Platinum-Group Elements and Gold Determination in NiS Fire Assay Buttons by UV Laser Ablation ICP-MS

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The direct analysis of nickel sulfide fire assay buttons by UV laser ablation ICP-MS was used to determine the platinum-group elements and gold in the following reference materials: UMT-1, WPR-1, WMG-1, GPt-4, GPt-6 and CHR-Bkg. The instrument was calibrated with buttons prepared using quartz doped with the appropriate standard solutions. Analytical precision (RSD) was generally better than 10%, although occasional higher RSDs may infer local heterogeneities within nickel sulfide buttons. Good or excellent agreement was observed between analysed and reference material values except Rh in UMT-1 and WMG-1, which suffered an interference from copper. Detection limits calculated as 10s quantitation limits were Au (1.7 ng g⁻¹), Pd (3.3 ng g⁻¹), Pt (8.3 ng g⁻¹), Os (1.3 ng g⁻¹), Rh (1 ng g⁻¹), Ru (5 ng g⁻¹) and Ir (0.7 ng g⁻¹).

Keywords: nickel sulfide, fire assay, laser ablation, LA-ICP-MS, platinum-group elements, gold.

L'analyse directe par ICP-MS couplé à un système d'ablation laser de pastilles obtenues par essai pyrognostique avec du sulfure de nickel est utilisée pour déterminer les concentrations en éléments du groupe du platine et en or dans les matériaux de référence suivants: UMT-1, WPR-1, WMG-1, GPt-4, GPt-6 et CHRBkg. L'instrument a été calibré avec des pastilles fabriquées en dopant du quartz avec les solutions standards appropriées. L'incertitude analytique (RSD) est généralement meilleure que 10% bien que des incertitudes plus élévées soient occasionnellement trouvées, probablement dues à des hétérogénéités locales au sein des pastilles. A l'exception du Rh dans UMT-1 et WMG-1, qui souffre d'une interférence avec le cuivre, l'accord est bon et même excellent entre les valeurs mesurées et recommandées. Les limites de détection (prises égales à 10s) sont: 1.7 ng g⁻¹ pour Au, 3.3 ng g⁻¹ pour Pd, 8.3 ng g⁻¹ pour Pt, 1.3 ng g⁻¹ pour Os, 1 ng g⁻¹ pour Rh, 5 ng g⁻¹ pour Ru et 0.7 ng g⁻¹ pour Ir.

Mots-clés : sulfure de nickel, essai pyrognostique, ablation laser, LA-ICP-MS, éléments du groupe du platine, or.

Nickel sulfide fire assay, used to collect the platinum-group elements (PGE: ruthenium, rhodium, palladium, osmium, iridium, platinum), is already a "classical" procedure to pre-concentrate those elements prior to analysis. The main reason for the extensive use of NiS fire assay is the possibility of easily accommodating large samples, necessary to eliminate any heterogeneity effects associated with the occurrence of these elements at low levels as discrete phases.

Considerable work has been done since Robért et al. (1971) used nickel sulfide as a collector to concentrate all noble metals by fire assay. In 1978,

Hoffman et al. described the determination of PGE and Au by neutron activation (INAA) after a NiS fire assay. However, despite the advances in analytical techniques allowing lower detection limits, contamination with reagents may hinder achieving them in real samples. In 1989, Asif and Parry showed that nickel sulfide buttons of reduced mass are still capable of collecting quantitatively the PGE. Besides allowing lower blanks levels, the use of buttons of reduced mass speeds up the analytical procedure, minimises the contact with toxic reagents such as nickel (Paukert and Rubeska 1993) and renders the whole procedure kinder environmentally.

The main reason why research interest in the NiS technique persists is because many authors still find losses at some steps of the assay. Using the conventional procedure, the button is separated from the vitreous slag, weighed, crushed and dissolved in concentrated hydrochloric acid. The reducing conditions then prevalent should prevent the dissolution of the PGE sulfides. When INAA analysis is used for the determination, the solution is filtered and the filter is irradiated directly. For other analytical techniques, like ICP-MS, some authors prefer not to filter the solution containing the PGE sulfides, but to add a tellurium precipitation step, to collect any dissolved PGE (Jackson et al. 1990, Sun et al. 1993, Reddi et al. 1994).

The direct analysis of the NiS button by INAA was proposed by Asif et al. (1992), but detection limits were not adequate. Later, Jarvis et al. (1995) described the direct analysis of the NiS buttons using an infrared laser ablation system coupled with ICP-MS. The results they obtained were promising, but detection limits were still too high to allow its general use. Here we describe the results obtained for PGE and Au determined directly in the NiS buttons, with an ultra-violet laser ablation system and a more sensitive ICP-MS instrument.

