

Determination of Metals in Industrial Wastewaters by Microwave Plasma-Atomic Emission Spectrometry

Elevated levels of metal and metalloid contaminants in the environment pose a risk to human health and are a source of considerable concern to agricultural, livestock and aquatic industries. Industrial wastewaters are the main source of these contaminants, which can persist indefinitely in the environment as they do not degrade with time, and have the potential to pollute not only farm and urban land but also surface and ground waters used for agriculture and drinking. Consequently, the determination of metals in wastewaters is an important aspect of environmental monitoring.

“The simplicity of the instrument and easy to-use MP Expert software is even suitable for novice analysts, with minimal training required for routine sample analysis”

This application note describes a new, simple, and relatively inexpensive analytical spectrometric method for the analysis of wastewater using microwave plasma-atomic emission spectrometry (MP-AES). This is a novel atomic emission spectroscopy method based on magnetically coupling microwave energy to generate a self-sustained atmospheric pressure nitrogen plasma. The Agilent 4100 MP-AES allows easy entrainment of sample aerosol, both aqueous and organic, produced by a conventional nebulizer and spray chamber system. The system provides good tolerance to aqueous and organic solvent loading. Refer to Reference [1] for more details about the operational characteristics of the MP-AES.

Experimental

Sample preparation

A series of unfiltered mine site wastewater samples were acidified at the time of collection. The samples were acid digested for the total metal determination using the following procedure: 0.5 mL of concentrated HCl and 0.2 mL of concentrated HNO₃ were added to 10 mL sample aliquots in 16 x 125 mm polypropylene tubes and digested at 90–100 °C in a sand bath on a hotplate until the final digested volume was 10 mL. If the sample volume was less than 10 mL, Milli-Q water was added to make up the sample volume to the 10 mL volume mark. All water and QC samples were digested, when applicable, accordingly. Results obtained by the 4100 MP-AES were compared with results provided by a commercial service provider.

Instrumentation

An Agilent 4100 MP-AES was used for the total metal determination of Al, B, Co, Cu, Mg, Mn, Ni and Zn in wastewaters. The viewing position and nebulizer pressures were optimized automatically using the Agilent MP Expert software. Table 1 lists the instrumental parameters used for sample analysis. Manual sample introduction mode was used.

Analytical calibration

Table 2 lists wavelengths, calibration fit types and maximum applicable analyte concentration. The criterion for wavelength selection was to (a) provide wide dynamic range and (b) avoid spectral interferences. Therefore, most of the analyte lines used for the final analyses were not the most sensitive line listed in the MP Expert software. The auto-background correction feature in MP Expert was used as the background correction method. Where there is a potential spectral interference on the analyte line, Fast Linear Interference Correction (FLIC), an Agilent proprietary spectral interference correction

Table 1: Agilent 4100 MP-AES operating conditions

Analyte	Wavelength (nm)	Read time (s)	Neb Pressure (kPa)	Background correction
Al	396.152	3	240	Auto
B	249.773	3	160	FLIC
Co	340.511	3	220	Auto
Cu	223.009	3	220	Auto
Fe	373.486	3	220	Auto
Mg	383.829	3	240	Auto
Mn	259.372	3	160	Auto
Ni	341.476	3	240	Auto
Zn	472.215	3	160	Auto

method, can be applied to allow effective removal of the spectral interference. For example, Fe interferences can occur due to the high level of Fe in the samples when determining B using the 249.773 nm primary wavelength. This type of spectral overlap can easily be corrected using FLIC.

Rational calibration fit is a non-linear curve fit of the type $y = (a + bx)/(1 + cx)$. This non-linear curve fitting allows an extended dynamic range so that sample analysis can be carried out using a single wavelength for a given analyte without time-consuming sample dilutions. Samples with analyte concentrations that exceed the maximum concentration given in Table 2 were diluted accordingly and re-analyzed. The acceptance criterion for calibration curve correlation coefficient is 0.999. At least four calibration standards, excluding the calibration blank, were used for calibration. Typical calibration curves for linear and nonlinear calibration curves are given in Figures 1 and 2.

