

Determination of major and minor elements in geological samples using the 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Mining, geochemistry, and metals

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Introduction

The development of atomic spectrometric methodologies for geochemical sample analysis presents many challenges to commercial laboratories. The range of concentrations in geochemical analysis varies from major elements that are present at percent levels, to trace elements that are present at sub-ppm levels. For example, Cu can be present at percent levels for target drillings, ppm levels in explorations and sub-ppm levels in selective leaches. In addition to the wide working range required for the analysis, high levels of total dissolved solids, spectral interferences due to emission line overlaps and non-spectral interferences due to easily ionizable elements (EIE) present challenges even to the experienced analytical chemist. Flame Atomic Absorption Spectrometry (FAAS) has long been the instrument of choice



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for geochemical analysis but with current trends in the market for lower detection limits, lower cost of analysis, improved ease of use and improved safety, the Agilent 4200 MP-AES is the ideal replacement for FAAS.

With the introduction of the 4200 MP-AES, the application range of the MP-AES has expanded to include challenging geochemical samples. The second generation 4200 MP-AES features an advanced microwave cavity and a torch designed to handle samples with high dissolved solids with better detection limits and increased working range than FAAS. The MP-AES runs off nitrogen, eliminating expensive and hazardous gases such as acetylene, increasing safety, and allowing for unattended operation of the instrument, even in remote locations.

The simplicity of the instrumentation and the user friendly MP Expert software facilitates easy instrument setup and method development with minimal training, even for novice laboratory technicians. This application note presents the base metals (Ag, Cu, Ni, Pb and Zn) results for geochemical certified reference materials analyzed by the 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES. Dewar nitrogen was used to run the MP-AES. Nitrogen can be supplied using either bottled gas or an Agilent 4107 Nitrogen Generator. The nitrogen generator alleviates the difficulties in sourcing gases in remote locations or in metropolitan areas where supply of analytical grade gases is difficult. A multi-

purpose sample introduction system configuration was used with an inert OneNeb nebulizer and a double pass glass cyclonic spray chamber, orange/green pump tubing and a pump speed of 10 rpm. This setup provided a well-controlled matrix loading to the plasma without sacrificing detection limits. The nebulizer gas flow is mass flow controlled, providing short and long-term sample nebulization stability during the high total dissolved solid sample analysis. The instrument operates in a fast sequential mode and with the peltier cooled CCD detector, background and spectral interferences can be simultaneously corrected easily and accurately using MP Expert software. The method parameters are given in Table 1.

Table 1. Method parameters used in the analysis

Parameter	Value
Nebulizer	OneNeb
Nebulizer flow rate	0.4 L/min
Spray chamber	Double pass glass cyclonic
Pump rate	10 rpm
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue
Internal standard pump tubing	Orange/green
Autosampler	Agilent SPS 3
Read time	5 seconds for Ag, 3 seconds for all others
Number of replicates	3
Fast pump during uptake	On
Sample uptake delay	30 seconds
Rinse time	120 seconds
Stabilization time	20 seconds
Background correction	Auto
Gas source	Dewar N ₂

Sample and calibration standard preparation

Two reference materials (GeoStats Pty Ltd) were analyzed to validate the method: GBM398-4 Low grade Cu/Pb/Zn with Laterite; and GBM908-14 Cu-Zn-Pb Sulphide Ore. The sample preparation procedure was a HNO₃-HCl-HClO₄-HF four-acid digestion with 0.4g of nominal sample weight. The mixture was taken to near dryness and after cooling, the digest was brought to a 100 mL final volume with 30% HCl solution. This represents a 250x nominal sample dilution. This four-acid digestion procedure provides near total digestion of samples for the analysis.

All calibration standards solutions were prepared in 6% HNO₃ and 19% HCl.

Wavelength selection and background correction

Table 2 gives the emission line selection, background and interference correction methods used. The selected wavelengths provide minimal spectral interferences, and wide dynamic range, eliminating time-consuming sample dilutions and reanalysis. An internal standard solution of 10 mg/L lutetium was delivered using orange/green tubing and a Y-connector was used to connect the sample tubing. Lutetium was selected as the internal standard element because it is rarely present in geochemical samples. The acceptance criteria for the calibration curve was a correlation

coefficient greater than 0.999, and less than 10% calibration fit error on each standard. A linear curve fit was used for all wavelengths.

