

# Determination of precious metals in rocks and ores by microwave plasma-atomic emission spectrometry for geochemical prospecting studies

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Methods were designed and developed for the quantitative determination of Au, Ag, Pt and Pd in several rock and ore reference samples by a new analytical technique, microwave plasma-atomic emission spectrometry (MP-AES). Two-gram samples dissolved in 100 ml using aqua regia digestion was directly used without any separation or a pre-concentration step for the determination of Au and Ag. On the other hand, NiS fire-assay technique followed by tellurium coprecipitation separation and pre-concentration step was adopted on 5 g samples to separate Pt and Pd from rock matrix for the determination of these two elements. Detection limits obtained are in the 0.5–5 ng/ml range for all these metals. MP-AES detection limits were compared with those of other well-established techniques, such as F-AAS, GF-AAS, INAA, ICP-AES and ICP-MS. The results obtained for Au, Ag, Pt and Pd were compared with those obtained by well-established analytical techniques such as F-AAS and ICP-MS. Precision and accuracy of the methods were demonstrated using replicate analyses of some international precious metal ore reference materials. Precisions of <5% RSD at practically 10–200 ng/ml levels of these elements in solution with comparable levels of accuracies were obtained which show good agreement with certified data. As there is limited literature on the application of MP-AES in geochemical and mineral exploration areas, this study forms one of the first application studies in these areas.

**Keywords:** Fire assay, geochemical prospecting, MP-AES, precious metals, rocks and ores.

PRECIOUS metals (Ru, Rh, Pd, Os, Ir, Pt and Au; sometimes Ag is also added to this list) are used in a variety of applications. Concentration and distribution of Au, Ag, Pt

and Pd in various types of rock formations have attracted enormous interest from explorers in recent times due to their rising demand in the technology sector owing to their applications as catalysts, biomedical tools (e.g. anti-cancer drugs), corrosion-resistant materials, high electrical conductivity materials, micro electronics and also in jewellery. As a result, the interest in better understanding the chemistry, mineralogy and geological occurrences, mining and extraction of these metals has been growing<sup>1</sup>. Accurate and precise determination of Au, Ag, Pt and Pd in hundreds to thousands of different types of rock and ore samples is required in exploration, mining and extraction activities<sup>2,3</sup>. Currently, a range of elemental analytical techniques, including flame and graphite furnace atomic absorption spectroscopy (F-AAS and GF-AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ICP mass spectroscopy (ICP-MS) are available for such studies. Despite striking advancements in analytical methods in recent times, a few elements such as Au, Pt and Pd remain the most poorly studied mainly due to the analytical difficulties in generating accurate data for these elements in rock and ore matrices, where the concentrations encountered are usually very low. In general, determination of these metals in geological samples is a two-step process though direct determination is also possible in some situations<sup>4</sup>. The first step involves preparation of representative samples and then separation of these elements from rock/ore matrix by a separation and pre-concentration technique such as nickel sulphide fire assay. The second step involves measurement of concentration by an instrumental analytical technique<sup>5</sup>. In recent times, yet another promising analytical technique, called microwave plasma-atomic emission spectrometry (MP-AES), which uses nitrogen as plasma gas, has been introduced by Hammer<sup>6</sup> with commercial instruments introduced by Agilent Technologies Inc., in 2011. Not many application studies have been reported using this technique so far, except a report on a prototype

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**Table 1.** Microwave Plasma-Atomic Emission Spectrometer operating parameters

Agilent 4100 microwave plasma-atomic emission spectrometer with 4107 nitrogen generator	
Plasma conditions	
Power of magnetron output	1 kW
Gas flows	
Plasma gas flow – nitrogen	20 l/min
Intermediate flow – nitrogen	1.5 l/min
Pre-optics protection gas – air	25 l/min
Nebulizer pressure	140–240 kPa (optimize for each element)
Nebulizer	OneNeb inert concentric for HF and high TDS solutions
Spray chamber	Double-pass glass cyclonic
Torch	Quartz torch
Plasma viewing	Axial
Acquisition parameters	
Sample uptake delay	8 sec
Stabilization time	60 sec
Read time	5 sec
No. of replicates	3
Background correction	Auto or FLIC (fast linear interference correction)
Optical system	Czerny–Turner design monochromator with 600 mm focal length and fixed entrance slit
Detector	Back-thinned solid state CCD detector (532 × 128 pixels)
Analytes (wavelength)	Au (267.595 nm), Ag (328.068 nm), Pt (265.945 nm), Pd (363.470 nm)

