JAAS
Journal of Analytical Atomic Spectrometry

Determination of platinum group elements and gold in geological materials using an ultraviolet laser ablation high-resolution inductively coupled plasma mass spectrometric technique†

Elisa K. Shibuya[a], Jorge E. S. Sarkis*[a], Jacinta Enzweiler[b], Alexandre P. S. Jorge[b] and Ana Maria G. Figueiredo[a]

[a]*Instituto de Pesquisas Energéticas e Nucleares IPEN/CNEN, Caixa Postal 11049, CEP 05508—900—São Paulo, SP, Brazil*
[b]*Universidade Estadual de Campinas—Instituto de Geociências, Campinas-SP, PO Box 6152, CEP 13083—970, Brazil*

In this work, a UV laser system coupled to high-resolution ICP-MS was used in the determination of platinum group elements (PGE) and gold in nickel sulfide buttons prepared by the fire assay technique. A Nd : YAG laser operating at 266 nm quadrupled frequency was used. The laser operating parameters were established by studying signal intensity and the precision for different energy beams and frequencies. The *F*-test was used to evaluate the homogeneity of the buttons, demonstrating that for most elements the distribution is homogeneous. The analyses were performed on three different sites in three replicates of the materials. The detection limits obtained (3σ) were in a range from 0.2 for Os (and Ir) to 7 ng g^{-1} for Pt. The accuracy of the results was better than 16.7% for most elements. The effects of isobaric interference on the ^{103}Rh signal ($^{206}Pb^{2+}$ and $^{40}Ar^{63}Cu^{+}$) were evaluated by analysing NiS buttons doped with lead and copper. For Au, Pt and Pd, the standard deviations obtained were higher than expected and are related to a non-homogeneous distribution of these elements in the buttons. The concentrations of the elements in the geological reference materials UMT-1 and WPR-1 were obtained by external calibration curves.

Keywords: *Laser ablation; inductively coupled plasma mass spectrometry; fire assay; platinum group element; gold*

The economic and geological importance of the platinum group elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt) and gold have led to considerable interest being given to developing reliable analytical methods to quantify them in natural samples. The natural abundance of PGEs and Au is very low (ng g^{-1} or sub-ng g^{-1}) and in general they occur in separate mineral phases which tend to be distributed heterogeneously in geological samples. Among the analytical procedures developed to determine the PGEs and Au in geological samples, fire assay with nickel sulfide[1] followed by an analytical detection technique with high sensitivity is one of the most accepted. For the fire assay, the sample (from 10 up to 50 g) is mixed with fluxes, nickel and sulfur in a fire clay crucible and fused at temperatures of around 1000 °C. During the fusion, the PGEs and Au present in the sample are collected by the nickel sulfide that is formed and deposited in the bottom of the crucible.

Nowadays, the most useful analytical detection techniques for the determination of these elements in pre-concentrated buttons are neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS) and, sometimes, inductively coupled plasma atomic emission spectrometry (ICP-AES). NAA is a very sensitive and versatile multi-element technique, allowing analysis of solid[2] or liquid[3] samples. However, in the case of NiS buttons, the mass of the collector material must be lower than 0.5 g, since Ni provides high background activity on irradiation, causing problems related with the reproducibility.[2] In addition, it is a very expensive and time consuming technique.

Plasma spectrometry has been widely employed for the major and trace element analysis of several types of geological materials. ICP-MS achieves better detection limits and is more sensitive than ICP-AES, being more suitable for trace analysis. In both cases, the most common method for sample introduction is the nebulization of a solution by means of a pneumatic or ultrasonic nebulizer, requiring the digestion of the sample. Owing to the usually high insolubility of geological materials, dissolution procedures become one of the most time consuming and complex steps of analytical method.

The main methods employed for the total digestion of the sample are open acid digestion, alkali fusion and microwave digestion.[4] They have been discussed and evaluated in a review by Totland *et al.*[5] During these procedures, the sample may be contaminated and can have the composition changed by losses of some of the volatile elements. Slurry nebulization can also be used.[6] The main difficulty with this method is the introduction of a representative amount of the sample into the plasma. The PGEs and Au do not have a homogeneous distribution along the geological matrix and, as a consequence, this heterogeneity can increase the detection limits. Therefore, it is desirable to avoid such procedures by using direct measurement techniques.

