

Analysis of Acid Rock Drainage (ARD) with Micro Plasma Atomic Emission Spectroscopy (MP AES) – Comparison with ICP-MS

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Abstract Analysis of dissolved metals in acid rock drainage (ARD) with an Agilent 4100 MP AES instrument that combines a nitrogen micro plasma with atomic emission detection (MP AES) was compared with an ICP-MS. Sample preparation consisted only of filtration, acidification (HNO₃ 1%) and addition of internal standard elements after appropriate dilution. In these complex matrices the systems gave identical results provided that care was taken to avoid ionization. This was easily done by addition of CsNO₃ which eliminated the need for matrix matching of calibration solutions. The use of internal standards is only needed for elements with known spectral interferences.

Keywords MP AES, ICP-MS, ARD, metal analysis.

Introduction

Since a couple of centuries the inductively coupled argon plasma (ICP) has been the most efficient energy source for metal analysis either with optical emission detection (OES) or mass spectrometry (MS). The ICP-systems are suited for multi element analysis in a wide range of matrices with detection limits in the high ng/L and the pg/L ranges for OES and MS, respectively. Interferences are reasonably well known and can be dealt with rationally. These techniques include matrix matching of calibration solutions, standard addition analysis and the use of internal standards (IS) as well as correction equations in MS. Most modern quadropole MS systems offer collision or reaction cells that physically minimize, or even eliminate, several severe isobaric interferences. A similar improvement has been made in ICP-OES by the introduction of more rational methods to correct for spectral overlaps and matrix interferences.

Both techniques are well suited for the analysis of acid rock drainage (ARD) but high cost for investment and operation might restrict their use. The latter is particularly important since a typical ICP consumes argon at a rate of 15 to 20 L/minute. Until recently, very few options to the argon plasma have been commercially available for multi element analysis. During the last twenty years, the micro plasma has been explored for different applications but not reached the market (Douglas and French 1981; Jankowski and Reszke 2013). This kind of plasma is induced by microwaves and can be operated with several different gases such as helium, oxygen and nitrogen. For the analysis of metals in complex matrices, such as ARD, the efficiency of the plasma to produce either excited atoms or ions has to be considered why nitrogen would be preferred from analytical as well as economic reasons.

A couple of years ago, Agilent Technologies released the MP 4100 AES which has a nitrogen micro plasma running on gas from a generator, although bottles are an alternative. The instrument uses atomic emission detection (AES) at pre-defined wavelengths. Positive results from analysis of metals in digests of animal feed and fertilizers (Li et al. 2013) indicate that the technology is suitable for complex matrices. In this study we present some experience of instrument performance when analyzing matrices with different complexity for Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb and Zn. The matrices in the comparison range from 1% nitric acid via tap water to ARD samples. The study includes the need for matrix matched calibration

solutions, the use of IS and the influence of ionization suppression. Hence, the suitability of both emission and ion lines were evaluated. An Agilent 7500cx with an octopole reaction cell was used for reference measurements of identical solutions.

Materials and methods

For preparation of solutions, 18.2 M $\cdot\Omega$ water was obtained from a central water purification unit and the nitric acid was produced from analytical grade acid by sub boil distillation. The quality of the water and the individual batches of acid were routinely checked with ICP-MS. The calibration solutions for ICP-MS were prepared volumetrically by dilution of a Merck VI multi element calibration solution. According to the manufacturer, the accuracy of the stock solution is 5% and the typical calibration range was 10 ng/L to 100 μ g/L except for Fe, Zn and As where it was 100 ng/L to 1000 μ g/L and Ca, where it was 1 μ g/L to 10,000 μ g/L. Single 1 g/L element solutions (CertiPure, Merck) were used to prepare mixed calibration solutions for the MP AES, from 0.01 to 10.0 mg/L. This limited calibration range was chosen to allow for more accurate measurements in the low concentration range. Instruments signals were evaluated with their original software, i.e. Mass Hunter and MP Expert (Agilent Technologies).

The ionization buffer solution with CsNO₃ was prepared by dissolving the salt (99.8%, Alfa Aesar) in 1% nitric acid. The internal standard mix of La, Lu and Y was prepared from single element solutions to give a final concentration of 1.0 mg/L when 100 μ L was added manually to each 10.0 ml sample. Light matrix samples were prepared from the Merck VI solution in 1% nitric acid. The intermediate matrix consisted of ordinary tap water that had been spiked with 1 mg/L Cd, Cu, Zn and Pb. The two complex matrices were a L/S 10 water leachate from historic sulphidic mine waste from Ljusnarsbergs mine waste site in Sweden and ARD from the same site. The samples were filtered through a 0.20 μ m polypropylene syringe filter (VWR) and preserved with nitric acid (1%). The solutions were split into one portion for ICP-MS analysis and one for MP AES and diluted with 1% nitric acid to fit the linear working ranges of the instruments.

