Application Note

Mining & Minerals Analysis

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Determination of Gold, Palladium, and Platinum in Noble Metal Ores Prepared by Fire Assay

Simple, safe, and fast multi-element method using the Agilent 4210 MP-AES with sampling valve

Authors

Andreia Maria de Souza
SGS Geosol Laboratory Brazil, Vespasiano, Minas Gerais, Brazil

Rodolfo Lorençatto
Agilent Technologies, Brazil

Introduction

Noble metals—especially Au, Pd, and Pt—have been extracted from ores for centuries. Due to their relative inert properties, the use of noble metals has evolved over time (*1-3*). Modern day uses of metals such as Au, Pt, Pd, Rh, Ir, and Ag still include jewelry, plus a range of other high value applications. Examples include semiconductor devices, catalytic converters, and alloys. Many methods have been used to quantify these metals over the years, from titrimetric techniques to high-end analytical instrumentation (*4-6*). When instrumental techniques are used to analyze noble metals in geological ores, samples are typically prepared for analysis using fire assay (*7, 8*).

A search of the literature shows Flame Atomic Absorption Spectrometry (FAAS) is often used for the determination of Au, Pd, and Pt in metal ores (*1, 9, 10*). FAAS offers acceptable sensitivity for the application. However, FAAS is typically a single element technique that requires the use of flammable (acetylene) and toxic (nitrous oxide) gases for its operation. As organizations look to reduce lab operation costs and improve productivity, the costs of hollow cathode lamps and expensive gases required for FAAS are challenging.

Microwave plasma atomic emission spectrometry (MP-AES) is an attractive alternative technique to FAAS because of its higher performance characteristics and lower operating costs. The Agilent 4210 MP-AES uses nitrogen as the plasma gas, achieving temperatures up to 5,000 K. The high temperature source can easily promote excitation states of elements that are difficult to analyze by FAAS or elements that have high detection limits, such as Pt, B, and P. The nitrogen needed for the microwave plasma can be extracted from compressed air using an Agilent 4107 Nitrogen Generator. This convenient gas supply significantly reduces the cost of ownership and impact on the environment, while improving lab safety. It also allows installation in remote locations or mobile labs where gas supplies may not be available.

The MP Expert software simplifies all aspects of instrument operation. The software is intuitive to use, with automatic background correction, auto optimization for nebulization and viewing, and quick start preset methods (applets). In addition, the Customer Diagnostic Dashboard gives real-time feedback on instrument status, enabling the user to monitor performance. If a question arises, information can be easily shared with Agilent's support team to ensure maximum instrument uptime.

In this work, Au, Pd, and Pt were determined in noble metal ores processed by fire assay using a single, multi-elemental MP-AES method.

Experimental

Samples and sample preparation

All standards were Atomic Absorption grade (Inorganic Ventures, Christiansburg, Virginia, USA). The following reagents were used: hydrochloric acid, nitric acid, and silver nitrate (Química Moderna, Barueri, São Paulo, Brazil); borax (Brasilbor, São Paulo, São Paulo, Brazil); sodium carbonate (Tassimin, Betim, Minas Gerais, Brazil); litharge (lead monoxide, Durox, Rio Claro, São Paulo, Brazil); quartz powder (Sulfal, Belo Horizonte, Minas Gerais, Brazil); and type 1 ultrapure water (Millipore, Burlington, Massachusetts, EUA). These materials were used for standard and sample preparation.

Gold, Pd, and Pt standard solutions were mixed and diluted with aqua regia solution (6.7% v/v) to give the following final concentrations: 0.500; 1.00; 2.00; 5.00; 10.0 and 50.0 mg/L.

To prepare the metal ore samples for analysis per the process outlined in Figure 1, a pre-determined amount of flux was added to 30 g of pulverized sample. Once the prill was obtained, it was dissolved in 0.75 mL of aqua regia, 4.25 mL of type 1 ultrapure water, homogenized, and placed into an autosampler rack.

Six different concentrations of Au, Pd, and Pt certified reference materials (CRMs) were bought from Geostats Pty Ltd (O'Connor, Western Australia, Australia): GPP-02, GPP-04, GPP-09, GPP-10, GPP-11, and GPP-12.