In recent years, the laser ablation technique coupled with an inductively coupled plasma mass spectrometer (LA-ICP-MS) has been developed as a powerful tool for the direct analysis of solid samples.[7–10] This technique allows a faster and simpler determination of major and trace elements, avoiding some of the polyatomic ion interferences of oxides and hydrides, which are undesirable and often result from wet analyses. It can also provide bulk analysis or analysis with high spatial resolution.

Jarvis *et al.*[11] used an IR laser (1064 nm) coupled with a quadrupole ICP-MS to analyse some PGE reference samples. They showed that the technique could give satisfactory results, but the detection limits (10–90 ng g^{-1}) were relatively high. The sensitivity values obtained were in a range between 234 and 690 counts s^{-1} μg^{-1} g. Compared with IR, the UV beam from a Nd : YAG laser, operating at a quadrupled frequency (266 nm) is more strongly absorbed by materials. The UV laser removes a larger amount of material, providing lower detection limits and a better spatial resolution than the IR laser system.[12]

In the present work, the use of a UV laser coupled with a high-resolution inductively coupled plasma mass spectrometer (LA-HR-ICP-MS) will be described for the determination of PGEs and Au in some reference materials prepared using the fire assay technique.

†Presented at the 1998 Winter Conference on Plasma Spectrochemistry, Scottsdale, AZ, USA, January 5–10, 1998.

EXPERIMENTAL

Sample preparation

The PGEs and Au in UMT-1 and WPR-1 (Canmet, Canada) reference materials were pre-concentrated by a fire assay technique using nickel sulfide as the collector in three replicate buttons. This method consists of a dry fusion in a fire clay crucible (950 °C for 30 min and 1050 °C for a further 30 min) of 15 g of material with a mixture of 10 g of sodium carbonate, 20 g of sodium tetrahydroborate(III), 1 g of nickel powder (INCO) and 0.75 g of purified sulfur (Merck). The crucibles were left in the furnace and allowed to cool overnight. After removing from the furnace, the crucibles were broken, the buttons were retrieved and weighed and the upper and lower surfaces were polished on a diamond lap.

The synthetic standards were prepared by the same method, doping quartz (analytical-reagent grade, Merck) with PGE and Au standard solutions (Spectre, ALFA AESAR). Blank buttons were prepared by using quartz only.

To evaluate the isobaric interference for Rh, three buttons with Cu and one button with Pb were prepared by the same technique, using ALFA AESAR (Johnson-Matthey) reagents.

Instrumentation

In this work UV Nd:YAG laser ablation (LUV 266 Gen3, Merchantek) coupled to an HR-ICP-MS instrument, Element, Finnigan MAT, was used.

The laser operates in a Q-switched mode ($t = 4$ ns) and is quadrupled frequency at 266 nm, producing shallow craters with uniform depth, as a consequence of a multi-mode laser output, which provides a relatively flat beam, rather than TEM_{00} distribution. The *xyz* movement of the sample chamber has an automated control system with 0.25 μm resolution. Laser beam parameters can be adjusted as shown in Table 1.

The ICP-MS consists basically of a plasma ion source (load coil), an interface (cones, skimmer and ion lenses), a mass analyser and a detector system. The Element analyser system consists of an entrance slit, a magnetic sector and an electrostatic analyser (Nier–Johnson reverse geometry) and an exit slit. It can be operated in three resolutions modes ($m/\Delta m$) of 300, 3000 and 7500. The ablated material is carried from the sample chamber to the plasma torch by an argon gas flow. Then it is atomised, ionised and introduced into the interface, where the ion beam is focused and introduced into the analyser system by the entrance slit. The magnetic field guides the incoming ions on circular paths, separating them as a function of their m/z rate. The ESA sector is an ion optical focusing element and, in combination with the magnetic sector, provides the double focusing. Finally, the ion beam is detected by using a conversion dynode and secondary electron multiplier (SEM), which can be operated in analog or counting mode.

Optimisation of LA-HR-ICP-MS system

(a) Operating parameters

The laser–material interaction depends directly on the thermal and optical properties of the material.[13] Thus, previous evaluation of the analytical conditions is necessary for each element in every type of material.[14]

In order to obtain stable signals with better statistics, a laser beam with an energy of 2.5 mJ on the target and a crater with a diameter of around 200 μm were used. The precision was improved by varying the frequency, as shown in the Fig. 1. The best value was obtained with a frequency of 10 Hz. The main parameters used are listed in Table 2.

In order to verify the reproducibility of the craters produced by the laser beam in the buttons, a scanning electron microscope (SEM XL30-Philips) and rugositymeter (Alpha Step 200, Tencor) were used.