Spectral interference corrections

Geological samples can contain a wide range of elements at varying concentrations which can result in spectral interferences. The 4200 MP-AES has continuous wavelength coverage across the available wavelength range and the MP Expert software contains an extensive wavelength database that helps to choose analytical wavelengths and identify possible interferences. A combination of Agilent Fast Linear Interference Correction (FLIC) and conventional inter-element corrections (IECs) were used for the samples analyzed in this matrix. FLIC is an advanced and easy to implement background correction method that corrects for spectral interferences as well.

Multiple line interferences on Ag 328.068 nm were corrected by using conventional inter-element correction (IEC). The IEC factors were developed using easy to use steps built into the MP Expert software. This involved using a 1 mg/L single element silver standard, and 100 and 1000 ppm single element interferent standards to generate the IEC factors. The concentration of interferent standards were selected to reflect the concentration of interferents in the samples.

Table 2. Analyte line selection, background, and interference correction methods

Element	Wavelength (nm)	Type	Background Correction	Interference Correction	Possible Interferences
Ni	305.082	Analyte	Auto		La
Ag	328.068	Analyte	Auto	IEC	Cu, Ti
Ti	334.940	IEC	Auto		
Pb	405.781	Analyte	Auto		La, Ti
Zn	481.053	Analyte		FLIC	La, Sr, and Ti
Cu	510.554	Analyte		FLIC	Al ₂ O ₃ and La
Lu	547.669	IS		FLIC	Ni, Ti

FLIC models were used for Zn, Cu and Lu to correct spectral interferences from Al, Ti, La and Sr. For example, if aluminium is present in samples at percent levels, an aluminium oxide emission can interfere with the Cu 510.554 nm line. Creating a FLIC model with a high concentration aluminium interference model will correct for the spectral contribution to the Cu 510.554 nm line. Figure 2 depicts Ni and Ti interference on Lu as corrected by FLIC.

Table 3 gives the FLIC sequence matrix for running the blank and single element analyte and interferent standards.

If samples contain other elements that create spectral interferences on analyte lines, more IEC corrections can be generated, or further FLIC models can easily be created in MP Expert.

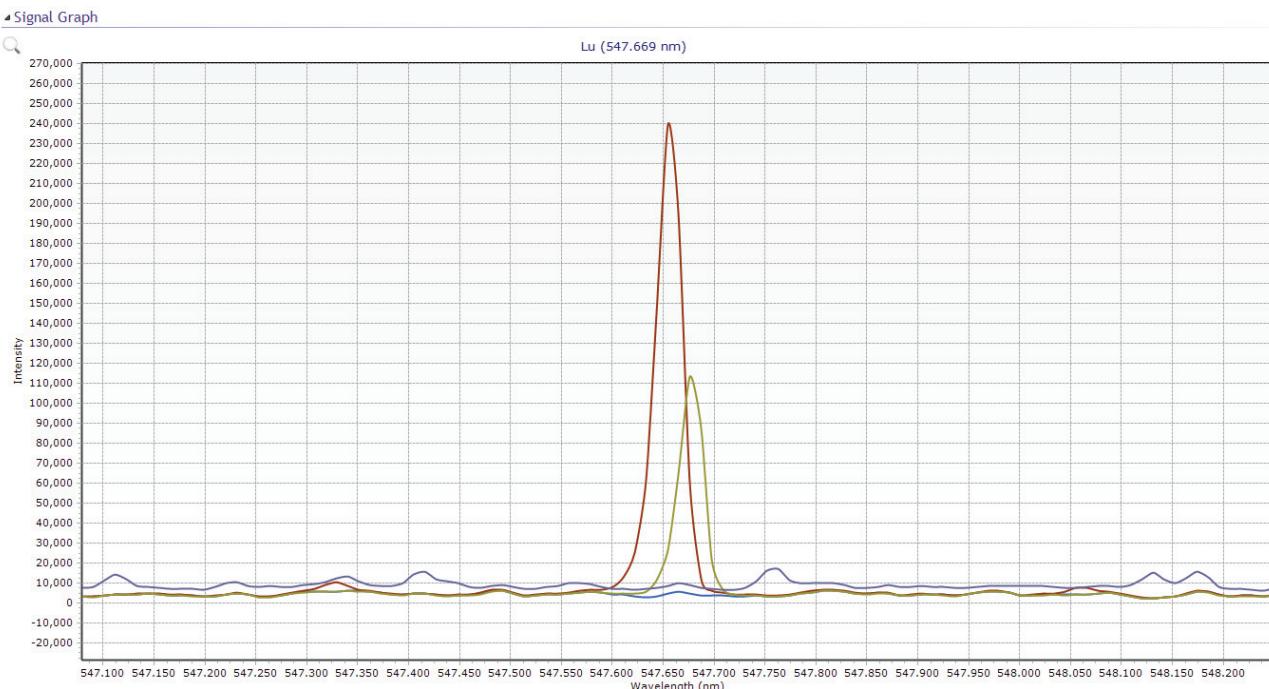


Figure 2. Ni and Ti interference on the Lu 547.669 nm line using FLIC with the blank (blue), Lu (red), Ni (green), and Ti (dark blue)