instrument by Zhang and Wagatsuma<sup>7</sup> on the matrix effects of easily ionizable elements and an application report on the determination of precious metals by Taylor<sup>8</sup>, though there have been a few other studies<sup>9–11</sup> on the microwave-induced plasma generated by other gases such as argon and helium. There is not much literature available at present on the application of MP-AES in geochemical and mineral exploration studies. In this study, an attempt is made to determine Au, Ag, Pt and Pd by MP-AES in several international geological precious metal reference materials by adopting aqua regia digestion (for Au and Ag) and nickel sulphide fire assay followed by Te co-precipitation method (for Pt and Pd).

## Experimental

### Instrumentation

The Agilent 4100 MP-AES with 4107 Nitrogen Generator was used in this study. The operating parameters used are presented in Table 1. This relatively new and simple instrumental technique is a fast sequential multi-element analytical technique that has a microwave-induced nitrogen plasma as an excitation source and optical dispersion and detection components similar to ICP-AES. This instrument uses a microwave excitation assembly to create a concentrated axial magnetic field around a conventional torch. This focuses the microwave energy where it is needed to produce a toroidal plasma with a cooler central channel that is suitable for stable introduction of liquid samples using a conventional sample introduction system. The principle of this technique is similar to any other emission technique such as a flame emission technique or

the well-known ICP-AES<sup>12</sup>. The intensity of each emitted line will be directly proportional to the concentration of a particular element. More details of the MP-AES atomic source, optical system and detector of the instrument are provided in Hammer<sup>6</sup>.

### Precious metal geological reference materials used

Sixteen international geological reference materials were utilized in this study for the determination of Au, Ag, Pt and Pd. Table 2 presents details of each sample, such as the rock/ore type and source of these reference materials.

### Materials and reagents

Anhydrous sodium carbonate, disodium tetraborate, sulphur, stannous chloride and fine granular quartz (silica), all of AR-grade quality produced by Merck (Darmstadt, Germany), Ni powder (-100 mesh) of 99.999% purity from Aldrich Chemical Company (Milwaukee, WI, USA) and tellurium powder (-385 mesh) of 99.998% purity from Alfa-Aesar (Wardhill, MA, USA), distilled HNO<sub>3</sub> and HCl (Merck) were used for sample preparation. These high-purity reagents and acids were chosen to minimize the procedural blank values. Millipore purified water (18 MΩ) was used in all studies.

### Sample decomposition methods

*For gold and silver in ore samples:* After roasting at 650°C in a muffle furnace, 2 g each of samples was weighed into individual 100 ml Borosil glass beakers and

**Table 2.** Details of precious metal reference materials utilized in the present study, type of rock/ore and their source

Sample name	Rock type	Source
SARM-7	Precious metal ore	MINTEK, P/Bag 3015, Randburg 2125, Republic of South Africa CCRMP-CANMET-MMSL (NRCan), 555 Both Street, Ottawa, Ontario K1A 0G1, Canada
PTC-1	Sulphide	
PTM-1	Ni–Cu matte solid	-do-
WMS-1	Massive sulphide	-do-
PTC-1a	Cu–Ni–sulphide concentrate	-do-
WPR-1	Altered peridotite	-do-
S9	Gold ore	ROCKLABS LTD 161 Neilson Street, Auckland, PO Box 18-142, Auckland, New Zealand
Ox 15	Gold ore	-do-
Ox 2	Gold ore	-do-
S-6	Gold ore	-do-
S-5	Gold ore	-do-
Ox-9	Gold ore	-do-
Ox-11	Gold ore	-do-
Ox-12	Gold ore	-do-
Ox-13	Gold ore	-do-
BND 3401.01	High-grade gold	National Physical Laboratory, New Delhi <sup>23</sup>

40 ml of freshly prepared aqua regia was added to each. These were then placed onto a hot plate at 200°C. The content was reduced to 10 ml after which 20 ml of freshly prepared aqua regia was added. The solution was heated until the volume reduced to 5 ml. The final solution was filtered and made up to 100 ml and stored in HDPE bottles. A couple of reagent blanks were also prepared in the same manner. Six replicates of each sample were dissolved in each case using the above sample dissolution procedure.