(b) Material transport system

A laser is a pulsed vaporisation source. As a consequence, the amount of ablated material may change during the analysis, increasing the relative standard deviation (RSD) of the measurements.[15] In order to evaluate this effect, the signal stability was studied by using two different conditions: (*i*) direct connection of the sample chamber to the ICP by a sample gas tube, providing a mean precision around 25%; and (*ii*) the system described previously was coupled to the mass spectrometer through the spray chamber, used as an expansion chamber, this configuration provided the most stable signal, with a mean fluctuation of around 8%.

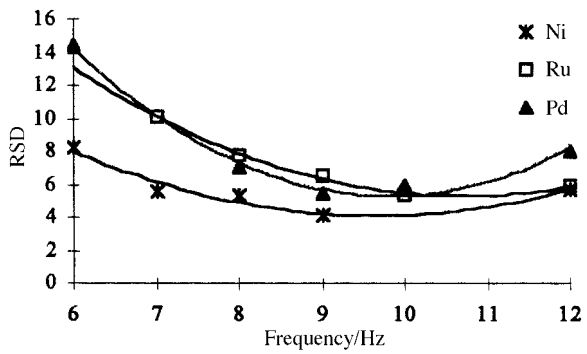

Fig. 1 RSD behaviour as a function of incidence laser frequency (laser energy = 2.5 mJ) in NiS standard button (concentration = 1.098 μg g^{-1}).

Table 1 Operating range of target laser beam parameters

	Range	
Laser parameter	Minimum	Maximum
Energy/mJ	0.01	4.00
Frequency/Hz	1.0	20.0
Spot size/μm	5	300

Table 2 Mass spectrometer and laser system operating parameters, selected by evaluating sensitivity and relative standard deviation of signal

(a) *Mass spectrometer*—	
Resolution	300
Outer gas flow	14.0 l min^{-1}
Aerosol carrier gas flow	0.96 l min^{-1}
Plasma power (rf)	1300 W
Intermediate gas	0.82 l min^{-1}
Scan mode	Escan
SEM mode (PGE, Au)	Counting
SEM mode (^{61}Ni)	Analog
Take-up time	60 s
Number of scans	60 (10 × 6)
Acquisition time	Around 300 s
(b) *Laser operating parameters*—	
Laser type	Nd:YAG
Frequency	266 nm
Operating mode	Q-switched
Energy on target	2.5 mJ
Diameter on target	200 μm
Frequency	10 Hz
Pulse duration	4 ns

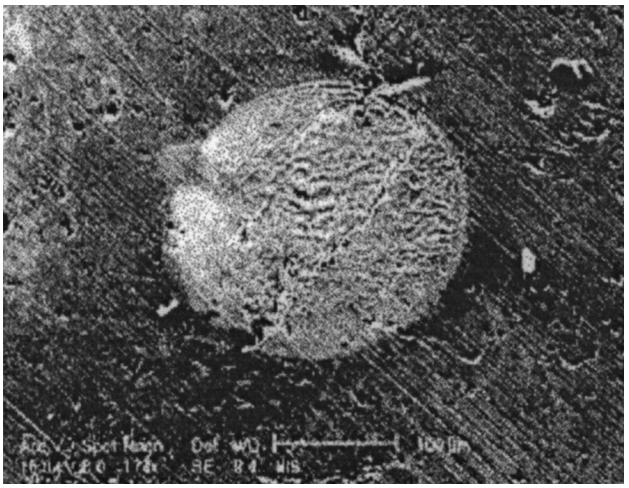

Fig. 2 Crater produced by single shot laser beam on the surface of an NiS button.

RESULTS AND DISCUSSION

Shown in Fig. 2 is one crater produced under the experimental conditions listed in Table 2(*b*) (single shot). As can be observed, the damage on the surface is minimal with a very superficial, circular and homogeneous ablation. The reproducibility of the craters was better than 5%. The values obtained, for 4 min ablation, were 177 ± 7 μm diameter and 80 ± 3 μm depth. The most common spectroscopic interferences that occur in ICP-MS are isobaric overlap, doubly charged ions and polyatomic ion interferences. Thus, prior to analysis, the existence of any of these interferences must be evaluated for each isotope to be measured.

In the present work, it was observed that the presence of Pb and Cu could introduce isobaric overlap on ^{103}Rh, affecting the accuracy of the results. In addition, ^{63}Cu can form ^{40}Ar^{63}Cu^{+} with ^{40}Ar and ^{206}Pb can form doubly charged ions. As Pb has the second ionisation potential lower than the first ionisation energy of Ar (16 eV),[16] this can occur to a significant degree. These effects were verified by analysing buttons containing only these elements. An interference of about 30% was observed in the intensities of Rh. This allowed the correction of the final Rh concentration values.