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Table 2: Calibration parameters used for the sample analysis

Analyte	Wavelength (nm)	Calibration fit	Weighted fit	Through blank
Al	396.152	Rational	On	On
B	249.773	Linear	On	On
Co	340.511	Linear	On	On
Cu	223.009	Rational	On	On
Fe	373.486	Linear	On	On
Mg	383.829	Rational	On	On
Mn	259.372	Linear	On	On
Ni	341.476	Linear	On	On
Zn	472.215	Rational	On	On

Quality control

General QC criteria used by routine analytical laboratories were used. This includes the analysis of an initial calibration verification (ICV) solution, a method blank (MB), a laboratory control sample

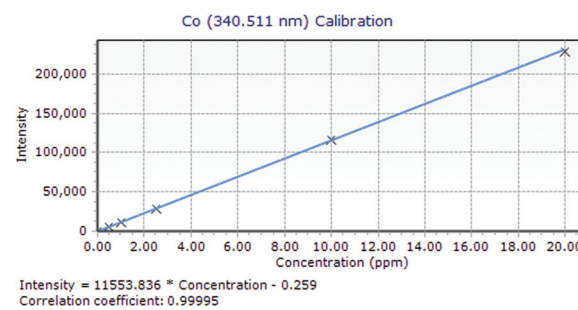


Figure 1. Typical linear calibration curve for Co at the 340.511 nm wavelength

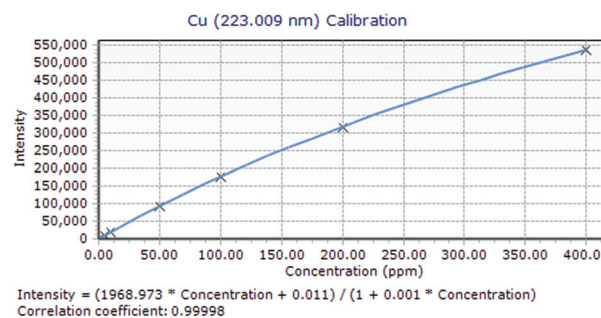


Figure 2. Typical non-linear calibration curve for Cu at the 223.009 nm wavelength. Note the extended range

(LCS), duplicate samples (DUPs), matrix spikes (MSs), and a continuing calibration verification solution (CCV). For every 20-sample QC batch, one MB and LCS, and at least two sets of DUPs,

one set of MS, and one CCV were analyzed. An ICV solution prepared using a different source was used to verify the integrity of the analytical calibration. The CCV solution measures instrument drift during the sample analysis. These QC samples, when applicable, were digested according to the digestion procedure given in the 'Sample preparation' section. Instrumental detection limits (IDL) were determined by analyzing seven blank solutions and applying a factor of 3.14 times the standard deviation of those results. Limit of reporting (LOR) was set at 10 times the IDL.

Results and discussion

The acceptance criterion for QC standards (ICV and CCV) is ±10% unless otherwise stated. For QC samples, acceptance criteria vary. The acceptable limit for LCS is ±10%, and that for MS recovery is ±25%. The spike concentration for the determination of MS recovery is 10 ppm, and if a sample contains an analyte concentration greater than four times the spike concentration, MS recovery is not determined (ND). Matrix spike recovery is determined only for key analytes; for example, MS recovery for Mg is not determined because Mg is considered to be a part of the matrix. The acceptance criteria for duplicate analyses are as follows:

No %RPD criteria for results < 10xLOR

%RPD < 50% for 10xLOR < result < 20xLOR

%RPD < 20% for 20xLOR < result, where

%RPD is the Relative Percent Difference.

The method blank value should be less than the LOR.