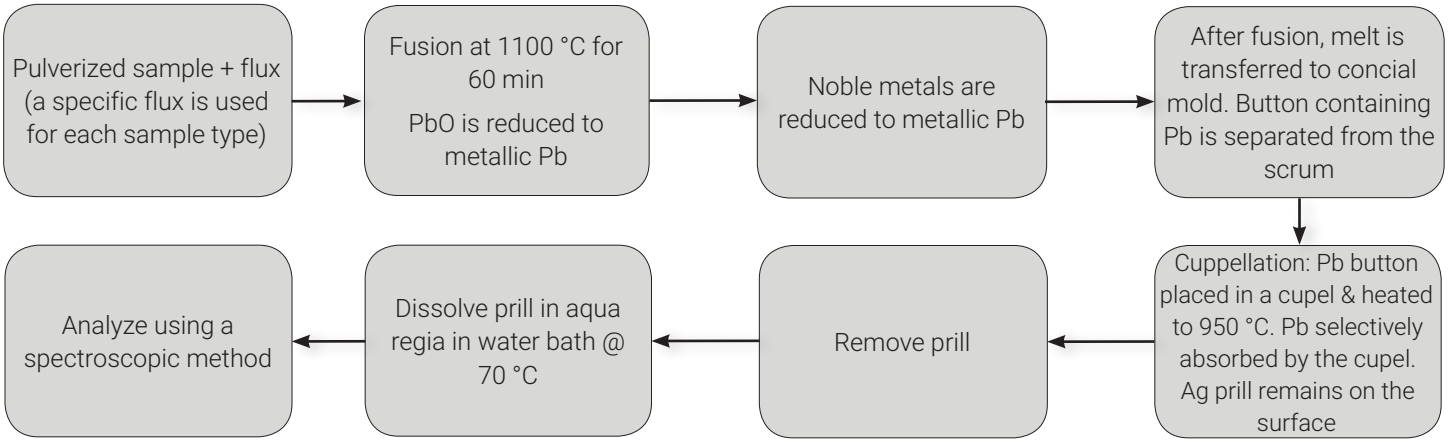


Figure 1. Noble metal ore preparation by fire assay. (A prill is a metallic bead that contains the precious metals).

Instrumentation

An Agilent 4210 MP-AES was fitted with a OneNeb Series 2 nebulizer, double-pass glass cyclonic spray chamber, and easy-fit torch. Sample introduction was via an AVS 4 four port switching valve and SPS 4 autosampler.

The AVS 4 is fully integrated into the 4210 MP-AES instrument hardware and controlled through the MP Expert software. The valve quickly switches between rinse and sample. This switching minimizes exposure of sample introduction components to high matrix samples, such as fire assay samples, prolonging the lifetime of consumable items.

Black-black tubing was used for sample pumping and blue-blue tubing was used for drainage. Using the automated optimization feature of MP Expert for nebulization flow and plasma viewing position, all wavelengths were adjusted to maximize the signal to root background ratio (SRBR) using 1 mg/L of Au, Pd, and Pt. Instrument operating conditions are shown in Table 1.

Table 1. Method conditions for the measurement of Au, Pd, and Pt by MP-AES.

Parameter	Au 267.595 nm [2]	Au 242.795 nm [1]	Pd 340.458 nm [1]	Pd 363.470 nm [2]	Pt 265.945 nm [1]	Pt 299.796 nm [2]
Background correction	Auto					
Read time (s)	3					
Nebulizer flow (L/min)	0.40	0.45	0.60	0.70	0.40	0.85
Viewing position (steps)	0	10	10	0	20	10
Replicates	3					
Pump speed (RPM)	15					
Uptake time (s)	25 (with fast pump)					
AVS 4 switch delay (seconds)	20					
SPS 4 rinse time (seconds)	10 (with fast pump)					
Stabilization time (seconds)	10					
Sample pump tubing	Black/black					
Carrier pump tubing	White/white					

