Ultra-fast determination of base metals in geochemical samples using the 5100 SVDV ICP-OES

Application note

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Introduction

Traditionally, geological samples are analyzed using flame atomic absorption (FAAS) and/or radial ICP-OES with a vertical torch.

Achieving high sample throughput at a low cost per analysis for geochemical samples can be challenging when using these techniques. The samples often have a wide range of element concentrations, requiring multiple dilutions, particularly when using FAAS. The samples also have high levels of total dissolved solids (TDS), which requires frequent cleaning of the sample introduction system.

In this application note, the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES was used to analyze geochemical samples containing up to 2.5% TDS. As well as demonstrating the accuracy and flexibility of the instrument, the sample measurement rate and argon consumption per sample were determined.

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Experimental

Instrumentation

The 5100 SVDV ICP-OES can be operated in synchronous vertical dual view (SVDV), vertical dual view (VDV), radial or axial modes for full flexibility with established methods and application requirements [1]. In this study, the 5100 ICP-OES was operated in SVDV mode and was coupled to an Agilent SVS 2+ Switching Valve System to maximize sample throughput and minimize argon gas consumption per sample.

SVDV mode allows the UV wavelengths from the vertically-oriented plasma to be read axially. This is ideal for the analysis of heavy matrix samples such as geochemical samples as it provides much lower method detection limits (MDLs) than the radial view mode often used for geochemical samples.

The standard sample introduction system supplied with the 5100 ICP-OES was used for this study. This comprised a SeaSpray nebulizer, double-pass glass cyclonic spray chamber and a standard 5100 Dual View torch (demountable, quartz, 1.8 mm injector). The instrument's plug and play torch loader automatically aligned the torch and connected gases, allowing fast start up and reproducible performance, irrespective of the operator. Instrument operating conditions used are listed in Table 1.

Table 1. Agilent 5100 SVDV ICP-OES operating parameters

Parameter	Setting
Torch	Standard DV torch (1.8 mm ID injector)
Nebulizer	Standard Seaspray
Spray chamber	Standard double-pass glass cyclonic spray chamber
Read Time (s)	5
Replicates	3
Sample uptake delay (s)	0
Stabilization time (s)	10
Rinse time (s)	3
Fast pump (80 rpm)	Yes
Background correction	Left and/or right background correction
RF power (kW)	1.4
Nebulizer flow (L/min)	Default: 0.70
Plasma flow (L/min)	Default: 12.0
Aux flow (L/min)	Default: 1.0
Viewing height (mm)	Default: 8

The innovative SVS 2+ is a 7 port switching valve that more than doubles the productivity of the 5100 ICP-OES by reducing sample uptake, stabilization times, and rinse delays. The SVS 2+ includes a positive displacement pump that can achieve up to 500 rpm and rapidly pumps sample through the sample loop. It also features a bubble injector to help with sample washout.

SVS 2+ operating parameters are given in Table 2.

Table 2. SVS 2+ operating parameters

Parameter	Setting
Loop uptake delay (s)	4.5
Uptake pump speed (refill) (rpm)	375
Uptake pump speed (inject) (rpm)	130
Sample loop size (mL)	0.5
Time in sample (s)	3.5
Bubble inject time (s)	4.3

Standard and sample preparation

A geochem base metal Certified Reference Material (CRM) OREAS 45e (ORE Research & Exploration P/L, Victoria, Australia) was used to validate the method.

The sample preparation procedure consisted of an Aqua Regia (AR) digestion on a hot plate. 1.0 g sample in 12 mL AR was refluxed at 60 °C for 0.5 hours and then at 110 °C for 2.0 hours. The solution was made to a total volume of 40 mL with Milli-Q water, resulting in a 30% AR final acid concentration, which is equivalent to 2.5% TDS.

All calibration standards solutions were prepared in 30% AR.

An internal standard solution of 20 ppm Lu and 200 ppm Rb was delivered using orange/green tubing which was connected to the white-white sample tubing via a T-connector (port 7 on the SVS 2+). Lu is rarely present in geochemical samples making it ideal as an internal standard. The Lu 261.541 nm wavelength was used used to correct the UV wavelengths.