The results presented in Tables 3 to 5 indicate that all QC analyses were within the acceptable limits, except in a few instances. While the recovery of the Zn ICV was about 78%, the recovery of the CCV

Table 3. Limit of Reporting for determined analytes and results for method blank (MB), initial calibration verification (ICV) and continuous calibration verification (CCV) solution

Analyte	Wavelength (nm)	LOR (ppm)	MB (ppm)	ICV recovery (%)	CCV-1 recovery (%)	CCV-2 recovery (%)	CCV-3 recovery (%)
Al	396.152	0.02	<LOR	102	103	104	-
B	249.773	0.02	<LOR	ND	ND	ND	98.4
Co	340.511	0.06	<LOR	95.5	99.1	101	-
Cu	223.009	0.25	<LOR	97.1	99.7	101	-
Fe	373.486	0.10	<LOR	ND	100	102	-
Mg	383.829	0.10	<LOR	ND	ND	ND	93.5
Mn	259.372	0.02	<LOR	103	100	101	-
Ni	341.476	0.02	<LOR	97.9	105	105	-
Zn	472.215	0.20	<LOR	77.9	99.7	101	-

Table 4: Results for LCS recoveries and %RPD for duplicate analysis

Analyte	Wavelength (nm)	LCS-1 recovery (%)	LCS-2 recovery (%)	Sample-1 (ppm)	%RPD	Sample-2 (ppm)	%RPD	Sample-3 (ppm)	%RPD
Al	396.152	94.9	100	28.1	4.17	117	2.03	68	2.07
B	249.773	ND	ND	0.02	66.6	0.06	18.1	0.02	22.2
Co	340.511	93.5	89.9	3.57	0.28	1.63	1.22	1.04	0.19
Cu	223.009	96.1	96.7	1520	3.82	63	0.02	83.7	1.56
Fe	373.486	96.9	95.6	40.9	3.40	100	1.77	291	5.13
Mg	383.829	ND	ND	64.5	0.23	266	0.75	47.8	1.29
Mn	259.372	99.1	92.7	56.4	1.02	88.6	0.19	24.3	0.40
Ni	341.476	97.6	98.7	0.26	12.2	0.21	4.65	0.18	0.55
Zn	472.215	96.7	94.9	2784	0.69	28.1	1.02	15.6	0.92

Table 5. Results for matrix spike recoveries

Analyte	Wavelength (nm)	Sample-1 (ppm)	Spike recovery (%)	Sample-2 (ppm)	Spike recovery (%)	Sample-3* (ppm)	Spike recovery (%)
Al	396.152	7.91	107	245	ND	†	ND
B	249.773	0.01	ND	0.14	ND	0.78	ND
Co	340.511	-0.03	92	4.04	97.2	14.8	113
Cu	223.009	6.07	85.4	145	100	26.8	76.2
Fe	373.486	90.9	ND	54.4	97.6	†	ND
Mg	383.829	1.23	ND	476	ND	165 †	ND
Mn	259.372	0.18	97.7	164	119	15.2	76.8
Ni	341.476	0.00	95.9	0.6	107	2.41	109
Zn	472.215	2.81	88.9	88.1	123	32.8	67.2

* Sample-3 was subsequently diluted for analysis due to high concentration of Al and Fe. † Overage result

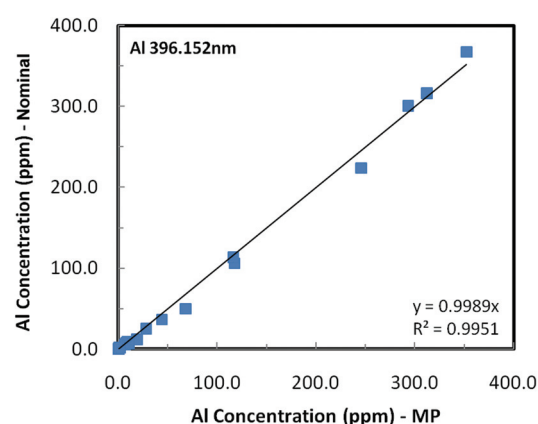


Figure 3a: Correlation between MP-AES results and nominal values for determination of Al