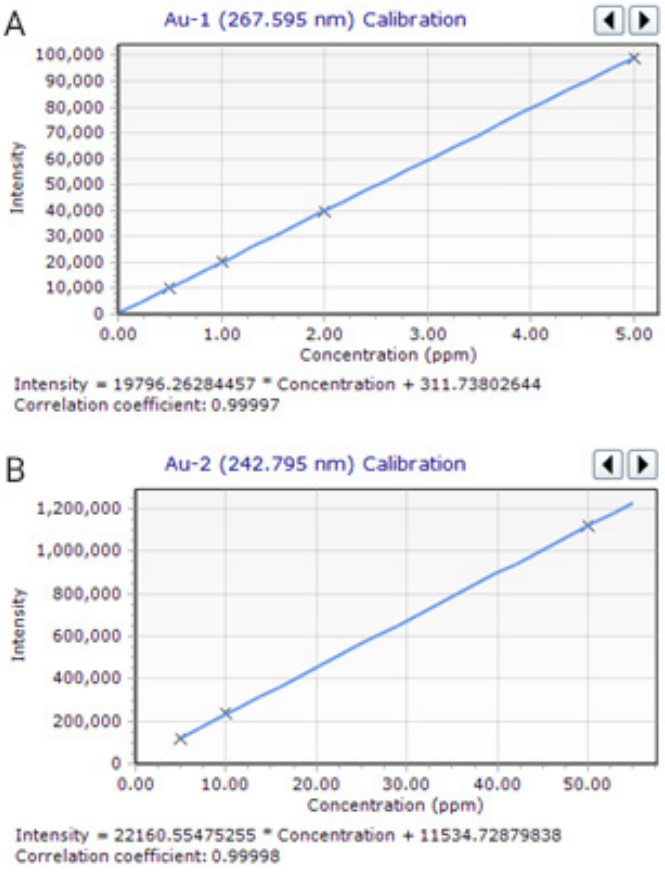
[1] More sensitive wavelengths
[2] Less sensitive wavelengths

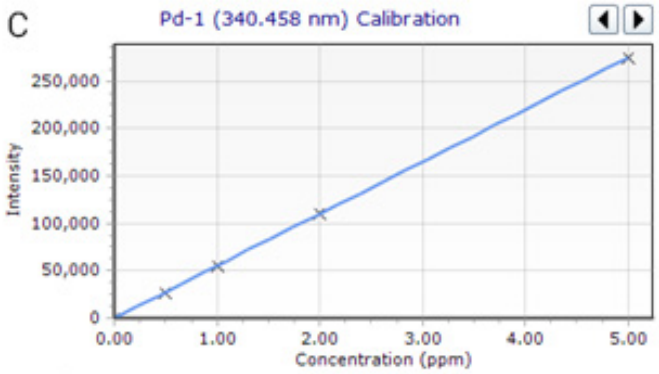
Benefiting from the MultiCal feature of the software, two wavelengths of the same element were selected to expand the linear dynamic range of the method (*11*). Lower concentrations were assigned to more sensitive wavelengths, and less sensitive wavelengths were used for higher concentrations. MultiCal provided a linear dynamic range from 0.500 to 50.0 mg/L, or 3 orders of magnitude, with a low impact on analysis time. The total time required to run a sample was about 1 minute and 20 seconds.

