Journal of Radioanalytical and Nuclear Chemistry, Vol. 244, No. 3 (2000) 623–625

NAA and UV laser ablation ICP-MS for platinum group elements and gold determination in NiS fire assay buttons: A comparison between two methods

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(Received November 22, 1999)

NAA and UV laser ablation ICP-MS were used to determine platinum group elements (PGEs) and gold in the geological reference materials UMT-1, WPR-1, WMG-1, GPT-4 and GPt-6, after NiS fire assay. Both methods presented results were good agreement with the recommended values. NAA gave more accurate values for Ir (relative errors between 0 to 9%) and UV-LA-ICP-MS presented better results for Pt (relative errors less than 12%, except for WPR-1). UV-LA-ICP-MS showed better sensitivity than NAA for Pd and Os. On the other hand, NAA showed lower detection limits for Ir and Au. Advantages and disadvantages of each method are discussed.

Introduction

The natural abundance of PGE (ruthenium, rhodium, palladium, osmium, iridium, platinum) and gold is very low (ng·g^{-1} or sub ng·g^{-1}) and the usual methods for the determination of these elements in geological samples consist of a pre-concentration procedure followed by detection using a high sensitive analytical technique. The nickel sulfide fire assay, used as a collector to concentrate all noble metals, is a classical pre-concentration method, due to the possibility of using large samples, eliminating problems of heterogeneous distribution in geological matrices.[1] Neutron activation analysis (NAA) was one of the first analytical techniques to provide PGE determination in geological samples at ng·g^{-1} levels,[2] but presents the disadvantage of requiring small quantities of the sample (up to 500 mg). The association of fire assay with NiS and NAA is a solution to this problem. After the fire assay, the NiS button is dissolved in concentrated hydrochloric acid, the solution is filtered and the filter is directly irradiated with neutrons. The direct analysis of the NiS button by NAA has been described,[3] but with a significant loss in sensitivity. In more recent years, laser ablation ICP-MS has been used as a mean of analyzing the NiS buttons directly, with the main advantage of avoiding problems of contamination and losses during dissolution.[4]

In the present paper, NAA after NiS fire assay was used to determine PGE and gold in the geological reference materials UMT-1 (ultramafic ore), WPR-1 (altered peridotite) and WMG-1 (mineralized gabbro), provided by Canadian Certified Reference Material Project, CCRMP, Canada, and GPt-4 and GPt-6 (pyroxene peridotite), provided by the Institute of Geophysical and Geochemical Exploration, IGGE, China. The results obtained were compared with previous works,[5,6] where PGE and gold were determined in the same reference materials, after NiS fire assay, by UV laser ablation ICP-MS. Accuracy, precision, detection limits, advantages and disadvantages of each method are discussed.

Experimental

Fire assay

NiS buttons were prepared by mixing thoroughly the sample (10–15 g) with the fusion mixture, consisting of 10 g of sodium carbonate (anhydrous extra pure, Merck), 20 g of sodium tetraborate (anhydrous GR, Merck), 1 g of nickel powder (INCO Metals) and 0.75 g of purified sulfur (Merck). The mixture was transferred into a fire clay crucible and fused at 950 °C for 30 minutes, and for another 30 minutes at 1050 °C. After cooling, the crucible was broken, and the NiS button was retrieved and weighed.

For NAA, the NiS buttons were crushed and dissolved in 20 ml of concentrated hydrochloric acid (analytical grade, Merck), at 85–90 °C. The resulting solution was filtered through a Millipore filter (HAW 04700, 0.45 μm) and the precipitate was rinsed with deionized water. The filters containing the PGEs and Au were dried in a desiccator and packed in polyethylene vials.