The Rb 780.026 nm wavelength is suitable for K correction as it is a group 1 element with similar properties.

Inter-element correction (IEC) factors were setup using the ICP Expert v7 software to correct for spectral interferences. Once the factors were determined, they were stored in a template and reused in subsequent analyses.

Results and discussion

Method Detection Limits and CRM recoveries

The Method Detection Limits (MDLs) are based on a 1 g to 40 mL sample dilution ratio. The results shown in Table 3 are an average of 3 determinations over 3 separate days. The axially viewed, vertical torch in the 5100 is able to achieve much lower MDLs for geochemical samples compared to a radially viewed plasma.

Excellent recoveries were obtained when the CRM OREAS 45e was analyzed using the 5100 ICP-OES. Table 4 lists the average of 3 determinations over 3 separate days. Elements without a certified value were determined with a spike recovery test. The spike recoveries for all elements were within ±10% (Table 5). Spike recoveries were determined using an average of 3 replicate results.

Table 5. Spike recovery test for additional elements not certified in CRM OREAS 45e.

Element	Ag	Cd	Mo	Ti	Zr
Wavelength (nm)	328.068	214.439	202.032	334.188	343.823
Spike amount (mg/L)	0.25	4	5	20	0.5
Spike recovery %	104.3	90.9	97.8	107.0	108.9

Table 3. MDLs (mg/kg) for target elements

Element	Ag	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
Wavelength (nm)	328.068	236.705	188.980	233.527	370.602	214.439	228.615	266.602	222.778	273.358	766.491
MDL (mg/kg)	0.025	0.81	0.37	0.013	0.17	0.011	0.048	0.109	0.21	3.5	8.0
Element	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn	Zr
Wavelength (nm)	277.983	294.921	202.032	588.995	230.299	213.618	220.353	181.972	334.188	334.502	343.823
MDL (mg/kg)	0.48	0.021	0.072	1.9	0.057	0.34	0.23	2.7	0.03	0.9	0.015

Table 4. Recoveries for base metals in CRM OREAS 45e

Elements	Al	As	Ba	Ca	Co	Cr	Cu	Fe	K
Wavelength (nm)	236.706	188.981	233.528	370.603	228.616	266.603	222.779	273.359	766.492
Certified (mg/kg)	33200	11.4	139	320	52	849	709	226500	530
Measured (mg/kg)	33395	11.8	138	306	48	880	717	245789	487
SD (mg/kg)	2329	0.6	2	6	1	17	27	4139	20
% Recovery	100.6	103.5	99.6	95.5	91.7	103.6	101.1	108.5	91.9
Elements	Mg	Mn	Na	Ni	P	Pb	S	Zn	
Wavelength (nm)	277.984	294.922	588.996	230.3	213.619	220.354	181.973	334.503	
Certified (mg/kg)	950	400	270	357	290	14.3	440	30.6	
Measured (mg/kg)	974	398	244	341	301	12.9	426	29.0	
SD (mg/kg)	37	10	5	15	10	0.4	16	1.6	
% Recovery	102.5	99.4	90.4	95.6	103.8	90.1	96.9	94.9	

Calibration linearity

The Vista Chip II detector used in the 5100 ICP-OES has the fastest processing speed (1 MHz) of any charge coupled device (CCD) detector used in ICP-OES and provides a full 8 orders of linear dynamic range by reducing the likelihood of pixel saturation and signal over-ranging.

All calibration curves showed excellent linearity, with correlation coefficients greater than 0.999. Figure 1 shows the calibration curve for Fe, with each calibration point having less than 0.5% readback error. This demonstrates the ability of the 5100's 27 MHz solid state RF (SSRF) system to achieve linearity for all wavelengths over a wide concentration range (up to 10,000 mg/L in solution for Fe). This capability allows analysts to carry out single point calibration, simplifying operation.