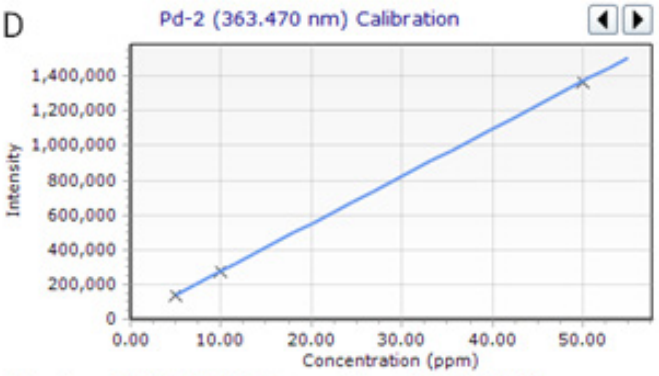
Results and Discussion

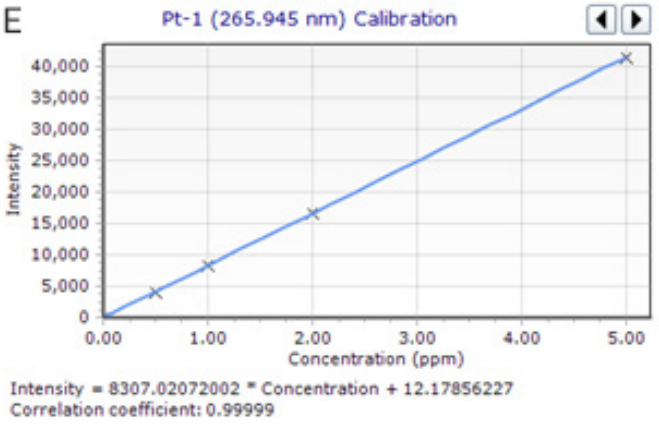
Working calibration range

The six calibration curves shown in Figure 2a-f highlight the working range for the 4210 MP-AES using MultiCal. All correlation coefficients were greater than 0.9999.









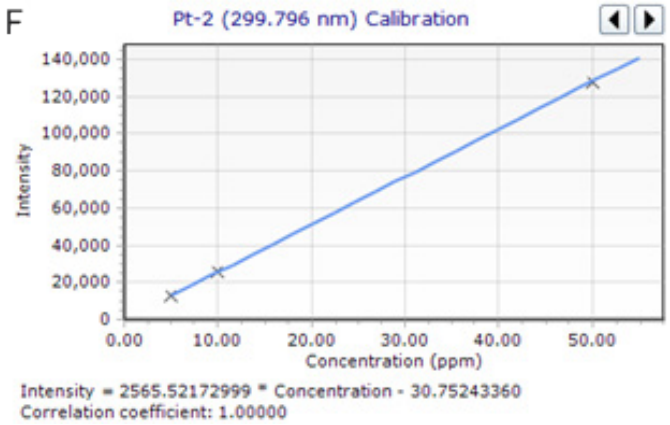


Figure 2a-f. Calibration curves for Au (a: 267.595 nm, b: 242.795 nm); Pd (c: 340.458 nm, d: 363.470 nm); Pt (e: 265.945 nm, f: 299.796 nm) using MultiCal.

Method Detection Limits

Method detection limits (MDL) and limits of quantification (LOQ) were calculated from the standard deviation of 10 fire assay blank solutions, using $3*\sigma_{blank}$ for MDLs and $10*\sigma_{blank}$ for LOQs. The most sensitive wavelength was used for each analyte, except for Au. Since the 267.595 nm line is less susceptible to spectral interference, it was used to calculate MDL and LOQ. Performance parameters are shown in Table 2. The MDLs demonstrate the suitability of the 4210 MP-AES method for the application.

Table 2. Agilent 4210 MP-AES MDL and LOQ for Au, Pd, and Pt.

Parameter	Au	Pd	Pt
MDL (mg/kg)	0.01	0.01	0.02
LOQ (mg/kg)	0.03	0.03	0.07
Linearity (using MultiCal)	0.05 – 50.0 mg/L; R > 0.9999		
Precision (% RSD)	< 1.5		

Long-term stability

A laboratory control sample containing 1 mg/L of Au, Pd, and Pt were measured for almost 7 hours. Figure 3 shows that excellent stability was obtained over the period, with less than 2.7% RSD for each metal. This demonstrates the robustness of the 4210 MP-AES with the AVS 4 switching valve for the analysis of high matrix samples. The AVS 4 directs sample away from the sample introduction system during uptake and rinse, minimizing exposure to the matrix present in the samples. In practical terms, more high-matrix samples can be analyzed before consumables need to be cleaned or replaced.

