

Ultra-fast ICP-OES determinations of base metals in geochemical samples using next generation sample introduction technology

Application note

Geochemistry, mining and metals

Author

John Cauduro

Agilent Technologies
Melbourne, Australia



Introduction

Mines, mineral processors and geologists involved in mineral exploration require accurate, precise analysis with rapid sample turn-around times. To remain viable in a competitive global environment, geochemical laboratories are analyzing increasing sample loads at lower and lower detection limits, making simultaneous ICP-OES the preferred analytical technique.

This work describes the high speed analysis of certified reference materials using the Agilent 725 simultaneous ICP-OES with a switching valve system (Agilent SVS 2) and an inert multipurpose nebulizer (Agilent OneNeb). The SVS 2 provides greater sample throughput and the OneNeb provides a robust sample introduction system capable of handling high throughput of challenging geochemical digests. The reference materials were prepared using the popular and effective 4-acid digest comprised of a combination of hydrochloric acid (HCl), nitric acid (HNO₃), perchloric acid (HClO₄) and hydrofluoric acid (HF).



Agilent Technologies

The new and innovative sample introduction system, termed the Switching Valve System 2 (SVS 2) comprises a software-controlled multi-port switching valve, a sample loop, and a high-speed, positive displacement pump. Using this system greatly reduces the sample-to-sample cycle, reducing argon consumption, while maintaining analytical accuracy. By limiting the amount of sample used during sample analysis, wear on components such as the nebulizer, torch and pump tubing is reduced, further minimizing operating costs.

The Agilent OneNeb nebulizer offers superior performance for this application over other comparable nebulizers. The OneNeb increases nebulization efficiency by generating an extremely fine aerosol, which greatly improves sensitivity and signal-to-noise ratio, and lowers detection limits. This allows lower volumetric flow rates to be used for analysis, reducing sample consumption.

Experimental

Instrumentation

An Agilent 725 simultaneous ICP-OES with radially-viewed plasma was used for the analysis. The Agilent 725 ICP-OES features a custom-designed CCD detector, which provides true simultaneous measurement with comprehensive wavelength coverage from 167 to 785 nm for fast, precise measurements of all elements of interest. The optical system is housed within a thermally-stabilized environment at 35 ± 0.1 °C and contains no moving parts, ensuring excellent long-term stability. For measuring elements that require low UV wavelengths (<190 nm) the optical path can be purged with either argon or nitrogen gas for improved performance, although this was not required for this analysis. The highly efficient RF generator produces a robust plasma, and the vertically-orientated radial plasma provides excellent solids handling, making it ideally suited to geochemical samples which typically have high concentrations of strong acids and high levels of total dissolved solids.

The Agilent 725 ICP-OES was fitted with a mass flow controller and a five-channel peristaltic pump. The five-channel peristaltic pump allows the sample, internal standard/ionization buffer solution, rinse solution and the waste to be simultaneously pumped.

A conventional one-piece radial torch was used. The sample introduction system consisted of the OneNeb nebulizer and a double-pass glass cyclonic chamber. Agilent ICP Expert II software was used for instrument operation.

A plasma gas flow of 10.5 L/min was used in the analysis, which reduced the overall argon consumption. This lower Ar consumption, coupled with the higher throughput with the SVS 2, offers significant cost savings.

Solutions were automatically presented to the spectrometer using the Agilent SPS 3 Sample Preparation System, controlled by the operating software. Tables 1 and 2 list the operating conditions used for the ICP-OES and the SVS 2 during this analysis.

Table 1. ICP-OES instrument operating parameters

Condition	Setting
Power	1.2 kW
Plasma gas flow rate	10.5 L/min
Auxiliary gas flow rate	1.5 L/min
Spray chamber type	Glass cyclonic (double-pass)
Torch	Standard one piece quartz radial
Viewing height	10 mm
Nebulizer type	OneNeb
Nebulizer flow rate	0.8 L/min
Pump tubing	Rinse/instrument pump: Black-black tabs (0.76 mm ID) Waste: blue-blue tabs (1.65 mm ID)
Pump speed	20 rpm
Replicate read time	3 s
Number of replicates	3
Sample uptake delay time	0 s
Stabilization time	20 s
Rinse time	0 s
Fast pump	Off

Table 2. SVS 2 operating parameters

Condition	Setting
Loop uptake delay	5.0 s
Uptake pump speed — refill	500 rpm
Uptake pump speed — inject	108 rpm
Sample loop size	1.0 mL
Time in sample	4.5 s
Bubble inject time	4.9 s

Inter-element corrections (IEC)

One of the main challenges when analyzing geochemical digests is that they often contain a diverse range of elements at varying concentrations. This leads to unpredictable spectral interferences that may not be resolved by the high-resolution polychromators found on today's ICP-OES instruments.

