

Ultra-Trace Analysis of Metals in Mineral Reference Materials

Quick and cost effective analysis in remote locations, without the use of flammable gases



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Introduction

There is a high demand from the mining industry for more accurate, reliable and cost-effective methods for the determination of metals in base metal ores. Accurate analysis is vital for determining the commercial value and feasibility of a mine. Achieving this can be challenging, as ore samples often contain metals over a wide range of concentrations from low parts per million to high percentage levels. The large number of core samples analyzed means that cost and speed of analysis are also important considerations when conducting ore analysis.

Base metal ore analysis is typically performed using flame atomic absorption spectroscopy (FAAS) or inductively coupled plasma optical emission spectroscopy (ICP-OES). The Agilent Microwave Plasma Atomic Emission Spectroscopy (MP-AES) is the ideal alternative for mining laboratories looking to transition away from FAAS to a higher performance, lower cost and safer technique.

The MP-AES uses a microwave-induced nitrogen-based plasma, eliminating the need for flammable or expensive gases and significantly reducing running costs compared to FAAS. The instrument can be operated unattended and in remote locations using an autosampler and nitrogen generator, meaning that samples can be analyzed on-site for fastest feedback. The nitrogen plasma also provides lower detection limits and a larger linear dynamic range than FAAS, making it ideal for accurate and repeatable determination of metals in ores over a wide concentration range.

Experimental

Instrumentation

An Agilent 4200 MP-AES was used for the determination of Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Ti, W, and Zn in digested base metal ores (this application is also applicable for a 4210 MP-AES). The instrument was fitted with a glass concentric nebulizer, double-pass glass cyclonic spray chamber and easy-fit torch. Nitrogen gas was supplied from a Dewar, however, the Agilent 4107 Nitrogen Generator could be used to perform this analysis in a remote location without the need to source gases. Method parameters are given in Table 1.

Table 1. 4200 MP-AES method parameters.

Parameter	Setting
Nebulizer	Meinhard glass concentric
Spray chamber	Double pass glass cyclonic
Pump rate (rpm)	10
Sample pump tubing	Black/black
Waste pump tubing	White/black
Nebulizer flow rate (L/min)	0.7-1.0
Read time (s)	3
Replicates	3
Sample uptake delay (s)	Co, Cr, Fe, Mo, Mn, Ni, Pb and Zn: 45, Cu: 50, Ti: 10 & W: 60*
Stabilization time (s)	20
Background correction	Auto
Gas source	Dewar

*Cu, Ti & W required different Sample Uptake Delay times and were run in separate worksheets

Wavelength selection

Details of wavelength selection are given in Table 2. The Agilent MP-AES features continuous wavelength coverage and the MP Expert software includes an extensive wavelength database that allows the selection of wavelengths to minimize spectral interferences. This is particularly important for the analysis of ore samples as metal concentrations can range from low ppm to high percent levels, causing many potential spectral interferences.

Table 2. Selected wavelengths for the determination of elements in base metal ores.

Element	Wavelength (nm)
Co	340.512
Cr	425.433
Cu	324.754
Fe	371.993
Mo	379.825
Mn	403.076
Ni	352.454
Pb	405.781
Sb	217.581
Ti	336.122
W	400.875
Zn	213.857

Standards and reagents

All solutions were prepared with ultra-pure de-ionized water (18.2 MΩ resistivity). Analytical grade nitric acid (68-70% m/v), hydrochloric acid (36.5-38% m/v), phosphoric acid (min. 85% m/v) and sulfuric acid (95-98% m/v) were used for sample digestion.

Calibration standards of 1.0, 5.0 and 10.0 mg/L were prepared for each element from 1000 mg/L single element standards purchased from High Purity Standards (Charleston, SC, USA). All standards were made up to volume in 1% (v/v) HNO₃.

Sample preparation

Chromite ore from a core sample was donated by Noront Resources Ltd. (Toronto, ON, Canada) for the determination of Cr and Fe. Ten sub-samples of this were analyzed to demonstrate the reproducible performance of the MP-AES.

