

Rapid determination of gold in geological samples using the Agilent 4210 MP-AES

Application note

Metals, mining, geochemistry

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Introduction

The accurate and repeatable determination of gold in geological samples is vital for companies involved in precious metal production and the laboratories that support them. With large numbers of samples to be analyzed, the cost-per-sample and analysis times are also important considerations when selecting the most suitable analytical technique for the application.

Geological samples that contain precious metals are typically prepared using the fire assay process and analyzed using flame atomic absorption

spectrometry (FAAS) or inductively coupled plasma optical emission spectrometry (ICP-OES). FAAS requires acetylene and nitrous oxide gases which are expensive and can be difficult to source in remote mining locations. In contrast, microwave plasma atomic emission spectrometers, such as the Agilent 4210 MP-AES, use a nitrogen-based plasma that can be sustained using a nitrogen Dewar or nitrogen extracted from air using a nitrogen generator. Eliminating the need for costly and flammable gases ensures more cost efficient and safer analysis compared to FAAS. Furthermore, the hotter plasma excitation source (5000 K) of MP-AES expands the application range of the technique by providing higher matrix tolerance, wider linear dynamic range and lower detection limits than FAAS.

The 4210 MP-AES combines the intuitive MP Expert software, easy-fit torch, and a fully integrated Advanced Valve System (AVS 4) switching valve to simplify instrument setup, method development and analytical performance. These innovative features ensure that samples can be analyzed quickly and accurately, improving productivity and data quality, while keeping operating costs low.

This application note describes the analysis of gold in geological samples prepared by fire assay using an Agilent 4210 MP-AES fitted with an AVS 4 switching valve.

Experimental

Instrumentation

All measurements were performed using the Agilent 4210 MP-AES with a fully integrated AVS 4 four port switching valve and configured with an SPS 4 autosampler and humidifier accessory. The instrument was fitted with a 5 channel peristaltic pump to allow a modified pump tubing configuration for faster sample uptake. The sample introduction system consisted of a Meinhard nebulizer, single pass glass cyclonic spray chamber, and easy-fit torch. Once in place, no further realignment of the torch was required.

The AVS 4, shown in Figure 1, is fully integrated into the 4210 MP-AES instrument hardware and controlled through the MP Expert software for optimum timing

and ease-of-use. The valve quickly switches between rinse and sample. This minimizes exposure of sample introduction components to high matrix samples, prolonging the lifetime of consumable items.



Figure 1. Agilent 4210 MP-AES with Agilent Advanced Valve System (AVS 4) four port switching valve

The operating parameters used for the 4210 MP-AES and AVS 4 switching valve are shown in Tables 1 and 2. Read time was decreased to 1 s for maximum sample throughput and the ideal nebulizer flow was easily determined using the Optimize Nebulizer Flow tool in the MP Expert software. All other method parameters used default settings.

To speed up sample delivery to the plasma, the flow rate of sample through the autosampler probe was increased based on the “rapid flow” concept—where the sample flow rate from the autosampler to the peristaltic pump is increased. To increase the sample flow rate, without overloading the nebulizer, an additional sample peristaltic pump tube was introduced to the system via a T-piece inserted between the end of the autosampler line and the start of the sample peristaltic pump tubing so that sample would flow through two sample peristaltic pump tubings instead of one. One of the peristaltic pump tubes was directed to the AVS 4 switching valve (to go to the nebulizer), and the other to waste, which avoided overloading the nebulizer with sample (Figure 2). By having sample flow through two pump tubings, the sample flow rate (through the autosampler probe up to the point where the T-piece was inserted) was increased, thus reducing sample uptake time by 40%.