A reliable method for analyzing geochemical samples must overcome these interferences. The continuous wavelength coverage and comprehensive wavelength database in ICP Expert II makes finding a wavelength free of interferences easy, but when this is not possible the IEC feature in ICP Expert II provides an easy-to-use solution to spectral interferences.

An example is shown in Figure 1. Silver (Ag) at 328.068 nm has a spectral interference from zirconium (Zr). Manganese and molybdenum also present possible interferences, but are not shown here. Hence IECs were used for this and other lines, giving excellent results particularly when close to the limit of detection (LOD). Off-peak background correction is the recommended form of background correction when using IECs.

Samples and sample preparation

Ore-grade Certified Reference Materials (Geostats) were prepared by taking 0.4 g and performing a 4-acid digestion using a combination of HF, HClO₄, HCl, and HNO₃ at temperatures up to 260 °C. Hydrofluoric acid is used in to dissolve silicates, resulting in a near-total digestion. The 4-acid digestion is a very effective dissolution procedure for multi-element analysis for a wide range of elements. However, the method is not suitable for volatile elements such as B, As, Pb, Ge, Sb or rare earth elements (REE).

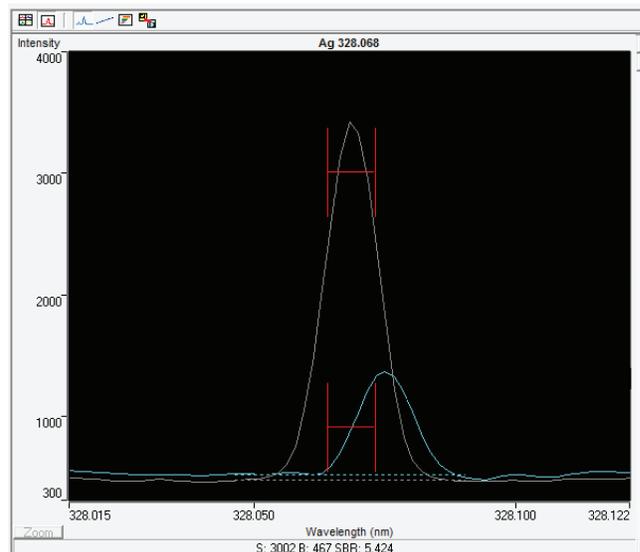


Figure 1. Zirconium interference shown to the right of the silver line at 329.068 nm

Calibration solutions were prepared from custom-grade single-element solutions, supplied by Merck, ACR chemical reagents and Inorganic Ventures Inc. The calibration standards and calibration blank solutions were prepared in deionized water (> 18 MΩ·cm) supplied from a Millipore system and stabilized with 30% v/v HCl (Merck).

Table 3 lists the selected elemental wavelengths and concentration range covered by the calibration standards for each element. Sensitivity, linear dynamic range and freedom from spectral interferences were taken into consideration during wavelength selection.

Results and discussion

Certified concentrations of base metals in the respective ore reference materials are reported in Table 4. Analyses were performed in various combinations and the error reported for each result represents the largest variation from the mean value. The LOD is based on three sigma of ten replicate analysis of the blank solution during the analytical run. Table 5 shows the detection limits (in the solid) for the analysis. Detection limits are well below those required for the analysis, with the exception of As in some ore materials.

Table 3. Element wavelength, CCV concentration and IEC concentration ranges for the elements (mg/L)

Element	Wavelength (nm)	Calibration range (mg/L)	CCV (mg/L)	IEC (mg/L)	Analyte (mg/L)
Ag	328.068	0.1–4.0	2		10
Al	237.312	10–500	200	200	500
As	193.696	2.0–100	50		500
Ba	233.527	1.0–50	20	50	500
Cd	226.502	0.5–25	10		25
Co	237.863	2.0–100	50	10	50
Cr	267.716	1.0–50	20	20	50
Cu	327.395	2.0–500	50	200	500
Fe	239.563	20–1000	500	500	500
Mn	257.61	2.0–100	50	100	500
Mo	284.824	10–500	100	100	500
Ni	231.604	2.0–500	50	500	500
Pb	405.781	2.0–100	50		500
Zn	206.200	2.0–100	50		500
Zr	343.823	0.5–10	10	2	10

Although a small amount of precipitate was observed in the digestion, the overall measured concentrations were in good agreement with the certified data.