A range of ore Certified Reference Materials (CRMs) purchased from Geostats Pty. Ltd. (O'Connor, WA, Australia), Ore Research & Exploration Pty. Ltd. (Bayswater North, VIC, Australia), CANMET Mining and Mineral Science Laboratories (Ottawa, ON, Canada) and National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA) were used to validate the method for all elements.

A sample size of approximately 0.2 g was digested for all ore samples and CRMs. All sample digests were carried out using an infrared-based digestion system (1) from ColdBlock Technologies Inc. (St. Catharines, ON, Canada). The target analytes and digestion method for each ore sample and CRM are summarized in Table 3.

Various acid mixtures were used for digestion depending on the nature of the ores. Aqua regia digestions used a mixture of 6 mL HCl and 2 mL HNO₃. Reverse aqua regia digestion used a mixture of 6 mL HNO₃ and 2 mL HCl. Phosphoric acid digestion used 6 mL H₃PO₄. A mixture of 4 mL H₃PO₄ and 2 mL H₂SO₄ was used for phosphoric/sulfuric acid digestion. A mixture of 2 mL H₂SO₄ and 4 mL HNO₃ was used for sulfuric/nitric acid digestion. All samples were made up to the volume of 25 mL following digestion.

Table 3. Description of samples and CRMs.

Sample/CRM Name	Description	Analytes of Interest	Digestion Method
Noront core sample	Chromite ore	Cr, Fe	Phosphoric/sulfuric acid
GBM398-1	Copper-lead-zinc cap rock	Cu, Ni, Pb, Zn	Aqua regia
GBM909-15	Nickel sulphide concentrate	Cu, Ni, Pb, Zn	Aqua regia
GBM309-16	Copper-lead-zinc-silver massive sulphide ore	Cu, Pb, Zn	Aqua regia
GIOP-117	High-grade (hematite) iron ore	Fe	Phosphoric acid
GIOP-33	Titano-magnetite iron ore	Fe, Ti	Phosphoric acid
GCR-06	High-grade chromite ore	Cr, Fe	Phosphoric/sulfuric acid
OREAS 78	Nickel-cobalt sulfide	Co, Ni	Aqua regia
OREAS 171	Manganese ore	Mn	Aqua regia
OREAS 189	Nickel laterite ore	Fe, Mn, Ni	Phosphoric acid
OREAS 701	High-grade tungsten-copper-gold-magnetite ore	Cu, Fe, W	Phosphoric acid
CCU-1d	Sulfidic copper concentrate	Cu, Fe, Pb, Zn	Reverse aqua regia
NIST 333a	Molybdenum sulphide concentrate	Mo	Sulfuric/nitric acid

Results and discussion

All calibration curves were linear with a correlation coefficient greater than 0.999 with the calibration curve for Ni 352.454 nm presented in Figure 1.

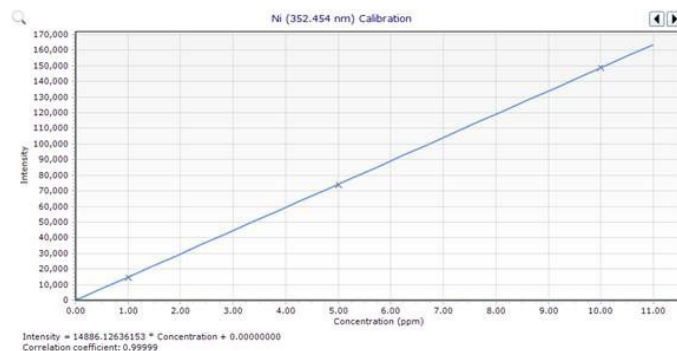


Figure 1. Calibration curve for Ni 352.454 nm.

Cr and Fe recoveries from the Norant chromite ore are listed in Table 4. The RSDs of all measurements taken from ten different locations in the core (core sections A-J) were found to be no more than 1.5% for both Cr and Fe, demonstrating the precision and repeatability of the MP-AES method for the determination of metals in real base metal ore samples.

Table 4. 4200 MP-AES recovery of Cr and Fe in the Norant chromite ore.