Intensity = 133.51 * Concentration + 11.17
Correlation coefficient: 1.00000
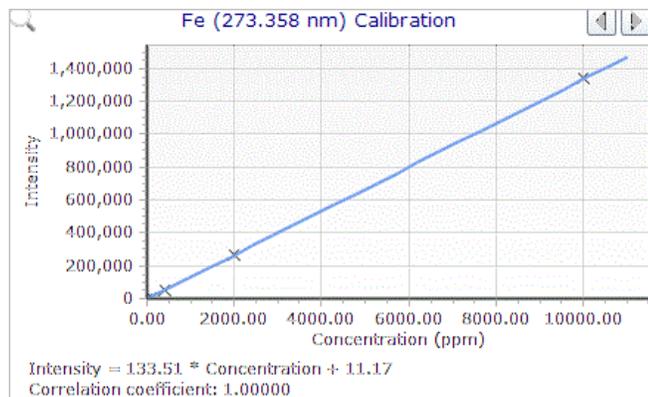
Standards	Concentration (ppm)	% Error
Blank	0	N/A
Standard 1	100	0.05
Standard 2	400	0.08
Standard 3	2000	0.39
Standard 4	10000	0.47

Figure 1. Calibration curve for Fe 273.358 nm line

Long Term Stability (LTS)

The 27 MHz SSRF in the 5100 is able to deliver a robust plasma capable of excellent long term analytical stability, even with tough samples.

To evaluate the long term stability of the method, an ore sample was run over an 8 hour period. Results were normalized to 100 per the first sample and are shown in Figure 2. The long term %RSD were all below 2.1%. Cd was spiked in the sample as the concentration was originally less than the MDL.
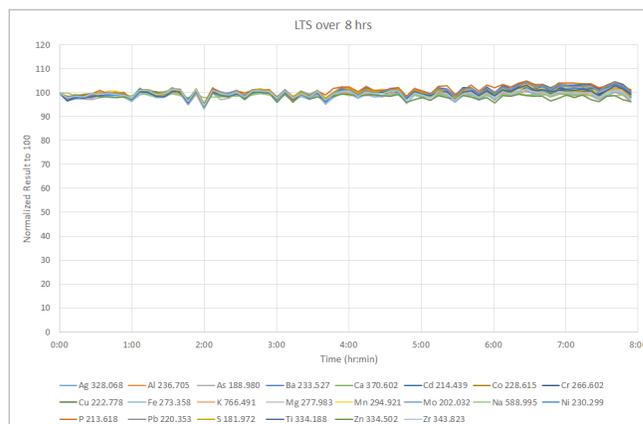

Figure 2. Long term stability over 8 hours.

Fast sample throughput and low argon consumption

The sample throughput of the 5100 ICP-OES is enhanced by:

- SVDV mode, which measures all wavelengths at once

- the SVS 2+, which reduces sample uptake, stabilization times, and rinse delays

- the fast Vista Chip 2 detector, that reads all wavelengths in a single measurement,

- and the design of the sample introduction system, with its short tubing lengths. This reduces sample uptake time and stabilization time

These factors delivered a sample analysis time of 40 seconds during this study. This equates to 90 samples per hour or 720 samples over an 8 hour day. The total Ar consumption was only 14 L/sample.

When running the 5100 SVDV without the SVS 2+, the additional rinse (45 sec) and uptake times (12 sec) increased the sample time to 96 seconds. When running in Dual View mode the analysis time was 113 seconds.

The times between the different operating modes of the same instrument are shown in Table 6.

Table 6. Comparison of operating modes: synchronous vertical dual view (SVDV) and vertical dual view (VDV)

	SVDV + SVS 2+	SVDV	VDV + SVS 2+	VDV
Sample to Sample time (sec)	40	96	57	113

Conclusions

Agilent's 5100 SVDV ICP-OES with a vertical torch provides the robust analytical performance required for the analysis of tough geochemical samples while achieving rapid sample throughput and low Ar gas consumption.

The geochemical base metal reference material OREAS 45e was prepared using an Aqua Regia digestion. It was then successfully analyzed using the 5100 ICP-OES in SVDV mode.

In addition to excellent MDLs, spike recoveries, and linearity, sample throughput of 40 seconds per sample was achieved using the SVS 2+ switching valve, without any compromise in performance. This enabled the measurement of 90 samples per hour and reduced argon consumption to just 14 L/sample.

Reference

1. Benefits of a vertically oriented torch— fast, accurate results, even for your toughest samples, Agilent publication, (2014), 5991-4854EN

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