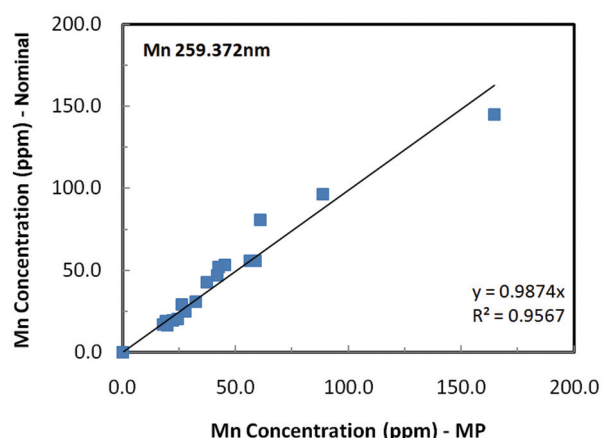


Figure 3e: Correlation between MP-AES results and nominal values for determination of Mn

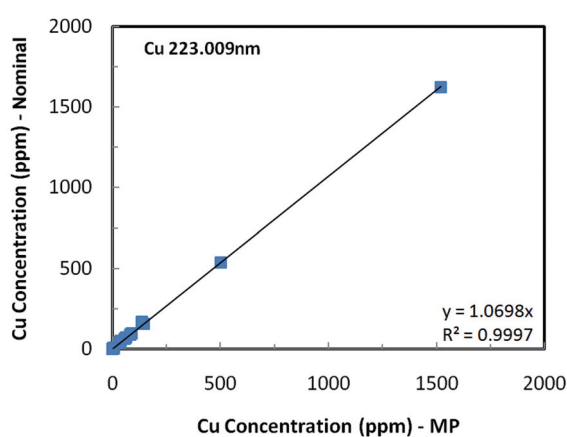


Figure 3b: Correlation between MP-AES results and nominal values for determination of Cu

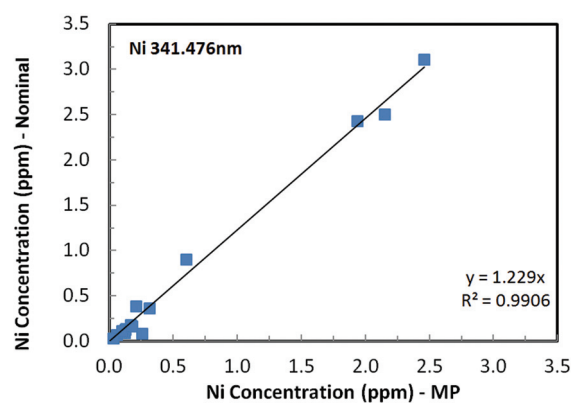


Figure 3f: Correlation between MP-AES results and nominal values for determination of Ni

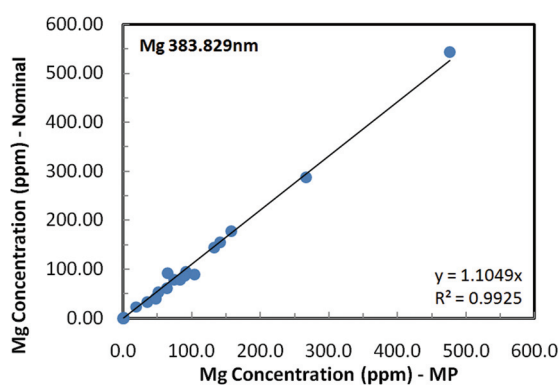


Figure 3c: Correlation between MP-AES results and nominal values for determination of Mg

