was included since the response should be independent of the ionization suppressor. Unfortunately, this line has several interferences with iron (atom lines at 422.545 nm, 422.417 nm and 422.743 nm) which might limit the use in an iron rich matrix. The selected magnesium lines were 285.213 nm and 279.553 nm. The first is an atom line that is sensitive and relatively free from interferences while the second is an ion line where notably manganese will interfere (atom lines at 279.482 nm and 279.827 nm). Both of these lines are more sensitive than that for magnesium.

For these elements the atom signals were quite independent on the concentration of $CsNO_3$ when it was below 2 g L^{-1}. At higher concentrations the response was lowered which indicate that the capacity of the plasma has been exceeded. For magnesium the 5 mg L^{-1} calibration solution gave 970,000 counts and 26,000 counts for the lines at 285.213 nm and 383.829 nm, respectively. For calcium the responses were 819,000 counts and 578,000 counts at 393.366 nm and 422.673 nm, respectively. The atom lines at 285.213 nm and 422.673 nm were chosen for further evaluation since their response would be less dependent on the presence of the ionization suppressor. However, the performance of the calcium line at 393.366 nm was included.

The calibration functions for the selected wavelengths had high linear correlation coefficients (r^2 0.9999) when the 1.25 mg L^{-1} $CsNO_3$ solution was present in the sample stream. The presence of $CsNO_3$ up to this concentration had no impact on the response for magnesium but it went down at higher concentrations. For the digests the ionization suppressor improved the correspondence between the MP AES and ICP-MS measurements (Table 2). Although the reason is not known in detail it seems reasonable to conclude that the digests contained components that impacted the production of excited manganese. The use of IS in the evaluation of the MP AES signal had no discernible impact on the correspondence between the techniques when either the calibration solutions or the digests were analyzed.

For calcium the signal intensities of the selected atom line at 422.673 nm were independent on $CsNO_3$ concentrations up to 1.25 g L^{-1} when the calibration solutions were analyzed. At this line the deviation between ICP-MS analysis of the digests was around 5%. It was lowered by the use of IS and “off-peak left + right” background correction to give compatible data with the ICP-MS. For the Merck VI solution the MP AES reported 9.98 mg L^{-1} of the expected 10.00 mg L^{-1}.

At the 393.366 nm ion line the concentration for the Merck VI solution was found to be 10.02 mg L^{-1}, which is close to the expected 10.00 mg L^{-1}. For the digests, however, there was a systematic underestimation in the range of 10–20% and there was also an increased variation between the replicate measurements of each sample solution. No improvements were found by the use of IS while the ionization efficiency depended on the sample matrix itself. To summarize, the best analytical performance of the MP AES was found for the atomic line and the use of IS. Further, the use of 1.25 g L^{-1} of $CsNO_3$ did not impact the quality of the analysis.

3.3. Lithogenic metals

3.3.1. Aluminium, iron and manganese

Aluminium has two quite sensitive atom lines at 396.152 nm and 394.401 nm. Since they are relatively free from spectral interferences, with the exception of dysprosium on the latter, they are typically recommended. For iron the ion line at 259.940 nm and the atom line at 371.993 nm were chosen since the main interferences are from rare earth elements at rather low responses. The former line is relatively free from interferences but iron has another ion line at 259.837 nm whose impact should be considered at high iron concentrations. In addition, when using an ionization suppressor, such as $CsNO_3$, the performance of ion lines must be monitored. Manganese has a sensitive atom line at 403.076 nm and a less sensitive ion line at 259.372 nm. In ICP-OES it is common to use the 257.610 nm ion line but it was omitted in this study because of lower sensitivity than the 259.372 nm ion line when the nitrogen MP is used. The ion line at 259.372 nm is relatively free from interferences unless iron is present since it has an atom line at the same wavelength. Fortunately, this iron line has a very low response and would contribute to the signal only at high iron concentrations. There are no direct overlaps with common elements for the manganese atom line at 403.076 nm, except a weak atom line for iron at 403.079 nm and an intense ion line for lanthanum at 403.169 nm. Thus, it becomes important to control the ionization of lanthanum since it is present in the IS mixture.