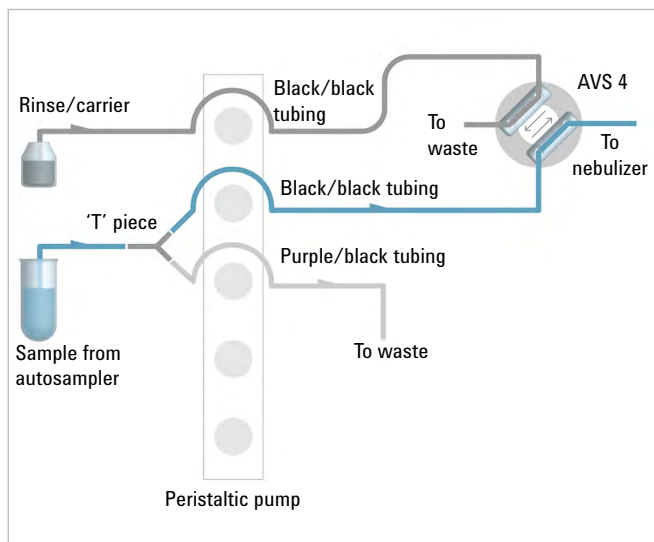


Figure 2. The “rapid flow” concept setup to increase the sample flow rate.

Table 1. Agilent 4210 MP-AES instrument and method parameters.

Parameter	Setting
Element	Au
Wavelength (nm)	267.595
Read time (s)	1
Replicates	3
Pump speed (rpm)	15
Fast pump during uptake and rinse (rpm)	80
Nebulizer flow (L/min)	0.85
Viewing position (mm)	0
Nebulizer	Meinhard
Spray chamber	Single pass glass cyclonic
Torch	Easy-fit torch
Sample pump tubing	Black/black (to AVS 4) Purple/black (to waste)
Carrier pump tubing	Black/black
Waste pump tubing	Blue/blue
Background correction	Auto

Table 2. Agilent AVS 4 settings.

Parameter	Setting
Uptake delay (s)	9
Switch delay (s)	7
Rinse time (s)	5
Stabilization time (s)	5

Samples and sample preparation

Six geological samples, two gold certified reference materials (CRMs) and a custom reference material (RM) were used in this study: SL76 and OxP116 (Rocklabs Reference Materials, New Zealand) and BP-13 (customer reference material—not commercially available). All samples and CRMs were prepared by a third party laboratory using a standard fire assay procedure. Ultrapure de-ionized water (18 MΩ resistivity, Millipore) and analytical grade hydrochloric acid (37% m/v, fuming) and nitric acid (69% m/v) were used for the preparation of all CRMs and samples. The final acid concentration of all solutions was 30% aqua regia.

Calibration standards of 2.5, 5, 10, 20, 50 and 100 mg/L were prepared from a 1000 mg/L Au single element standard. Standards were also prepared in 30% (v/v) aqua regia.

Calibration linearity

Au 267.595 nm was calibrated from 1 ppm up to 100 ppm for this method, with a correlation coefficient of greater than 0.999. This wide linear dynamic range allowed accurate determination of Au in geological samples from 1 ppm to over 60 ppm without the need for time consuming dilution and re-analysis of samples.

Results and discussion

Method detection limits

The procedure for determining the method detection limit (MDL) was based upon 40 CFR 136 Appendix B [1]. MDLs were calculated as three times the average standard deviation of ten replicate readings of a 150 µg/L solution measured after calibration with a 150 µg/L standard. The MDL was determined three times on two different instruments to give a total of six runs. The average of these six MDL measurements is given in Table 3.

Table 3. Agilent 4210 MP-AES method detection limit for Au 267.595 nm.

Element and wavelength (nm)	Average MDL (µg/L), n = 6
Au 267.595	7.2

Reference Material recoveries

To validate the method, various samples and CRMs were analyzed in triplicate using the 4210 MP-AES. The average Au value is presented in Table 4, with comparative results from FAAS analysis and certified values (in solution) for the three CRMs. There was no significant difference between the results obtained using FAAS and MP-AES, and the CRM recoveries were within $\pm 10\%$ of the certified value.

Using the AVS 4 switching valve, and modified pump tubing setup, the method was optimized to give a sample-to-sample analysis time of less than 30 seconds.