*For platinum and palladium (NiS fire-assay decomposition followed by Te co-precipitation method):* Five grams of the finely powdered sample, 2 g of Ni, 1.2 g of S, 20 g of Na<sub>2</sub>CO<sub>3</sub>, 80 g of Borax, 6 g of SiO<sub>2</sub> and 1.5 g of CaF<sub>2</sub> were mixed and transferred into a fire clay crucible. Under reductive conditions, the sample was fused in a preheated furnace for 80 min at 1050°C. The melt was then quickly poured into an iron mould and allowed to cool for an hour. The NiS button was separated from the slag and crushed into small chips (> 1 mm in diameter) in an agate mortar. The NiS chips were transferred into a 250 ml beaker and dissolved with 100 ml of purified conc. HCl at 150°C over a hot plate, until the volume reduced to about 50 ml and dissolution was complete. After reducing the volume of the solution to about 50 ml, an equal amount of deionized water was added and the solution was heated to boil on a Bunsen burner. Then 2 ml of 1000 µg/ml Te was added to the completely dissolved solution, the solution was stirred and 5 ml of 20% SnCl<sub>2</sub> (freshly prepared) solution was added drop-wise. The black Te-precipitate formed was heated to coagulate at about 80–90°C for 60 min. The solution was then cooled and filtered through a 0.45 µm cellulose nitrate membrane filter paper using the Millipore vacuum filtra-

tion system, for a quantitative transfer of the platinum group elements (PGE)-containing Te-precipitate onto the filter paper. The residue was washed with 10 ml of 10% HCl and followed by washing with few millilitres of deionized water. The filter paper was transferred to a 100 ml clean, dry glass beaker and 4 ml of freshly prepared aqua regia was added. The contents were heated on a hot plate at 150 ± 10°C for 2–3 min till the PGE residue dissolved and a clear solution was obtained. The solution was transferred to a 50 ml volumetric flask and the volume was made to 50 ml with deionized water. These final solutions were immediately used for determining Pt and Pd by MP-AES. Six replicates of each sample were dissolved in each case using the above sample decomposition procedure.

### Analysis

During the analysis, the nebulizer system was washed with 1% HNO<sub>3</sub> and deionized water in that order in each case and the data on each sample/standard/blank were acquired after 60 sec of nebulization to stabilize the plasma. Procedural blanks, calibration solutions, sample solutions and reference sample solutions were analysed in that order.

### Results and discussion

Precious metal exploration studies usually involve various stages, such as reconnaissance study, detailed follow-up, anomaly delineation and target definition, resource estimation and reserve calculation. In all these stages, documenting Au, Ag, Pt and Pd distributions in a particular area and identifying anomalous high concentrations

are essential to locate and develop precious metal mine sites and to understand the dispersal of these metals in geological systems. Large numbers of rock and ore samples collected in such exploration programmes are usually analysed for these elements. Hence, the methods developed must be simple, easy, cost-effective and environmentally friendly.

Aqua regia is a 3 : 1 mixture of HCl and HNO<sub>3</sub> and is a strong oxidizing mixture that can attack Au, Ag, Pt and Pd. It can also decompose sulphides, including pyrites, arsenides, selenides and some Mo and W minerals<sup>13</sup>. Although some workers<sup>14</sup> preferred use of HF during decomposition of the sample to recover Au completely, earlier studies in our laboratory<sup>4</sup> revealed that, in a majority of the cases, significant differences are not observed in the extraction efficiency of gold when HF was added to the reaction mixture. However, there have been several reports<sup>5,15</sup> that aqua regia attack is virtually completely efficient in solubilizing Au and Ag from geological samples, particularly when the attack is made after roasting the sample at 650°C. It is also possible to vary the sample size from 2 g up to 20–50 g depending on the sample homogeneity, target elements and their expected concentrations. Since all the gold reference materials used in this study are well-homogenized samples, 2 g sample size and only aqua regia attack were preferred.