In the chosen calibration range the atom lines for these elements gave linear (r^2 0.9999) calibration functions and no signal depression was found when 1.25 g L^{-1} $CsNO_3$ was present. For aluminium the atom line at 396.152 nm was chosen for further evaluation because the good agreement with ICP-MS indicated that that there were no interferences in the digests (Table 2). There was also a good agreement between the expected and found aluminium concentrations in the Merck VI solution of 0.100 mg L^{-1} and 0.102 mg L^{-1}, respectively. The signal intensity for the 5 mg L^{-1} calibration solution was 75,800 counts which would suffice for accurate determinations below the lowest calibration standard of 0.100 mg L^{-1} in this study. No improvement was found when using the IS elements for signal correction. Hence, in this kind of matrix the MP AES seems to provide ICP-MS compatible results without the use of IS and it tolerates $CsNO_3$ at concentrations required to control the ionization of other elements.

The iron ion line at 259.940 nm gave 22,400 counts while the atom line at 371.993 nm gave 33,800 counts for the 5.00 mg L^{-1} calibration standard. However, in the digests the ion line at 259.940 nm gave concentrations that were roughly 15–40% less than those determined with ICP-MS, in the presence of 1.25 g L^{-1} $CsNO_3$. Even the less complex matrix in the Merck VI solution resulted in an underestimation since 0.982 mg L^{-1} iron was found instead of the expected 1.000 mg L^{-1}. This deviation is not satisfactory and it is likely that although the ionization suppressor was present small matrix differences resulted in different ionization efficiencies. No improvements were found when using any of the three IS elements for signal correction. The atom line performed better and the concentration in the Merck VI solution was determined to be 0.998 mg L^{-1}, in the presence of $CsNO_3$. There was also a fair agreement with ICP-MS measurements of the digests since the differences were usually within a few μg L^{-1} (Table 2). No improvement was found when using the IS correction to correct the response at the atom line.

For manganese both selected wavelengths gave almost identical calibration results (r^2 0.9999) in the presence of $CsNO_3$, provided that the interference from lanthanum on the atom line at 403.076 nm is corrected for. The reason for choosing 403.076 nm, apart from being the more sensitive of the two lines, is that it gave less variation for the digests. The same process as for the iron line probably also for the manganese ion line, i.e. matrix components influencing the ionization. The 5.0 mg L^{-1} solution gave 103,700 counts so the calibration can be extended downwards in comparison with the lowest calibration standard (0.100 mg L^{-1}). Analysis of the Merck VI solution gave 0.101 mg L^{-1} for the atom line which is quite close to the expected 0.100 mg L^{-1}. The same applies to the comparison with ICP-MS determinations of the digests (Table 2) where the results are essentially the same. These results were obtained without the use of IS in the calculations.

3.4. Trace metals

Vanadium is usually present in plants in trace concentrations and the element could not be quantified with MP AES neither at the atom line at 437.923 nm nor the most sensitive ion line at 309.311 nm. The ICP-MS results showed that the concentrations in the digests were 0.2–0.4 μg L^{-1}, which is below the detection limit of MP AES. The latter gave a linear (r^2 0.9999) calibration function for both wavelengths in the selected concentration range. For the Merck VI solution at 0.100 mg L^{-1} the ion line underestimated the concentration by 70% which indicates a change in ionization efficiency and possibly also the interference from aluminium at 309.271 nm. Also the atom line gave an underestimation of 10% but the use of yttrium as IS lowered it to 0.1%.

According to the ICP-MS analysis of the digests their chromium concentrations were 1.3–2.8 μg L^{-1} which is in the lower range of the capability of the MP AES at the 425.433 nm chromium atom line (Table 2). This wavelength has approximately the same response as the atom line at 357.868 nm but does not suffer from rather intense interferences with scandium that might be present in the plant digest. The response at 425.433 nm was 112,400 counts for the 5.0 mg L^{-1} solution and the linearity was good (r^2 0.9999) which would allow for accurate quantifications below 0.100 mg L^{-1}. An average of 0.099 mg L^{-1} was found in the Merck VI solution where the expected value was 0.100 mg L^{-1}.