Long term stability

Three fire assay samples and one CRM were measured continuously for 3 hours without re-slope or recalibration to demonstrate the long term stability of the 4210 MP-AES.

Figure 4 shows the stability plot of the samples and CRM which were measured every 10 samples. All samples demonstrated excellent long term precision with a %RSD of less than 2% over the 3-hour analysis period (Table 5). This demonstrates the exceptional reliability and stability of the 4210 MP-AES with the AVS 4 switching valve for this analysis.

As the AVS 4 directs sample away from the sample introduction system during uptake and rinse, exposure to the matrix present in the samples is minimized resulting in increased lifetime of consumables, such as the nebulizer, spray chamber and torch. This means more high-matrix samples, such as these geological digests, can be analyzed before consumables need to be replaced, which decreases ongoing instrument running costs.

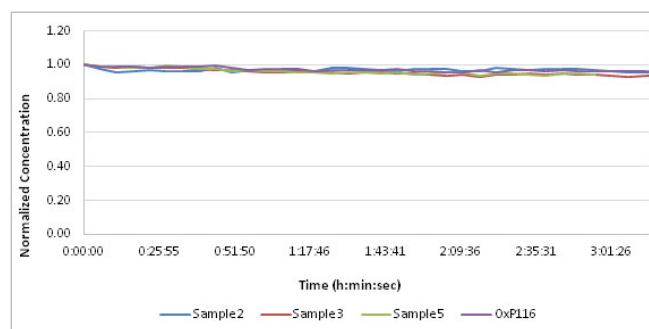


Figure 4. Normalized concentration of Au in geological samples measured over 3 hours.

Table 4. Comparative Au recovery results for samples and CRMs in solution obtained using MP-AES and FAAS.

Sample/Reference Material	Gold Certified Value (mg/L)	FAAS Measured Value (mg/L)	FAAS Recovery (%)	MP-AES Measured Value (mg/L)	MP-AES Recovery (%)	Difference between FAAS & MP-AES results (%)
Sample 1	-	4.180	-	4.495	-	8%
Sample 2	-	1.089	-	1.157	-	6%
Sample 3	-	17.19	-	17.87	-	4%
Sample 4	-	62.80	-	62.76	-	0%
Sample 5	-	28.18	-	28.90	-	3%
Sample 6	-	1.663	-	1.786	-	7%
SL76	17.88	18.33	103	18.52	104	1%
BP-13	1.074	1.089	101	1.156	108	6%
OxP116	44.85	44.99	100	44.95	100	0%

Table 5. Long term stability %RSD results for Au in four geological samples.

Solution	Average Concentration (mg/L)	%RSD over 3 hours
Sample 2	1.171	0.9
Sample 3	17.21	1.9
Sample 5	28.27	1.8
OxP116	44.53	1.3

Conclusions

The Agilent 4210 MP-AES is a high performance, safe and cost effective alternative to FAAS for the analysis of Au in geochemical samples. In this study, the easy-to-use AVS 4 switching valve system minimized the exposure of the sample introduction components to high matrix fire assay samples, offering further long term cost savings for labs conducting routine geochemical analysis.

The 4210 MP-AES with AVS 4 switching valve showed:

- Rapid analysis capabilities with a sample-to-sample analysis time of less than 30 seconds.
- An impressive linear dynamic range allowing the determination of Au over a wide concentration range without the need for time consuming dilutions.
- High analytical performance with a method detection limit of 7.2 ppb and CRM recoveries within $\pm 10\%$ of certified values.
- Measured concentrations were within 10% of those determined with FAAS for all samples and CRMs analyzed.
- Excellent long term stability with %RSD values for four different samples below 2% over three hours.

References

1. US Environmental Protection Agency, 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11, July 2011, <https://www.gpo.gov/fdsys/granule/CFR-2011-title40-vol23/CFR-2011-title40-vol23-part136-appB/content-detail.html>

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Published September 1 2016

Publication number: 5991-7103EN



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