Although both lead and NiS fire-assay methods for the determination of Au, Pt and Pd are probably the most reliable methods of separation and pre-concentration sample preparation for analysis of most geological materials<sup>16–18</sup>, only NiS fire assay was chosen in this study for the determination of Pt and Pd. As all the samples taken in this present study are well-known PGE reference materials, sample homogeneity was ensured, and hence, 5 g sample size was used for the NiS fire-assay procedure. Because of the heterogeneous distribution of PGE in various types of rocks and ores, separation and pre-concentration of these elements by the NiS fire-assay technique is best suited as it can handle larger amounts of sample (5–50 g). The Te co-precipitation step enhances the recovery of PGE.

#### *Spectral interferences, calibration strategies and linearity and results*

Spectral line interferences in emission spectrometry can severely affect the accuracy of minor and trace element determinations, particularly in geological samples because of their complex nature. For all elements in this study, the most sensitive wavelengths in each case were utilized. In general, the interference effects from adjacent lines can be minimized by using a high-resolution spectrometer in the instrument, decreasing the width of the slits or using higher spectral orders. A high-resolution spectrometer (resolution <0.035 nm) has a definite advan-

tage for the analysis of spectrally complex materials. However, there is a practical limit to the resolution that can be achieved. This is determined by the natural line widths and the extent of broadening. Furthermore, even with a high-resolution monochromator, there may not be sensitive lines free from spectral interferences that can be used for trace element determinations in complex materials<sup>19</sup>. The analytical wavelengths for all four elements in this study and possible interfering lines of other elements present in the sample solutions are presented in Table 3. With the sample preparation procedures followed in the present study, such interference effects were found to be negligible. For example, Figure 1 presents the possible interferences on Pd analytical wavelength (363.470 nm). Possible line interferences from other concomitant elements are also depicted. As only tellurium and other PGE are expected to be present in the solutions, the expected interference effects from other elements (shown in Figure 1) are found to be negligible in this particular case.

The concentration or working range of an analytical technique is the range of concentration that can be measured accurately without the need to recalibrate or dilute the sample. In order to overcome matrix effects that are generally observed during the analysis of geological samples by a number of instrumental analytical techniques, several methods can be used. Dilution of the sample, use of internal standardization and matrix-matching calibration standards are some of the procedures generally adopted for obtaining precise and accurate data. In the present study, external calibration was performed using solutions of identically prepared international precious metal reference materials (Figure 2) to minimize possible matrix and other interference effects. Out of the reference materials studied here, a few were selected to cover the entire working range for calibration of all four elements in each case (Figure 2). This approach is beneficial in several ways. First, because the dilution factor is the same for all solutions in each case, the absolute (rock) concentration values for each element can be used for calibration so that quantification becomes straightforward for unknown samples. A second advantage is that, the possible errors arising due to dilution will be minimal. This approach also minimizes the possible inter-elemental and matrix (spectral and non-spectral) interferences. The calibration graphs shown in Figure 2 are linear in the concentration ranges of these studies for all four analytes. The linearity in the calibration curves in all cases was found to be better than flame AAS in general. In addition, AAS, MP-AES has the capability to do fast sequential measurement of different elements making it one of the rapid analytical techniques currently available to the exploration geochemists.

Au and Ag determined in 10 international gold reference materials, and Pt and Pd determined in 5 PGE international reference materials are presented in Tables 4