The concentrations of cobalt in the plant digests were 1.1–2.8 μg L^{-1} according to the ICP-MS, which is very similar to chromium. The 340.512 nm atom line was chosen for cobalt in spite of lower sensitivity and interference from palladium (340.458 nm atom line) in comparison with the line at 345.351 nm. The latter suffers from several interferences from REE, particularly holmium, which might be present in plant material. It is less likely to find high concentrations of palladium. The calibration was linear (r^2 0.9999) and the intensity 40,000 counts for the 5.0 mg L^{-1} calibration standard. No effects of the ionization suppressor at 1.25 g L^{-1} were found. The results for the digests were similar to those from the ICP-MS but very close to the LOD. Because of the low signals from the digests in the MP AES measurements the performance cannot be evaluated accurately. Also the result for the Merck VI solution deviated and the concentration found with the MP AES was 6% higher than expected. This was improved to 1% relative standard deviation by the use of lanthanum as IS.

Nickel has several recommended atom lines where those at 341.476 nm and 352.454 nm are sensitive but suffer from interferences, particularly with cobalt, iron and several REE. For the calibration of 0.100–5.000 mg L^{-1} both lines gave linear responses (r^2 0.9999) that were independent of the 1.25 g L^{-1} $CsNO_3$. The 5.0 mg L^{-1} standard gave some 85,000 counts. The 352.454 nm line was selected although it suffers from interferences from iron because of its higher sensitivity and lower sample variation (Table 2). The digests had relative standard deviations from 0.6% to almost 10% at nickel concentrations from 0.009 to 0.21 mg L^{-1}. These concentrations are not different from the results of the ICP-MS. Analysis of the Merck VI solution gave 0.101 mg L^{-1} while the expected concentration was 0.100 mg L^{-1}. The results were obtained without the use of IS but at higher concentrations of iron and cobalt correction models should be considered.

Copper gave linear responses (r^2 0.9999) for the selected atom lines at 324.754 nm and 327.395 nm in the chosen calibration range. Both the lines are rather sensitive and the 5.0 mg L^{-1} calibration solution gave 804,000 counts and 422,000 counts. The latter line is sometimes recommended although there is a potential interference from the calcium atom line at 327.467 nm. The response of the former line is about twice as high but several lines from iron (324.596 nm, 324.696 nm and 324.820 nm) and from lanthanum (324.935 nm) are potential interferences. The 324.754 nm line was selected for this analysis since plant material usually contains more calcium than iron. There was a fair agreement for the digests between ICP-MS and MP AES (Table 2) and also for the MP AES analysis of the Merck VI solution. These results were obtained by using lutetium as IS in combination with the off peak left+right background correction to narrow the range for background readings as well as 1.25 g L^{-1} $CsNO_3$. Evidently, some interferences were present because without IS and having the background correction in automatic mode the reported concentrations were 10–15% lower than the ICP-MS measurements. The nature of the interference is unknown but the iron concentrations are high enough to contribute, but less than what is expected from calcium at the copper line at 324.754 nm. Thus, in order to perform accurate readings in this kind of matrix the use of element specific interference correction models should be considered.

The zinc atom line at 213.857 nm has an excellent intensity and few interferences. In the digests, iron atom lines (213.859 nm and 213.970 nm) and possibly also one vanadium ion line (214.007 nm) are the most important interferences to consider. The latter should be minor in ordinary plant material and in the presence of the ionization suppressor. For the zinc atom line at 472.215 nm only lanthanum is a likely interfering element and then from the ion lines at 471.994 nm and 472.443 nm. Hence, lanthanum might be less suitable as IS unless the ionization can be minimized. The calibration functions were linear (r^2 0.9999) for both wavelengths. The 213.857 nm line was chosen for this application because it is some 60 times more sensitive and the 5.0 mg L^{-1} calibration standard gave about 74,000 counts. Without the use of IS the concentrations were overestimated by some 30% in the digests as well as in the Merck VI solution. This was corrected for by using lutetium as IS. Then the MP AES measurements corresponded well with ICP-MS and the Merck VI solution was only 0.2% off target (Table 2). It is suspected that the iron concentrations in the solutions caused the interferences.