Using the SVS 2 significantly improved throughput, cutting the sample-to-sample time by half, from 1 minute and 30 seconds per sample, to 45 seconds. This increases sample throughput from 40 samples an hour to 80 samples an hour, as shown in Figure 2. As an added benefit, the daily argon consumption was greatly reduced, as shown in Figure 3.

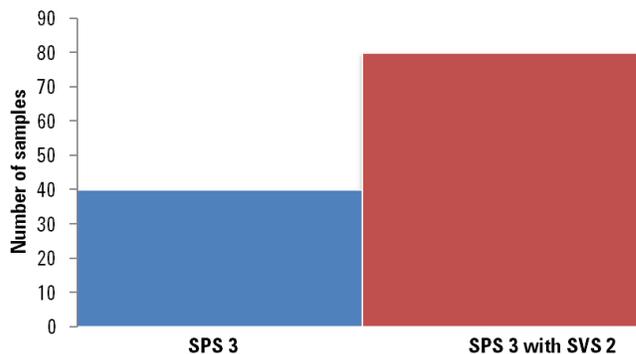


Figure 2. Time plot. Number of samples per hour.

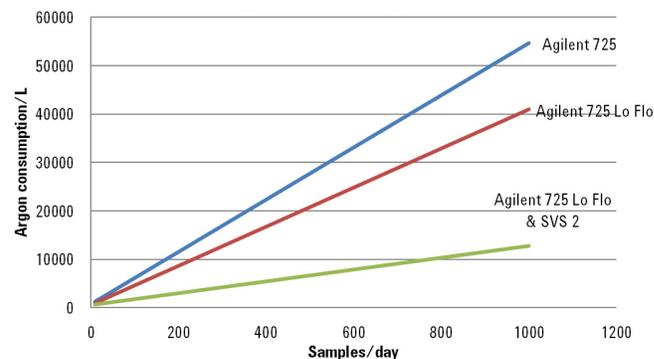


Figure 3. Daily argon consumption

Conclusion

This work has demonstrated the ability of the Agilent 725 simultaneous ICP-OES with radially-viewed plasma to accurately measure base metals in challenging geochemical samples. The highly efficient RF generator of the 725 ICP-OES transfers RF energy efficiently into the plasma to produce a robust, stable plasma even at low plasma gas flows of 10.5 L/min Ar. The low Ar plasma flow and efficient spectrometer purge use a total argon consumption of only 15.5 L/min, and when combined with the doubling of sample throughput from 40 samples an hour to 80 samples an hour using the SVS 2, running costs are slashed. The powerful and easy-to-use IEC feature in ICP Expert II means a reliable method can be set up to handle the wide range of unpredictable spectral interferences often encountered in geochemical samples.

Table 4. Comparison of results with Certified Base Metal Reference Material

CRM	Element	Units	Ag	As	Co	Cu	Ni	Pb	Zn
GBM398-4	Certified	mg/kg	48.7	12	1974	3891	4071	11714	5117
Triplicate analysis	SD		5.1	9	125	195	187	776	229
	Measured	mg/kg	50.14	<LOD	1877	3662	3780	11566	5188
	SD		0.44		26	104	33	157	43
	Recovery	%	103.0	<LOD	95.1	94.1	92.8	98.7	101.4
GBM399-5	Certified	mg/kg	24.2	320	46	29424	24412	21173	9493
Triplicate analysis	SD		1.5	27	5	1446	1248	1402	504
	Measured	mg/kg	24.60	297	45.3	26608	22899	21147	8752
	SD		0.27	11	2.2	286	216	160	90
	Recovery	%	101.6	92.7	98.5	90.4	93.8	99.9	92.2
GBM908-14	Certified	mg/kg	303.7	NA	NA	23715	NA	32955	42716
Single analysis	SD		21.9			704		1185	1503
	Measured	mg/kg	333.3	228	119	23727	15.0	35736	
	Recovery	%	109.7	NA	NA	100.1	NA	108.4	101.5

Table 5. Limit of detection results in mg/kg of sample

Element	Ag	As	Co	Cu	Ni	Pb	Zn
LOD	0.75	37	1.3	43	12	99	66

References

1. Hoobin, D. Ultra-fast ICP-OES determinations of oil and plant material using next generation sample introduction technology.
2. Hoobin, D. Ultra-fast ICP-OES determination of trace elements in water, conforming to US EPA 200.7 and using next generation sample introduction technology.
3. Kovachev, N. Development of a new liquid sample introduction system for ICP-OES and ICP-MS systems (poster).

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2012

Published August 27, 2012

Publication number: 5991-0876EN



Agilent Technologies