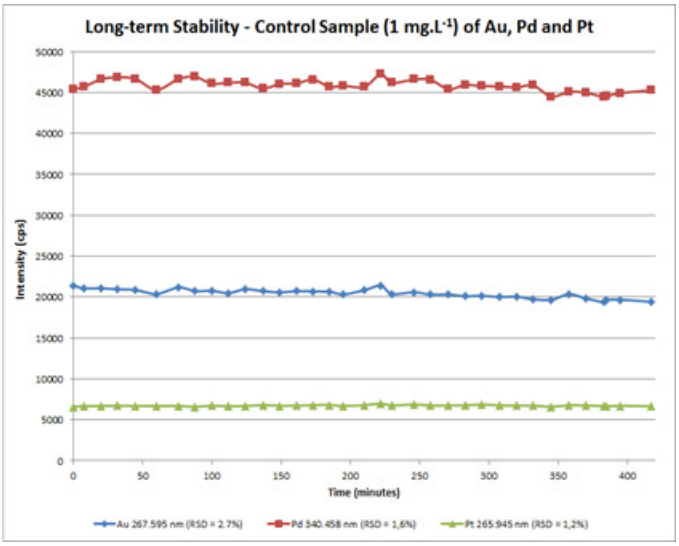


Figure 3. Long-term stability of 1 mg/L of Au, Pd, and Pt over approximately 7 hours.

CRM recoveries

To validate the method, various CRMs were analyzed for Au, Pd, and Pt using MP-AES, ICP-OES, and FAAS. To compare MP-AES performance with ICP-OES, six different CRMs were analyzed using the 4210 MP-AES and an Agilent Vista PRO Radial ICP-OES. The CRM recoveries obtained using MP-AES were within ±11% of the certified values in all cases. Also, there was no significant difference between the results obtained using MP-AES and ICP-OES (Table 3).

To compare MP-AES performance with FAAS for the analysis of Au, quantitative measurements of 22 CRMs were carried out. The results given in Figure 4 show good correlation between the two techniques and reference values.

Table 3. CRM analysis results measured using MP-AES and ICP-OES.

CRM		MP-AES			ICP-OES		
		Au 267.595 nm	Pd 340.458 nm	Pt 265.945 nm	Au 242.795 nm	Pd 340.458 nm	Pt 265.945 nm
GPP-02	Result (mg/kg)	0.921	0.529	0.493	0.920	0.501	0.512
	Certified result (mg/kg)	0.929	0.523	0.505	0.929	0.523	0.505
	Recovery (%)	**99**	**101**	**98**	**99**	**96**	**101**
GPP-04	Result (mg/kg)	0.082	0.098	0.086	0.079	0.096	0.081
	Certified result (mg/kg)	0.08	0.098	0.088	0.08	0.098	0.088
	Recovery (%)	**102**	**100**	**98**	**99**	**98**	**92**
GPP-04 (Dup)	Result (mg/kg)	0.086	0.095	0.084	0.079	0.091	0.083
	Certified result (mg/kg)	0.08	0.098	0.088	0.08	0.098	0.088
	Recovery (%)	**108**	**97**	**95**	**99**	**93**	**94**
GPP-09	Result (mg/kg)	0.597	0.423	0.346	0.602	0.415	0.358
	Certified result (mg/kg)	0.603	0.408	0.343	0.603	0.408	0.343
	Recovery (%)	**99**	**104**	**101**	**100**	**102**	**104**
GPP-10	Result (mg/kg)	1.464	2.105	2.365	1.489	2.041	2.529
	Certified result (mg/kg)	1.576	2.008	2.349	1.576	2.008	2.349
	Recovery (%)	**93**	**105**	**101**	**94**	**102**	**108**
GPP-11	Result (mg/kg)	0.677	0.578	0.580	0.724	0.592	0.620
	Certified result (mg/kg)	0.722	0.567	0.592	0.722	0.567	0.592
	Recovery (%)	**94**	**102**	**98**	**100**	**104**	**105**
GPP-12	Result (mg/kg)	0.046	0.045	0.042	0.041	0.040	0.047
	Certified result (mg/kg)	0.05	0.048	0.047	0.05	0.048	0.047
	Recovery (%)	**93**	**93**	**90**	**82**	**84**	**100**
GPP-12 (Dup)	Result (mg/kg)	0.048	0.046	0.042	0.046	0.044	0.044
	Certified result (mg/kg)	0.05	0.048	0.047	0.05	0.048	0.047
	Recovery (%)	**96**	**96**	**89**	**92**	**92**	**94**