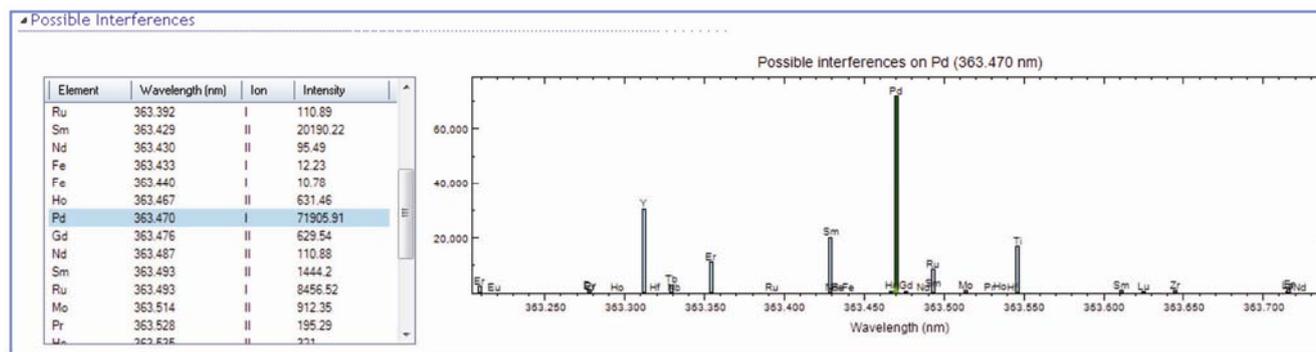


Figure 1. Possible interferences on Pd line (363.470 nm). Resolution <0.05 nm.

Table 3. Possible interferences for Au, Ag, Pt and Pd by MP-AES (resolution < 0.050 nm)

Analyte	Wavelength (nm)	Interference effects by different elements
Au	267.595	Nb: 267.594 nm; Ta: 267.590 nm; Cr: 267.715 nm
Ag	328.068	Rh: 328.055 nm; Sc: 328.078 nm
Pt	265.945	Ta: 265.941 nm; Ru: 265.962 nm
Pd	363.470	Ho: 363.467 nm; Gd: 363.476 nm; Fe: 363.440 nm

Table 4. Concentration ( $\mu\text{g/g}$ ) of gold in some international geological reference materials determined by MP-AES after aqua regia digestion