LA-ICP-MS

A UV Nd:YAG laser ablation system (LUV 266 Gen3, Merchantek) coupled to a HR-ICP-MS Instrument, Element, Finnigan MAT, was used. The instrumental parameters and the isotopes used are described elsewhere.[6]

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0236–5731/2000/USD 17.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

INAA

Irradiation was carried out at the research nuclear reactor IEA-R1m of IPEN. Synthetic standards were prepared by using PGE and Au standard solutions (Specpure ALFA AESAR). Samples and standards were irradiated for 5 minutes at a thermal flux of $5 \cdot 10^{11}$ n·cm^{-2}s^{-1}, and counted for 3 minutes after a 3-minute decay to determine Rh and Pd. Samples and standards were re-irradiated for 8 hours at a thermal flux of about 10^{12} n·cm^{-2}·s^{-1}. After 48-hour decay, samples and standards were counted for 30 minutes for Pt and Au. A third series of counting was performed after 2–3 weeks after irradiation, for Ru, Os and Ir.

The measurements of the induced gamma-ray activity were carried out in a GMX20190 hyperpure Ge detector (Canberra). The multichannel analyzer was a 8192 channel Canberra S-100 plug-in-card in a PC computer. The gamma-ray spectra were processed by using the program VISPECT, developed by Piccot,[7] from Saclay, France. This program locates peak positions and calculates gamma-ray energies and net areas.

Results and discussion

The results obtained for the geological reference materials analyzed using both analytical techniques are presented in Table 1. The errors associated with the data represent one standard deviation. The uncertainty of recommended values corresponds to 95%.

Table 1. Results obtained for PGE in the standard reference materials UMT-1 and WPR-1 (CCRMP, Canada), GPt-4 and GPt-6 (IGGE, China), in NiS buttons by LA-ICP-MS[5] and INAA (in ng·g^{-1})

	Ru	Rh	Pd	Os	Ir	Pt	Au
UMT-1							
LA-ICP-MS (n^* = 3)	12.1 ± 1.4	13.8 ± 0.9	113 ± 6	8.4 ± 0.6	10.3 ± 0.9	144 ± 35	48 ± 3
INAA (n^* = 14)	8.4 ± 2.1	9.1 ± 1.8	90 ± 18	6.9 ± 1.1	9.1 ± 2.9	110 ± 20	43 ± 7
Recommended	10.9 ± 1.5	9.5 ± 1.1	106 ± 3	(8)	8.8 ± 0.6	129 ± 5	48 ± 2
WPR-1							
LA-ICP-MS (n^* = 3)	17.1 ± 5.0	14.6 ± 3.5	170 ± 30	12.6 ± 3.5	11.7 ± 3.0	198 ± 48	28 ± 5
INAA (n^* = 9)	20 ± 3	11.3 ± 1.0	235 ± 42	15.4 ± 3.4	13.6 ± 3.4	207 ± 36	41 ± 8
Recommended	22 ± 4	13.4 ± 0.9	235 ± 9	(13)	13.5 ± 1.8	285 ± 12	42 ± 3
WMG-1							
LA-ICP-MS (n^* = 2)	36.2 ± 1.1	57 ± 10	416 ± 30	30.2 ± 1.1	55.5 ± 3.5	742 ± 20	99 ± 4
INAA (n^* = 6)	25.5 ± 5.2	18 ± 6	319 ± 53	24.1 ± 0.9	44 ± 6	524 ± 220	91 ± 22
Recommended	35 ± 5	26 ± 2	382 ± 13	(24)	46 ± 4	731 ± 35	110 ± 11
GPT-4							
LA-ICP-MS (n^* = 2)	3.85 ± 0.78	6.65 ± 0.35	92.5 ± 3.5	2.35 ± 0.07	7.90 ± 0.14	64 ± 1	3.7 ± 1.1
INAA (n^* = 4)	2.1 ± 1.0	2.6 ± 0.7	54 ± 24	3.2 ± 3.4	4.3 ± 0.7	22.5 ± 9.9	2.8 ± 1.7
Recommended	2.5 ± 0.2	4.3 ± 0.8	60 ± 9	2.4 ± 0.4	4.7 ± 1.1	58 ± 5	4.3 ± 0.3
GPT-6							
LA-ICP-MS (n^* = 1)	9.8 ± 1.0	26 ± 4	586 ± 66	13.3 ± 0.5	36 ± 3	449 ± 126	57 ± 33
INAA (n^* = 5)	10.5 ± 3.4	17.4 ± 3.5	444 ± 50	16.4 ± 4.1	28.0 ± 4.6	202 ± 57	35 ± 6
Recommended	13 ± 1	22 ± 3	568 ± 51	15.6 ± 2.0	28 ± 7	440 ± 37	(45)

n^* – Number of determinations.