The MP 4100 sample introduction system had a sample line with a 0.89 mm i.d. tygon tubing connected with a Y-piece to the 0.19 mm i.d. tubing that delivered the ionization buffer solution. The sample was delivered from an Agilent SPS-3 autosampler to a concentric nebulizer (Meinhard, TR-30-K1) fitted to a double pass cyclonic spray chamber. The analytical cycle consisted of: i) 30 seconds at 40 rpm for rinsing with 1% nitric acid; ii) 25 seconds of sample uptake at 40 rpm; iii) 20 seconds of equilibration at 10 rpm and iv) reading at 10 rpm. Wavelength calibration was performed at the beginning of each working day. Both the viewing angle and the nebulizer pressure were optimized before each analytical sequence. The selected wavelengths were: Al (394.401, 396.152 nm), Ca (393.366, 422.673 nm), Cd (226.502, 228.802 nm), Cu (324.754, 327.395 nm), Fe (259.940, 371.993 nm), K (766.491, 769.897 nm), La (394.910 nm), Lu (261.452 nm), Mg (285.213, 383.829 nm), Mn (403.076, 403.307 nm), Na (588.995, 589.592 nm), Pb (368.346, 405.781 nm), Y (371.029 nm) and Zn (213.857, 481.053 nm). Ion lines are given in italics. Integration times were 3 seconds for principal and 5 seconds for trace elements. Background correction was made with the automatic mode option in the software.

A MicroMist nebulizer fitted to a 1.02 mm i.d. tygon tubing sample line and a Scott type double pass spray chamber were used on the Agilent 7500cx ICP-MS. The analytical cycle consisted of: i) rinsing of the probe with 18.2 M $\cdot\Omega$ water for 30 seconds at 0.40 rps; ii) rinsing of the sample line with 18.2 M $\cdot\Omega$ water for 20 seconds at 0.40 rps; iii) rinsing of the sample line with 1% nitric acid for 30 seconds at 0.40 rps; iv) sample uptake for 60 seconds at 0.40 rps; v) stabilization for 20 seconds at 0.10 rps; and vi) reading at 0.10 rps. The internal

standard consisted of ^{103}Rh that was added manually to all solutions at a concentration of 10 $\mu\text{g/L}$. The following isotopes were used: ^{27}Al , ^{43}Ca , ^{111}Cd , ^{63}Cu , ^{56}Fe , ^{39}K , ^{24}Mg , ^{55}Mn , ^{23}Na , $^{206+207+208}\text{Pb}$ and ^{66}Zn . The octopole reaction cell was operated in collision mode for the quantification of Fe. For these elements, the cell conditions were set to a flow of He at 5 mL/min with octopole RF and Bias parameters at 180 V and -20 V, respectively.

Results and discussion

When the MP was calibrated with the easily ionized Na and K in the 0.10 to 10.0 mg/L range, the response was non-linear at all wavelengths, with higher response at high concentrations. Although the software's rational model for calibration gave an excellent fit ($r^2 > 0.9999$), this behavior indicates ionization interferences. For the light matrix solutions the addition of 1.0 g/L CsNO_3 gave an increased response and a linear calibration. At concentrations above some 2.5 g/L, the signal was reduced, indicating that the capacity of the plasma had been exceeded. For spiked tap water and ARD samples the signals for these elements became constant at CsNO_3 concentrations above 1 mg/L and the signal suppression began around 2 g/L. Hence, a CsNO_3 concentration of 1.25 g/L was chosen as a compromise. The use of matrix matched calibration solutions, where Na and K were replaced with Ca and Mg, performed equally well. Its practical use can be questioned, since matrix matched solutions requires more time and chemicals.

Table 1 Metal concentrations in spiked tap water samples ($n=12$) determined with ICP-MS and the recovery by the MP AES as well as the recovery from a Merck VI solution ($n = 10$).

Element	ICP-MS		MP AES	
	Conc. (mg/L)	RSD (%)	Tap water Recovery (%)	Merck VI Recovery (%)
Al	0.116	0.4	98-102	98-101
Ca	14.167	0.9	101-103	99-104
Cd	0.999	0.3	101-104	100-103
Cu	3.573	0.6	98-100	96-101
Fe	0.005	1.1	89-116	96-104
K	1.788	1.2	104-109	99-103
Mg	2.383	0.6	97-101	98-100
Mn	0.016	0.6	92-106	98-101
Na	5.620	1.1	105-107	99-104
Pb	1.003	0.8	96-101	89-106
Zn	1271	0.6	98-99	96-99

Table 2 Metal concentrations in L/S 10 leachates ($n= 22$) and ARD ($n = 16$) from sulphidic mine waste determined with ICP-MS and the corresponding recovery by the MP AES.