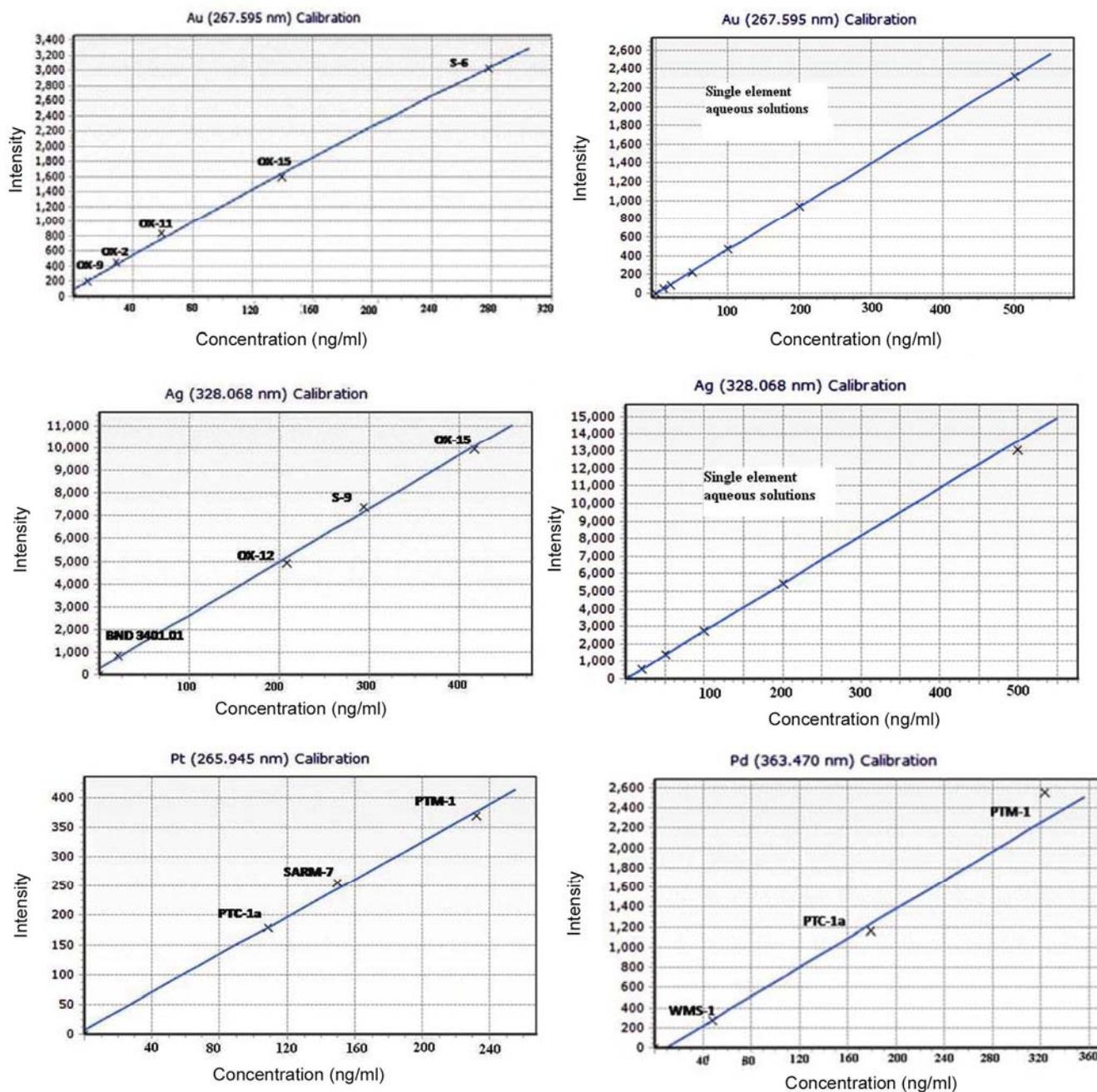
Sample	Au ( $\mu\text{g/g}$ )					Ag ( $\mu\text{g/g}$ )			
	This study				Average % RSD	This study			Average % RSD
	CAL 1	CAL 2	DIBK-F-AAS <sup>20</sup>	RV <sup>+</sup>		CAL 1	CAL 2	RV <sup>+</sup>	
S9	5.62	5.82	–	5.23	1.3	14.73	15.2	14.72	1.7
Ox-15	6.68	6.87	–	6.98	0.9	20.26	20.08	20.86	2.3
Ox-2	1.84	2.02	1.40	1.42	3.8	BDL	BDL	NA	–
S-6	13.6	13.55	–	13.89	0.5	17.37	17.10	17.08	1.7
S-5	5.30	5.51	–	5.00	1.4	9.49	9.24	NA	1.4
Ox-9	0.52	0.45	0.48	0.46	5.1	BDL	BDL	NA	–
Ox-11	3.17	3.47	2.92	2.94	1.4	8.91	9.19	NA	0.7
Ox-12	6.07	6.44	6.59	6.60	1.3	9.69	10.07	10.40	0.8
Ox-13	1.85	2.11	–	1.77	3.6	BDL	BDL	NA	–
BND 3401.01 (ref. 23)	12.49	12.63	12.22	12.10	0.8	1.08	1.07	1	3.1

$n = 6$ ; <sup>+</sup>Certificates of analysis issued by ROCKLABS, New Zealand; <sup>-</sup>Not available. CAL1 – Against matrix matching calibration standards; BDL – Below detection limit; CAL2 – Against aqueous calibration standards; NA – not available.

and 5 in comparison with certified data. Au and Ag results obtained in these studies (Table 4) demonstrate that MP-AES is a powerful analytical technique which allows fast and direct measurement of these elements without the need for adopting any separation or pre-concentration procedures. In general, the MP-AES data for these two elements compare well with reference values, wherever values are available for comparison. The values obtained for Pt and Pd in some of the international PGE reference samples (Table 5) compare favourably with reported values proving that MP-AES is an extremely valuable technique for the detection and determination of Pt and Pd in rocks and ores after separating and pre-concentrating these elements from the rock matrix by NiS and

Te co-precipitation methods. The data for Pt and Pd also compared favourably with those generated by a well-established NiS fire-assay ICP-MS technique (Table 5). These results for Pt and Pd suggest that MP-AES when combined with NiS fire assay can also generate data of sufficient quality for exploration studies.