According to the ICP-MS measurements the digests contained 0.1–0.3 μg L^{-1} arsenic and 4.4–9.7 μg L^{-1} molybdenum but neither could be detected with the MP AES. Determination of arsenic was made at the atom lines at 193.695 nm and 234.984 nm. Both of them are rather insensitive and suffer from several interferences from elements in the plant material. The 193.695 nm line is interfered by several iron atom lines (193.663 nm, 193.390 nm, and 194.002 nm). The usefulness of the 193.695 nm line would however depend on the concentrations of the elements since the iron lines have rather low response. When using this rather short wavelength it is recommended to fill the detector with nitrogen to avoid absorption from oxygen in the air. This was not done in this study. At 234.984 nm an iron ion line (234.830 nm) might be a problem but should be minimized by the ionization suppressor although both of these lines have roughly the same response. The same applies to the cobalt ion line at 234.737 nm. In addition, the beryllium atomic line at 234.861 nm is more than 400 times stronger than arsenic at 234.984 nm and might be a serious problem if the element is present. Therefore, if this atomic line should be used for the determination of arsenic it is recommended to also monitor beryllium at 234.861 nm. In the digests as well as in the Merck VI solution the arsenic line at 193.695 nm overestimated the concentrations by some 50% and the use of IS did not improve the conditions. At this wavelength the rational calibration function was used since the response was not completely linear. It is likely that at this short wavelength the combination of iron and colloids/particles in the solution caused the deviation. At the 234.984 nm line the recovery of arsenic in the Merck VI solution was 99.5% if lutetium was used as IS.

The performance for cadmium was evaluated with the atomic line at 228.802 nm and the ion line at 226.502 nm. The 226.502 nm line is relatively free from interferences from common elements although a few REE (rhenium, osmium, tellurium, and hafnium) are important, as well as iron at high concentrations. The 228.802 nm line has almost the same set of interferences such as the REE but here also arsenic, cobalt and nickel might contribute, particularly at high concentrations. In the presence of $CsNO_3$ at 1.25 g L^{-1} both lines gave linear (r^2 0.9999) calibration functions. The responses for the 5.0 mg L^{-1} calibration standard were 12,800 counts and 152,000 counts. Because of the expected low concentrations in the digests the 228.802 nm line was chosen. An estimate showed that in the digest the sum of interfering elements reached some 10% of the intensity of the analytical signal. If the ionic line for cobalt at 228.615 nm was suppressed by the ionization suppressor the interferences would be even less. Evidently, these interferences were of minor importance since the uncorrected results from the MP AES were close to those from the ICP-MS (Table 2). There was also good agreement for the Merck VI solution where 0.099 mg L^{-1} was found of the expected 0.100 mg L^{-1}.

For barium several atom and ion lines are available but it is questionable if the atom lines are sensitive enough, so in this study we evaluated the lines at 455.403 nm and 614.171 nm. The sensitivity is excellent at the 455.403 nm line and in the digests only the iron line at 455.613 nm might possibly interfere since other interferences come from REE. The same applies to the 614.171 nm line but in this case lanthanum is the element of interference since it has an atom line at 614.298 nm. In addition, the matrix in the digests might influence the production of ions. Both wavelengths gave linear (r^2 0.9999) calibration functions in the presence of 1.5 g L^{-1} $CsNO_3$. There was also a fair agreement with the ICP-MS measurements of the digests, provided that yttrium was used as IS to correct for the signals in the MP. Without the IS correction the overestimation was around 20%, at both wavelengths. Evidently some element in the digests had an impact on the intensity of the signals since the Merck VI solution gave concentrations 0.001 mg L^{-1} higher. According to these results it might be possible to use the ion lines for barium in this kind of plant digests. However, it is recommended that the impact of the matrix should be carefully controlled before these lines are used.

Lead has several atom lines to choose from but most of them have interferences from elements that are more or less abundant in plant material. For these reasons we selected the atom lines at 368.346 nm and 405.781 nm since they are the most sensitive. The 283.305 nm atom line was discarded because of interferences with notably chromium and iron. They are in fact so prominent that they would have required element specific corrections, i.e. FLIC. The 405.781 nm line was selected because of its sensitivity although the digests might contain interfering concentrations of manganese (atom lines at 405.555 nm and 405.894 nm) in particular. The calibration functions were linear (r^2 0.9999) for both lines in the presence of 1.5 g L^{-1} $CsNO_3$. Unfortunately, no ICP-MS results were available for the digests because of contamination of the blank. The MP AES overestimated the concentration of lead in the Merck VI solution with 0.3% but this could be lowered to 0.1% by using lutetium as IS. The lead concentrations in the digests were between 0.146 mg L^{-1} and 0.156 mg L^{-1} which seems likely since the plants were grown on a lead rich substrate. These values are also similar to ICP-MS measurements of other digests of the same plant material that gave 0.159–0.164 mg L^{-1}.