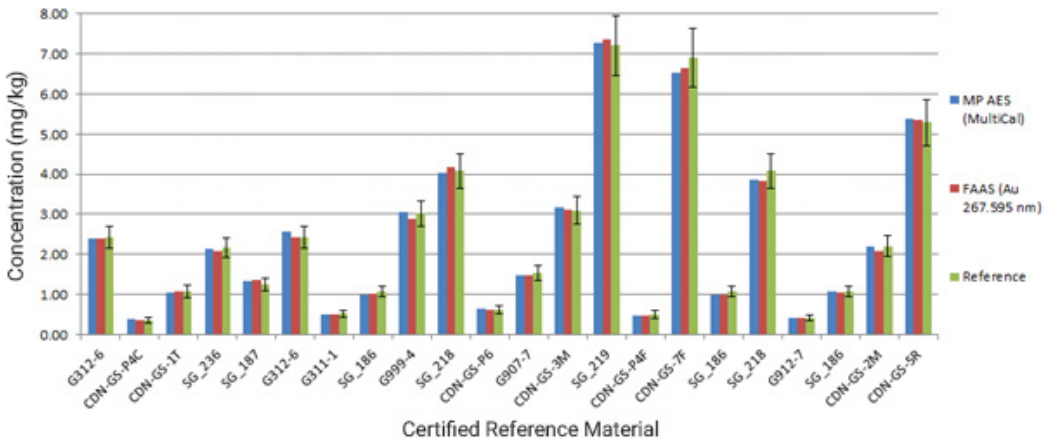


Figure 4. CRM analysis for Au using MP-AES and FAAS.

Actual sample analysis

Several noble metal ore samples were analyzed using the 4210 MP-AES with AVS 4. Quantitative results for 10 samples are shown in Table 4. As expected, the concentration of each metal varied in each sample. However, the data was obtained without the need for further dilution, maintaining a good level of productivity. To analyze the same samples for the three metals by FAAS would require additional sample dilution steps and reanalysis, requiring more time and resources.

Table 4. Quantitative results for Au, Pd, and Pt in noble metal ore samples by MP-AES.

	Au (mg/kg)	Pd (mg/kg)	Pt (mg/kg)
Sample 1	0.36	4.45	0.72
Sample 2	0.15	4.12	1.71
Sample 3	0.14	3.64	1.58
Sample 4	3.27	< 0.03	< 0.07
Sample 5	8.86	5.29	5.36
Sample 6	< 0.03	< 0.03	< 0.07
Sample 7	0.68	0.97	0.84
Sample 8	4.09	< 0.03	< 0.07
Sample 10	0.28	10.64	3.59

Conclusions

The Agilent 4210 MP-AES with AVS 4 delivers the robustness, dynamic range, and sensitivity required for the accurate quantification of multiple elements in noble metal ores.

Following preparation by fire assay, Au, Pd, and Pt were measured in 10 geological ore samples. The AVS 4 switching valve system minimizes the exposure of the sample introduction components to high matrix fire assay samples. It also optimizes sample throughput and enhances LTS—important considerations in high throughput labs. A complete sample run was completed in approximately 80 seconds.

Using the MultiCal feature of the MP Expert software, a combination of wavelengths of different sensitivity can be measured for the same element. MultiCal simply and effectively extends the dynamic range for the element, avoiding the need for extra sample dilution steps. This saves time and minimizes any contamination that may occur during further dilution of the samples. Since the MP-AES is fully controlled by the MP Expert software, analytical conditions can be optimized with minimal operator input or expertise.

The data presented in this report demonstrates how MP-AES exceeds FAAS performance in terms of sensitivity (MDLs and LOQs), speed, and robustness (long-term stability).

MP-AES represents a low-cost, higher performance alternative technique to FAAS for the analysis of geological metal ores. Also, when fitted with a nitrogen generator, the technique can be safely used in remote areas or field locations.

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