Another important aspect is that there is an excellent agreement of the data obtained using simple aqueous single-element calibration curves for both Au and Ag with certified data (Table 4). The data obtained thus for these two elements also match with those obtained by calibrating with certified reference materials (Table 4). For Au, the data generated by this method also compare favourably well with the established DIBK-F-AAS procedure<sup>20</sup>.



**Figure 2.** Calibration curves for Au (aqueous and matrix), Ag (aqueous and matrix), Pt (matrix) and Pd (matrix) constructed by analysing reference materials of different concentrations.

This proves that the matrix effects are minimal or negligible in the MP-AES technique, at least with respect to Au and Ag in geological samples. On the other hand, such agreement was not obtained in the case of Pt and Pd. More studies are needed in this direction for a comprehensive understanding. One of the principles of all geoscientific research is that, sufficient details should be provided in any research publication that will allow an independent investigator working in an independent laboratory to replicate and confirm any published mea-

surement<sup>21</sup>. Our reported results here conform to this requirement.

*Accuracy, precision and detection limits*

The variation for the mean of three separate dissolutions run in duplicate (each element determined six times) is indicated in Tables 4 and 5. Overall, precisions < 5% RSD with comparable accuracies were obtained for most

**Table 5.** Concentration ( $\mu\text{g/g}$ ) of Pt and Pd in international platinum group element geological reference materials determined by MP-AES after NiS fire assay-Te co-precipitation separation and pre-concentration method

Sample	Pt ( $\mu\text{g/g}$ )				Pd ( $\mu\text{g/g}$ )			
	This study	NiS-ICP-MS method <sup>18</sup>	RV	% RSD	This study	NiS-ICP-MS method <sup>18</sup>	RV	% RSD
WMS-1	1.99	–	1.74	0.54	1.19	–	1.19	1.82
PTC-1A	2.98	–	2.72 $\pm$ 0.11	4.32	4.13	–	4.48	0.85
PTM-1	5.83	–	5.8	4.86	8.29	–	8.1	0.44
SARM-7	3.84	3.81	3.74 $\pm$ 0.05	2.15	1.64	1.55	1.53	1.26
WPR-1	2.81	2.76	2.85 $\pm$ 0.12	0.52	2.41	2.45	2.35 $\pm$ 0.09	1.11
PTC-1	2.83	–	3	0.25	12.98	–	12.7	1.16

$n = 6$ ; RV, Certified values from GEOREM (<http://georem.mpch-mainz.gwdg.de>); –, Not available.

**Table 6.** Detection limits in solution ( $\text{ng/ml}$ ) for Au, Ag, Pt and Pd by MP-AES in comparison with other well-established contemporary analytical techniques

Analyte	Wavelength (nm)	Detection limits ( $\text{ng/ml}$ )					
		MP-AES (This study)	F-AAS <sup>17</sup>	GF-AAS <sup>3</sup>	ICP-AES <sup>16,24</sup>	ICP-MS <sup>18</sup>	HR-ICP-MS <sup>25</sup>
Au	267.595	1.82	20	0.03	6	0.010	0.0012
Ag	328.068	0.5	10	–	2	0.020	0.028
Pt	265.945	5	100	0.6	30	0.004	0.054
Pd	363.470	1.9	20	0.3	44	0.010	0.00640

determinations. However, precision was highly dependent on the absolute concentration in the material. Determinations made close to the MP-AES detection limit gave the poorest precision, as in the case of Ox-9, for example, in Table 4. More consistent results were obtained for elements at relatively higher concentration levels, with many yielding RSDs much better than  $\pm 2\%$ . This range of precisions is expected many times in the determination of Au, Ag, Pt and Pd, because of the heterogeneity effects in their distribution in natural materials and also due to possible insufficient recoveries of Pt and Pd in the NiS bead and the follow-up solution chemistry procedure.