The homogeneity of PGEs and Au in the polished surface of an NiS matrix was verified by using the *F*-test.[17] For this purpose, two buttons of UMT-1 were ablated at ten different sites, randomly chosen. The critical *F*-value calculated was 1.986 with a 95% confidence interval. The results are presented in the Fig. 3. It can be observed that, except for Au, the buttons can be considered to be relatively homogeneous. Thus, the analyses were performed at three different sites on each button.

The calibration curves were obtained by analysing nine multi-element buttons at the following concentrations: 0.086, 0.188, 0.502, 0.68, 0.928, 1.082, 1.098, 4.02 and 5.16 μg g^{-1} (for Os, owing to the low concentration in the analysed samples, the calibration curve was prepared with seven standards of up to only 1.098 μg g^{-1}).

To correct signal fluctuations ^{61}Ni was used as an internal standard.[11] The signal variation during acquisition of the results is shown in Fig. 4. The same behaviour for all elements is verified, denoting that ^{61}Ni is a good internal standard for these isotopes.

The detection limits (3σ),[18] related to the original samples, were calculated considering six replicates in the blank button and are listed in Table 3. The sensitivity for the analytes are also presented in Table 3 and refer to pre-concentrated samples. The concentration values obtained for the analysed reference materials are listed in Table 4. They represent a mean value for three different analyses in buttons 1, 2 and 3 ($n=9$). The results are in good agreement with the recommended values for most elements. For Au, Pd and Pt, the concentration values show good accuracy but a high standard deviation due, mainly, to the non-uniform distribution observed on the surface of the button. This indicates that the behaviour of these elements, during the sample preparation method, should be evaluated. Despite this, the accuracy for these elements is better than 16.7% (Au for WPR-1).

In the UMT-1 reference material, the accuracy was better than 13.7%. In the WPR-1, the concentration obtained for Os

Table 3 Detection limits related to the original samples

Element	Detection limit/ ng g^{-1}	Sensitivity*/ counts s^{-1} μg^{-1} g
Ru	3.5	551.1
Rh	0.3	4032.0
Pd	1.4	1111.4
Os	0.2	1799.9
Ir	0.2	6491.9
Pt	7	2033.4
Au	0.7	6002.5

* Refers to the sensitivity in the NiS button.

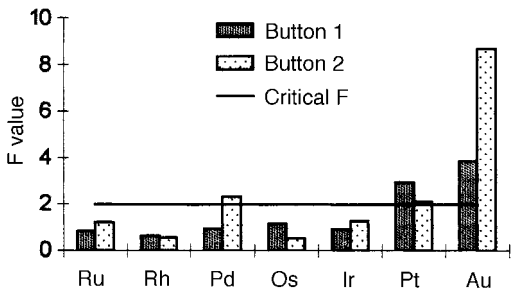

Fig. 3 *F*-values obtained ($n=10$; $k=10$) to evaluate the superficial distributions of elements. Pt and Au presented a non-homogeneous distribution along the surface. For Pd, button 2 presented some heterogeneity.

Table 4 Mean concentration values and standard deviations (1σ) in ng g^{-1} of PGEs and Au in original UMT-1 and WPR-1 reference material, considering three replicated buttons ($n=9$). The Rh concentration values were corrected for interferences

	UMT-1		WPR-1	
Element	Obtained	Recommended	Obtained	Recommended
Ru	10.7 ± 1.4	10.9 ± 1.5	20.5 ± 3.8	22 ± 4
Rh	8.5 ± 0.9	9.5 ± 1.1	13.7 ± 0.9	13.4 ± 0.9
Pd	108 ± 14	106 ± 3	249 ± 42	235 ± 9
Os	6.9 ± 0.7	(8)	17.1 ± 1.6	(13)
Ir	9.0 ± 0.8	8.8 ± 0.6	15.6 ± 1.2	13.5 ± 1.8
Pt	140 ± 30	129 ± 5	325 ± 30	285 ± 12
Au	50 ± 21	48 ± 2	49 ± 16	42 ± 3