Table 3. FLIC sequence

Anayte (nm)	Blank	Analyte mg/L	Interferent				
			1 Al mg/L	2 Ti mg/L	3 La mg/L	4 Sr mg/L	5 Ni mg/L
Zn (481.053)	Cal Blank	10	x	100	100	100	x
Cu (510.554)	Cal Blank	10	1000	x	100	x	x
Lu (547.669)	Cal Blank	10	x	100	x	x	100

Results and Discussion

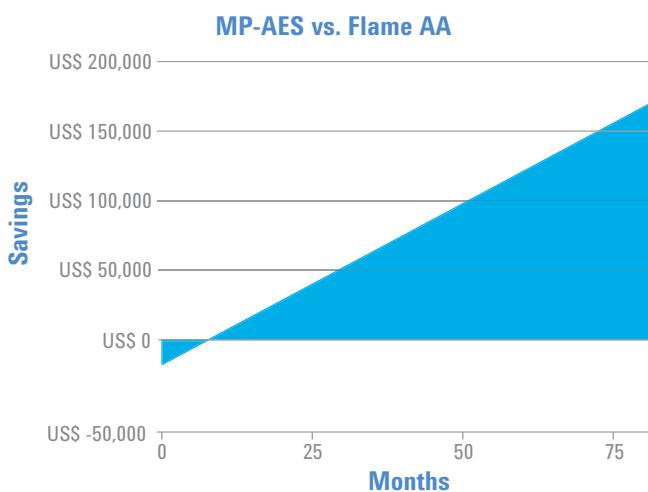
Results obtained on the MP-AES for the two reference materials are given in Table 4. Method detection limits (MDLs) were determined by analyzing 10 replicates of acid digested method blank under method conditions. The MP-AES results are within $\pm 10\%$ of certified concentrations (see Table 4).

The results show that the MP-AES is capable of measuring silver at low levels by using IEC to correct for spectral interferences. Elements such as Cu and Zn show excellent recoveries across a wide concentration range (0.39% to 2.37% for Cu, and 0.51% to 4.27% for Zn) demonstrating the capability of the MP-AES to measure samples over a wide dynamic range.

Cost savings with the 4200 MP-AES

The potential cost saving of using the 4200 MP-AES for this application was estimated by comparing an FAAS purchased with an air compressor and 1 year of consumables to an MP-AES purchased with air compressor, SPS 3, and 1 year of consumables. The analysis requirements were assumed to be 350 samples per week and 5 elements per sample. The calculation

assumes that the FAAS is run without an autosampler and that all elements are analyzed with air/acetylene. In this example the results show an estimated cost saving over US \$150,000 over a 7 year evaluation period. A global average gas cost was used in this calculation and results will vary from country to country.



This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements. For this calculation operator labor costs were set to US\$25/hour and electricity costs were set to US\$0.18 per kW.

Table 4. MDL and recoveries for reference materials determined by the 4200 MP-AES. All results shown for the solid sample.

Analyte	Units	MDL	GBM398-4			GBM908-14		
			MP-AES	Certified	Recovery (%)	MP-AES	Certified	Recovery (%)
Ag	mg/kg	1	45.8	48.7	94	298.7	303.7	98
Cu	wt %	0.002	0.37	0.39	95	2.30	2.37	97
Ni	wt %	0.002	0.39	0.41	97	-	nr	-
Pb	wt %	0.002	1.08	1.17	92	3.24	3.30	98
Zn	wt %	0.002	0.50	0.51	98	4.24	4.27	99

nr = not reported

Conclusion

The results of the analysis of geochemical reference materials obtained using the Agilent 4200 MP-AES indicate that MP-AES is an excellent technique for challenging geochemical sample analysis. The next generation waveguide and torch create a plasma that is capable of determining elements at ppm levels to percent levels in the sample. The continuous wavelength range and extensive wavelength database allow wavelengths to be selected that minimize spectral interferences and maximize the working range. In addition, spectral interferences were successfully corrected with the use of IECs and FLIC models.

By eliminating hazardous gases such as acetylene, the MP-AES greatly improves laboratory safety and provides significant reductions in running costs. The elimination of expensive hazardous gases also means that the MP-AES can run unattended and in remote locations.

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