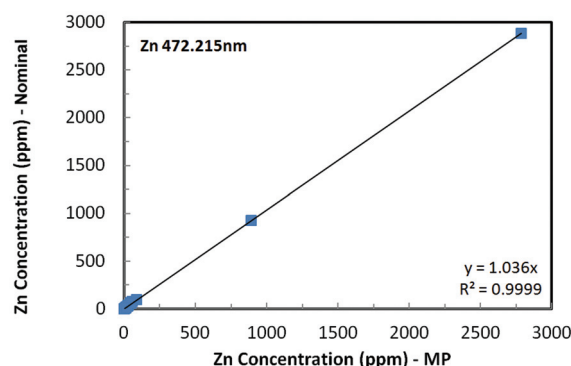


Figure 3g: Correlation between MP-AES results and nominal values for determination of Zn

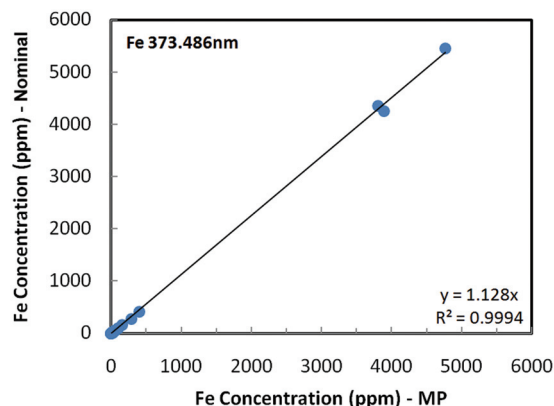


Figure 3d: Correlation between MP-AES results and nominal values for determination of Fe

standard is within $\pm 10\%$, and there is also very good agreement between results measured using the 4100 MP-AES and the nominal values. For MS recoveries, only the Zn MS recovery for spiked Sample-3 is outside the acceptable limit. However, it is not uncommon to have low MS recoveries for highly-impacted samples. In this particular sample, the sulfate concentration is about 1500 ppm. It should also be noted that the final CCVs (CCV2 and CCV3) were measured four and half hours after the first measurement (calibration blank), and the final CCV recoveries were still within $100\pm 5\%$ except for Mg. This indicates the capability of the instrument hardware and demonstrates that the 4100 MP-AES

remains stable during long analytical runs without requiring time-consuming recalibrations.

Figures 3a to 3g are correlation plots of the results obtained using the 4100 MP-AES compared to nominal values. It is clear from these plots that there is good agreement between both sets of results. The results for Boron were not plotted because they were lower than the LOR for B. It is therefore likely that any noticeable differences in the two sets of results are due to sample heterogeneity prior to digestion as these unfiltered samples contained sediments.

Conclusions

Results obtained using the Agilent 4100 MP-AES for the analysis of highly-impacted wastewater samples including QC standards (ICV and CCV) and QC samples (MB, LCS, DUPs and MS) clearly indicate that MP-AES is a suitable atomic emission spectrometry technique for the determination of metal contaminants in waters. Method development, instrument optimization and sample analysis can be easily carried out using the intuitive MP Expert software. The analytical range can easily be extended using non-linear rational curve fitting for a single wavelength, therefore eliminating the usual practice of measuring multiple wavelengths or sample dilutions. Spectral interferences can be easily corrected using an Agilent propriety correction method (FLIC). Matrix spike recovery is within the accepted data quality objectives and therefore indicates that microwave plasma is capable of minimizing the potential sample matrix effects. The CCV results indicate no significant instrumental drift after 5 hours of continuous operation. The highly stable, self-sustained atmospheric pressure nitrogen plasma ensures the running costs of MP-AES are low — a key advantage for busy commercial laboratories. The simplicity of the instrument and easy to-use MP Expert software is even suitable for novice analysts, with minimal training required for routine sample analysis.

Acknowledgement

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Reference

1. M. R. Hammer, A magnetically excited microwave plasma source for atomic emission spectroscopy with performance approaching that of the inductively coupled plasma, *Spectrochimica Acta*, 456-464, 63B, 2008.