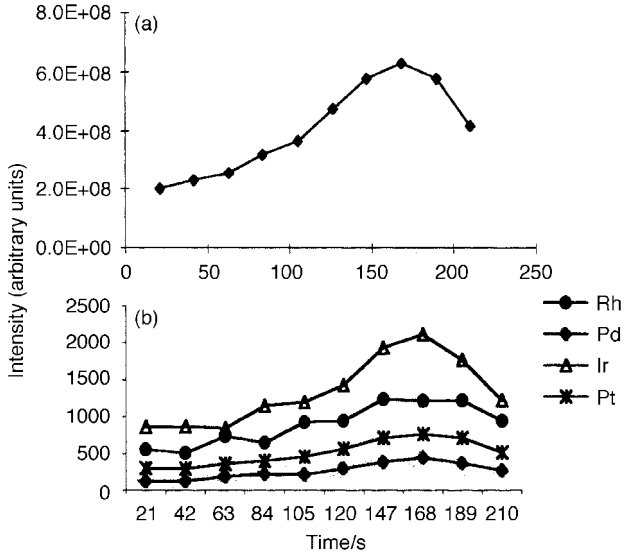

Fig. 4 (a) Behaviour of internal standard (^{61}Ni) during analysis. In this experiment, the acquisition time was around 3.5 min. These measurements refer to an NiS standard button (concentration = 0.188 μg g^{-1}). (b) Signal behaviour of Rh, Pd, Ir and Pt during ablation.

was 31.5% higher than recommended, and better than 16.7% for the other elements.

CONCLUSIONS

The UV laser ablation HR-ICP-MS technique seems to be a very promising analytical tool for the determination of PGEs and Au in geological materials. It presents better results than IR laser ablation quadrupole ICP-MS,[11] achieving higher sensitivity and better detection limits.

In the present work, the use of external calibrations with synthetic standards enables reliable results to be obtained. This procedure also presents the following advantages in relation to the calibration performed using reference materials: the standards can be prepared at a pre-determined concentration range; all standards consist of the same elements, avoiding interference from different isotopes; and it overcomes the difficulties related to the lack of reference materials.

The authors are grateful to FAPESP, FINEP, CAPES and CNPq for financial support.

REFERENCES

1 Asif, M., and Parry, S. J., *Mineral. Petrol.*, 1990, **42**, 321.
2 Jackson, S. E., Fryer, B. J., Goose, W., Healey, D. C., Longerich, H. P., and Strong, D. F., *Chem. Geol.*, 1990, **83**, 119.
3 Asif, M., Parry, S. J., and Malik, H., *Analyst*, 1992, **117**, 1351.
4 Totland, M., Jarvis, I., and Jarvis, K., *Chem. Geol.*, 1995, **124**, 21.
5 Totland, M., Jarvis, I., and Jarvis, K., *Chem. Geol.*, 1992, **95**, 35.
6 Totland, M., Jarvis, I., and Jarvis, K. E., *Chem. Geol.*, 1993, **104**, 175.
7 Gray, A. L., *Analyst*, 1985, **110**, 551.
8 Russo, R. E., *Appl. Spectrosc.*, 1995, **49**, 14A.
9 Longerich, H., Jackson, S., Fryer, B. J., and Strong, D., *Geosci. Can.*, 1992, **20**, 21.
10 Chen, Z., Doherty, W., and Grégoire, D. C., *J. Anal. At. Spectrom.*, 1997, **12**, 653.
11 Jarvis, K., Williams, J. G., Parry, S. J., and Bertalan, E., *Chem. Geol.*, 1995, **124**, 37.
12 Jeffries, T. E., Perkins, W. T., and Pearce, N. J. G., *Analyst*, 1995, **120**, 1365.
13 Moenke-Blankenburg, L., in *Laser Microanalysis*, ed. Winefordner, J. D., and Kolthoff, I. M., Wiley-Interscience, New York, 1989, pp. 37–38.
14 Cromwell, E. F., and Arrowsmith, P., *Appl. Spectrosc.*, 1995, **49**, 1652.
15 Miller, J. C., *Laser Ablation—Principles and Applications*, Springer-Verlag, New York, 1994, pp. 167–172.
16 Jarvis, K. E., Gray, A. L., and Houk, R. S., in *Handbook of ICP-MS*, Chapman and Hall, New York, 1992, ch. 5, pp. 125–144.
17 McCormick, D., and Roach, A., *Measurements, Statistics and Computation*, ed. Chapman, N. B., John Wiley, London, 1987, pp. 310–319.
18 Analytical Methods Comittee, *Analyst*, 1987, **112**, 199.

Paper 8/01477I
Received February 20, 1998
Accepted May 18, 1998