4. Conclusions

This study has demonstrated that nitric acid digests of plant material are a suitable matrix for the determination of principal metals (Ca, K, Mg, and Na), lithogenic metals (Al, Fe, and Mn) and several trace metals (Ba, Cd, Cr, Cu, Ni, Pb, V, and Zn) with MP AES. For these elements there was a high correspondence with ICP-MS. The method failed to quantify arsenic, cobalt and molybdenum because of concentrations below the detection limits. For most elements external calibration was sufficient for quantification but an ionization suppressor is required for easily ionizable elements. Care should be taken so that the concentrations of the ionization suppressor and the samples do not exceed the capacity of the plasma. It is advised to use atom lines since they in general provide less matrix dependent signals. Ion lines are detectable with the Agilent 4100 but their intensities depend on the plasma loading and the matrix components in the sample. These deviations cannot be corrected for by the use of internal standard(s). This approach was successfully used to improve the accuracy and precision of several elements by compensating for minor interferences.

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References

[1] Agilent. ⟨http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Atomic-Spectroscopy/4200-MP-AES/Pages/default.aspx⟩, 2014 (accessed 2305.14).
[2] J.A.C. Broekaert, V. Siemens, Spectrochim. Acta Part B 59 (2004) 1823–1839.

[3] M.D. Calzada, M.C. Quintero, A. Gamero, J. Cotrino, J.E. Sanchez Uría, A. Sanz-Medel, Talanta 39 (4) (1992) 341–347.
[4] J.F. Camuna, M. Montes, R. Pereiro, A. Sanz-Medel, C. Katschthaler, R. Gross, G. Knapp, Talanta 44 (4) (1997) 535–544.
[5] D.J. Douglas, J.B. French, Anal. Chem. 53 (1) (1981) 37–41.
[6] K. Fallgatt, V. Svoboda, J.D. Winefordner, Appl. Spectrosc. 25 (3) (1971) 347–352.
[7] M.R. Hammer, Spectrochim. Acta Part B 63 (2008) 456–464.
[8] K. Jankowski, R. Parosa, R. Ramsza, E. Reszke, Spectrochim. Acta Part B 54 (1999) 515–525.
[9] K.J. Jankowski, E. Reszke, Microwave Induced Plasma Analytical Spectrometry, first ed., Royal Society of Chemistry, Warzaw, Poland, 2010.
[10] K. Jankowski, E. Reszke, J. Anal. At. Spectrom. 28 (8) (2013) 1196–1212.
[11] H. Kawaguch, M. Hasegawa, A. Mizuike, Spectrochim. Acta Part B B27 (5) (1972) 205–210.
[12] W. Li, P. Simmons, D. Shrader, T.J. Herrman, S.Y. Dai, Talanta 112 (2013) 43–48.
[13] F.E. Lichte, R.K. Skogerboe, Anal. Chem. 45 (2) (1973) 399–401.
[14] T. Maeda, K. Wagatsuma, Microchem. J. 76 (2004) 53–60.
[15] H. Matusiewicz, M. Ślachciński, Microchem. J. 82 (2006) 78–85.
[16] H. Matusiewicz, M. Ślachciński, Microchem. J. 86 (2007) 102–111.
[17] H. Matusiewicz, M. Ślachciński, J. Anal. At. Spectrom. 25 (2010) 1324–1333.
[18] M. Moisan, C. Beaudry, P. Leprince, IEEE Trans. Plasma Sci. 3 (2) (1975) 55–59.
[19] A. Montaser, Inductively Coupled Plasma Mass Spectrometry, Wiley-VCH Inc., New York, 1998.
[20] A. Montaser, D.W. Golightly, Inductively Coupled Plasma Analytical Spectrometry, VCH Publishers, Inc., New York, 1992.
[21] J. Nolte, Emission Spectroscopy, A Practical Guide, Wiley-VCH, Weinheim, Germany, 2003.
[22] Y. Okamoto, J. Anal. At. Spectrom. 9 (1994) 745–749.
[23] Z. Zhang, K. Wagatsuma, Spectrochim. Acta Part B 57 (2002) 1247–1257.
[24] A.T. Zander, G.M. Hieftje, Anal. Chem. 50 (9) (1978) 1257–1260.