Core Section	Cr 425.433 Measurement (%)	RSD (%)	Fe 371.993 Measurement (%)	RSD (%)
A	26.1	0.9	13.4	0.9
B	27.2	0.8	13.7	1.0
C	27.6	1.2	13.5	1.2
D	28.5	1.3	13.5	1.0
E	28.6	1.2	13.8	1.4
F	30.0	0.8	14.7	0.7
G	30.0	0.8	14.4	1.2
H	28.9	1.1	13.5	1.5
I	29.3	0.8	13.9	0.8
J	29.9	0.6	13.8	0.6

Recoveries of various metals in the twelve ore CRMs can be found in Table 5. The measured metal concentrations in the ore CRMs ranged from approximately 0.20% to almost 70%. All results were within $\pm 10\%$ of the certified value with an RSD of less than 2.5%, showing the accuracy and precision of the MP-AES for determinations over a wide concentration range.

Table 5. 4200 MP-AES recovery of certified elements in ore CRMs.

CRM Name	Element	Certified Value ($\mu\text{g/g}$)	Measurement ($\mu\text{g/g}$)	Recovery (%)	RSD (%)
GBM398-1	Cu 324.754	14820	15300	103	1.0
	Ni 352.454	9436	9300	99	1.1
	Pb 405.781	26700	26300	99	1.1
	Zn 213.857	20300	21400	105	0.9
GBM909-15	Cu 324.754	13100	13400	102	0.7
	Ni 352.454	115900	10800	94	1.9
	Pb 405.781	2120	2020	95	1.7
	Zn 213.857	26600	25700	96	2.4
GBM309-16	Cu 324.754	52300	53000	101	1.4
	Pb 405.781	14800	14100	96	1.4
	Zn 213.857	105300	103000	98	1.1
GIOP 117	Fe 371.993	696300	698000	100	0.5
GIOP 33	Fe 371.993	493000	473000	104	1.1
	Ti 336.122	122000	118000	97	1.1
GCR-06	Cr 425.433	327900	326000	100	1.1
	Fe 371.993	201400	203000	101	0.9
OREAS 78	Co 340.512	237400	234000	99	1.0
	Ni 352.454	257900	253000	98	1.0
OREAS 171	Mn 403.076	351000	353000	101	1.2
OREAS 189	Fe 371.993	104500	101000	97	1.0
	Mn 403.076	1758	1730	99	1.2
	Ni 352.454	14800	14400	101	1.4
OREAS 701	Cu 324.754	4910	4900	100	2.1
	Fe 371.993	230200	230000	100	0.7
	W 400.875	24300	23900	98	2.0
CCU-1d	Cu 324.754	239300	248000	103	1.2
	Fe 371.993	292600	294000	100	0.8
	Pb 405.781	2620	2700	103	1.8
	Zn 213.857	26300	26400	100	0.7
NIST 333a	Mo 379.825	548600	550000	100	1.7

Conclusions

The Agilent MP-AES is the ideal technique for accurate, reliable, low cost analysis of metals in base metal ores. Determinations of Cr and Fe in ten sampled sections throughout a chromite ore core demonstrate the precise and reproducible performance of the MP-AES for analysis of real base metal ore samples. Accurate recoveries of 11 elements over 12 different CRM samples showcase the accuracy of the technique and its ability to overcome the spectral interferences common in geological samples with complicated metal compositions. The nitrogen-based plasma excitation source of the MP-AES means that expensive and flammable gases associated with FAAS are eliminated, resulting in safer, more cost effective base metal ore analysis.

Reference

1. Y. Wang, L.A. Baker, E. Helmecci, I.D. Brindle, Rapid high-performance sample digestion of base metal ores using high-intensity infrared radiation with determination by nitrogen-based microwave plasma optical spectrometry, *Analytical Chemistry Research*, **2016**, doi: 10.1016/j.ancr.2016.02.002

Verified for Agilent
4210 MP-AES



Results presented in this document were obtained using the 4200 instrument, but performance is also verified for the 4210 MP-AES

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