Element	Leachate		MP AES		ARD	
	ICP-MS Conc.(mg/L)	RSD (%)	Recovery (%)	ICP-MS Conc.(mg/L)	RSD (%)	MP AES Recovery (%)
Al	20.65	0.7	96-99	14.9	1.1	97-101
Ca	209.1	1.2	97-106	112.4	2.0	93-99
Cd	0.261	0.7	96-98	0.097	0.3	91-96
Cu	5.89	1.1	98-104	1.94	0.3	98-102
Fe	294.3	1.8	97-101	86.4	1.2	94-99
K	10.14	1.1	103-109	7.31	1.8	102-110
Mg	59.87	1.6	95-102	12.7	0.8	96-101
Mn	5.88	0.9	97-99	3.19	1.1	95-100
Na	9.36	1.5	106-118	8.67	1.3	104-112
Pb	1.94	0.8	91-98	0.74	1.4	89-99
Zn	17.14	1.2	96-102	6.37	1.1	95-102

For Na and K the use of IS was limited. The signal to IS ratio ranged from 0.98 to 1.00 in the calibration range. For the samples, the ionic strengths were too high for IS compensation. Hence, the recommended procedure would be either to use matrix matching or addition of an ionization buffer. With the latter procedure, the recoveries of Na and K were quantitative in all tested matrices (tables 1, 2). It should be noted that the MP AES gave slightly higher concentrations but it has not been possible at this stage to conclude if it is real or a result of slightly different calibration solutions.

Calcium has a number of atom as well as ion lines with different sensitivities and interferences. Here, we selected sensitive lines at 393.366 nm (ion) and 422.673 nm (atom). The latter is particularly important for measurement of ARD since it has several known interferences from iron (atom lines at 422.545 nm, 422.417 nm and 422.743 nm). The magnesium lines of choice were 285.213 nm (atom) and 279.553 nm (ion). The first line is relatively interference free while the second has interferences from manganese (279.482 nm and 279.827 nm). All lines were influenced by ionization but with addition of 1.25 g/L CsNO₃ they gave linear ($r^2 > 0.9999$) calibration functions and excellent recoveries of the Merck VI solution (table 1). When analyzing the samples, the ion lines were too dependent on the matrix composition in order to be recommended. The atom lines, however, gave identical (p 0.05) results with the ICP-MS for all test matrices, including the Merck VI solution.

For Al, Fe and Mn, the results were similar to Ca. In the presence of the ionization buffer the calibration functions are linear ($r^2 > 0.9999$) but in the samples their matrix compositions have a large impact on the signal from ion lines. A signal depression in all solutions is noted at CsNO₃ concentrations above 2.0 mg/L. When using the excitation lines and 1.25 g/L CsNO₃ the recoveries are quantitative in relation to the ICP-MS as well as expected concentrations in the Merck VI solution.

Both the ion and atomic line for cadmium gave linear responses ($r^2 > 0.9999$) in the calibration, when CsNO₃ was present at 1.25 g/L. In the samples, only the atom line gave results that were compatible with the ICP-MS (tables 1-3). In addition, copper gave linear ($r^2 > 0.9999$) calibration functions for the selected atom lines. The 327.395 nm line is sometimes recommended although there is a potential interference from calcium at 327.467, which must be examined. Also the Cu 324.754 nm line suffers from interferences, particularly from iron (324.596 nm, 324.696 nm and 324.820 nm) and from lanthanum (324.935 nm). No impacts from interferences were found in the Merck VI sample or the spiked tap water but they were substantial in the ARD samples. The 324.754 nm line was selected for further optimization, because of its sensitivity. A good agreement with ICP-MS was found when Lu was used as IS in combination with the left+right background correction model in the software. The lead atom lines suffer from spectral interferences from several elements such as Cr, Fe and Mn. This was not noticed in the calibration solutions and although the response is low for lead, the calibration functions were linear ($r^2 > 0.9999$). The recovery was excellent for the Merck VI and spiked tap water samples (table 1). In the ARD samples the combination of rather high concentrations, the use of Lu as IS and optimizing the right+left background correction model gave satisfactory results. It is however recommended that each sample matrix should be evaluated and the use of more specific background correction models such as FLIC (fast linear interference correction). In the presence of the ionization buffer both atom lines for zinc gave linear calibration functions and gave reliable data for the Merck VI and tap water samples (tables 1-3). In the ARD the atom lines from Fe (213.859 nm, 213.970 nm) interfered with the 213.857 nm line of Zn why the 472.215 nm line was chosen. This line showed some interference with La (472.443 nm) from the IS mix but only at low Zn

concentrations and much less than Fe on the former Zn line as evidenced from the results in tables 1–3.

Conclusions

The study shows that the MP AES gave metal concentrations no different ($p < 0.05$) from ICP-MS, even for matrices as complex as ARD. Excitation lines should be used since they are less prone to interferences than ion lines why the use of an ionization buffer (CsNO_3) is recommended. The concentration of the buffer should be kept at a minimum in order to maintain the capacity of the plasma. It is also recommended that the matrices in question be scanned for elements with potentially interfering lines with the analytes. Such problems can to a high extent be corrected for by the use of internal standard elements and optimized background correction, at least for metal concentrations typical for ARD.

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