In general, determination of precious metals in geological samples is a challenging task because of the extremely low concentration levels ( $\text{ng/g}$  or  $\text{pg/g}$ ) of these elements, varied and complex geological matrices and their heterogeneous distribution. Extremely sensitive analytical techniques, which can offer very low limits of detection (LODs), are required to detect and accurately determine these elements in a variety of geological materials. LODs are a measure of instrument performance. Comparative detection limits are presented in Table 6. Undoubtedly, high-resolution ICP-MS (HR-ICP-MS) is the most sensitive analytical technique available today. The detection limits for all precious metals studied by MP-AES here are found to be in the 0.5–5  $\text{ng/ml}$  range. During the last four decades, AAS was the leading analytical technique, especially for Au and to a lesser extent for Pt and Pd analysis. The classical lead fire-assay col-

lection technique in association with F-AAS is normally the method used to determine these elements for the evaluation of ore-grade material<sup>6,17</sup>, but the method cannot offer the required sensitivity for these elements, due to interference effects of PGE with each other. Besides AAS methods, colorimetric and titrimetric methods were also in use during this period. Instrumental neutron activation analysis (INAA) is capable of detecting Au directly in solid samples at  $\text{ng/g}$  levels, but is not sensitive enough for similar measurements of Pt and Pd. Though INAA offers very low detection limits, it requires regular access to a nuclear reactor. It is not suitable for routine analysis, but it is particularly useful for checking other methods. Its contribution to the exploration studies is limited because usually it cannot handle large volumes of samples. ICP-AES methods are also characterized by lower sensitivity and prone to interference effects, particularly from transition metal lines for the determination of precious metals in geological materials. However, these effects can be successfully overcome by the selection of alternative analytical lines and/or adopting matrix separation procedures<sup>22</sup>. This technique enabled accurate PGE determinations at relatively higher concentration levels in geological materials. However, during the last three decades, INAA, GF-AAS and ICP-MS have proved to be sufficiently sensitive for the determination of noble metals at geochemical background levels. In general, methods based on GF-AAS, ICP-AES, INAA and ICP-MS have proved to be reliable and efficient for the de-

termination of ng/g– $\mu$ g/g level concentrations of precious metals as a matter of routine on the very large number of samples collected during any exploration programme. The present study proves that the MP-AES technique possesses the required sensitivity together with accuracy for the analysis of rock and ore samples in precious metal exploration studies. This technique also compares favourably with other well-proven techniques such as F-AAS, GF-AAS and ICP-AES for the determination of precious metals because it offers the required sensitivity, minimal interferences and is also simple and relatively inexpensive.

## Conclusion

This study considers the importance of choosing proper sample decomposition, separation and pre-concentration methods before the application of an instrumental analytical technique for the detection and determination of Au, Ag, Pt and Pd in rock and ore samples. MP-AES is relatively a new analytical technique; the commercial instruments were released only in 2011. This study of precise determination of Au, Ag, Pt and Pd at sub- $\mu$ g/g levels in rock and ore materials (ng/ml in sample solutions) at the required accuracy and precision levels demonstrates the potential of this technique for precious metal exploration studies. Matrix effects were found to be minimal in the determination of Au and Ag in rocks and ore samples by the MP-AES technique. Also, the results obtained by MP-AES in this study compared well with those of the established techniques such as F-AAS and ICP-MS. Since the instrument uses a microwave-induced nitrogen plasma as an excitation source, running costs are significantly reduced as only nitrogen is required for plasma operation. This instrument also offers low-cost elemental analysis with improved laboratory safety as no gas cylinders are required as a nitrogen generator with air compressor can be used instead of a nitrogen cylinder for generating the nitrogen plasma. MP-AES is an ideal instrumental analytical technique for any elemental analysis in the laboratory, especially in remote sites and mobile laboratories where regular supply of different gases such as acetylene, nitrous oxide and argon is expensive and problematic, particularly in remote areas. Finally, this study reveals that MP-AES is a good addition to the already existing array of established analytical techniques for an analytical chemistry laboratory. Compared to flame AAS, this technique provides improved linear dynamic range, superior detection limits and fast sequential measurement. Using the sample preparation procedures described in this study and MP-AES, a large number of rock and ore samples can be analysed easily and quickly in a limited time required in any precious metal exploration programme. Further detailed studies in this direction, particularly the inter-elemental interference

and other matrix effects are necessary to understand the complete potential of this technique.

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