Table 2. Detection limits (3σ) (in $ng \cdot g^{-1}$)

	Ru	Rh	Pd	Os	Ir	Pt	Au
LA-ICP-MS	3.5	0.3	1.4	0.2	0.2	7	0.7
INAA	3	0.3	6	1	0.01	7	0.02

The detection limits (3σ) for LA-ICP-MS, calculated by averaging values obtained for six different measurements performed on two blank buttons,[6] and experimental quantitative detection limits for the analytical conditions described for NAA, calculated considering the CURRIE criterion,[8] are shown in Table 2.

Table 1 shows that both methods gave results in good agreement with the recommended values. We can observe that, in general, NAA showed results lower than the recommended values. This tendency was attributed to losses of PGEs during the NiS button dissolution, also reported by PARRY.[10] The direct analysis of the NiS button, eliminating the chemical dissolution step, is one of the greatest advantages of the laser ablation ICP-MS technique.

The results presented in Table 1 show that NAA was more accurate for the determination of Ir, with relative errors better than 9%. To a lesser extent, NAA gave more accurate results than UV-LA-ICP-MS for Rh and Pd. In the case of the determination of Rh in the reference materials UMT-1 and WMG-1, the relative errors obtained by using NAA were 4% and 31%, respectively, in comparison to 45% and 119% when UV-LA-ICP-MS was employed. The higher Rh values were attributed to the isobaric interference of the $^{63}Cu^{40}Ar$ species, formed in the plasma. When such interference was corrected,[6] a rhodium concentration of 8.5± 0.9 $ng \cdot g^{-1}$ in UMT-1 was determined, which compares favorably with the certified valued.

The determination of Rh and Pd by NAA showed, in some experiments, the interference of the radioisotope ^{38}Cl ($T_{1/2}$=37.29 min), produced by neutron activation of chlorine from the hydrochloric acid used in the dissolution of the NiS button remaining in the filter containing the PGE. The high activity of ^{38}Cl interferes in the gamma-ray spectra of the short lived radioisotopes ^{104m}Rh and ^{109m}Pd. Platinum was more accurately determined by UV-LA-ICP-MS, mainly in the reference materials WMG-1, GPt-4 and GPt-6 (relative errors less than 10%). In the determination of the elements Os, Ru and Au, some results were more accurate when NAA was used, such as in the analysis of Os in WMG-1 (relative error of 0%) and Ru and Au in WPR-1 (relative errors of 9 and 2%, respectively), and some when UV-LA-ICP-MS was employed, like in the determination of Os in WPR-1 and GPT-4 (relative errors of 3 and 0%, in comparison of 18% and 33% when NAA was used). These results indicate that both analytical techniques gave similar results for the determination of Os, Ru and Au.

The NAA technique presented larger deviations between replicates, especially in the samples with lower concentration of PGE, as in the case of GPt-4. In this sample, the recommended values are of the same order as the detection limits for some elements, like Ru and Os. In the case of NAA, the precision may be improved by increasing the length of irradiation and counting time, minimizing counting statistics errors.

NAA presented better detection limits for Ir and Au (Table 2). This is explained by the particularly favorable nuclear characteristics of these elements for thermal neutron activation. On the other hand, UV-LA-ICP-MS showed lower detection limits for Os and Pd. For the other PGE's (Ru, Rh and Pt), the detection limits obtained by both analytical techniques were similar.

In conclusion, we can say that both analytical techniques are accurate and precise to determine PGE and Au in different geological matrices. The well known accuracy of NAA has made it a reference technique, and NAA remains essential in the certification of standard reference materials. Nevertheless, the number of nuclear research facilities is decreasing all over the world, while LA-ICP-MS instruments are becoming more common in analytical laboratories; its shorter turnaround time, compared to NAA, makes it an important tool for routine work.

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The authors thank the Brazilian agency FAPESP for financial support.

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