The lower detection limits achieved allowed for the analysis of some of the PGE reference materials distributed by the CCRMP (Canada) and IGGE (China). The chromitite CHR-Bkg distributed by SARM (CRPG, France) was also analysed. The overall aim of this work was to show that the direct determination of PGE in the NiS buttons makes analysis much faster and eliminates any problems with contamination or losses during the dissolution or any other procedures used in conventional methods.

Experimental

Fire assay

The preparation of the NiS buttons was similar to the procedure described by Jarvis et al. (1995), with a few minor modifications. Buttons were prepared by adding the sample (10.0 or 15.0 g) to a 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). For the chromitite sample, sodium tetraborate was substituted

for lithium tetraborate and 3 g of quartz was added to the flux. After mixing thoroughly, the blend was transferred to a new 250 ml fire clay crucible and inserted into a furnace already heated to 650 °C. The temperature was raised and fusion was carried out at 950 °C for 30 minutes, followed by another 30 minutes at 1050 °C. The crucibles were left in the furnace and allowed to cool overnight. After removing them from the furnace, each crucible was broken open, to release the nickel sulfide button, which was retrieved and weighed. For the laser ablation ICP-MS analysis, the upper and lower surfaces of the buttons were polished on a diamond lap.

For calibrating the LA-ICP-MS, NiS buttons were prepared by substituting quartz for the sample. The quartz was analytical grade (Merck) and had been previously doped with a PGE standard solution (Specpure, ALFA AESAR) and left to dry at room temperature. Quartz (10 g) was weighed on a watch glass, the PGE standard solution was added with a micropipette and the weight recorded. This weight was used to calculate the concentration of PGE in the nickel sulfide button, taking into account the concentration of analytes in the standard solution, its density and the mass of the nickel sulfide button. In these calculations, the following assumptions were made: the PGE are quantitatively collected by the NiS and are homogeneously distributed in the buttons. The final concentration of PGE and Au in the NiS buttons used to calibrate the instrument were: 0.086; 0.188; 0.502; 0.928; 1.082; 1.098; 4.02; 4.77; 5.16; 8.68 and 9.45 µg g⁻¹. This wide concentration interval was necessary because of the large range of PGE concentrations in the reference samples analysed. Blanks were prepared using only quartz.

LA-ICP-MS measurements

Laser ablation ICP-MS measurements were made at IPEN (Instituto de Pesquisas Energéticas e Nucleares), São Paulo, Brazil, using an UV Nd:YAG laser ablation system (LUV 266 Gen3, Merchantek) coupled with a HR-ICP-MS instrument (Element, Finnigan MAT). The conditions used are summarized in Table 1. The isotopes used are shown in Table 2. The ^{61}Ni isotope was also measured because it was used as an internal standard (Jarvis et al. 1995). In this study, ^{101}Ru was not measured, due to the interference from ^{61}Ni^{40}Ar. Other isobaric interferences may also be present, like ^{63}Cu^{40}Ar on rhodium and ^{65}Cu^{40}Ar on ^{105}Pd.

Table 1.
Instrumental parameters

Laser ablation	
Instrument	LUV266 Gen3 Merchantek™ EO
Laser type	Nd:YAG, frequency quadrupoled, 266 nm
Operation mode	Q-switched
Laser output, PFM	70%, 2.5 mJ/pulse
Pulse duration	4 ns
Frequency	10 Hz
Approximate pit size	180-200 μm
Pre-ablation time	1 min
Focus condition	On sample surface

ICP-MS	
Instrument	Element, Finnigan MAT
Resolution	300
Plasma power	1300 W
Sample gas	0.99 l min⁻¹
Auxiliary gas	0.82 l min⁻¹
Cooling gas	14 l min⁻¹
SEM acquisition	Analogue for ^{61}Ni and counting, other isotopes
Counting statistics	10 X 6 (runs and passes)

Table 2.
Isotopes used during LA-ICP-MS analysis of the NiS buttons and their abundances (%)

^{61}Ni	^{99}Ru	^{103}Rh	^{105}Pd	^{188}Os	^{189}Os	^{193}Ir	^{194}Pt	^{195}Pt	^{197}Au
1.16	12.7	100	22.2	13.3	16.1	62.6	32.9	33.8	100

Results and discussion

The average diameter of the nickel sulfide buttons used in the present study was 13 mm and the craters formed by the laser ablation, observed by scanning electron microscopy, had a diameter of approximately 200 μm.

All nickel sulfide buttons, including blank buttons and standard buttons obtained with pure and doped quartz respectively, were analysed at three different positions and ten acquisitions were made for each position. The measured intensities for each position were averaged. In a separate evaluation, ten different positions on one NiS button of the reference sample UMT-1 were analysed and the intensities were statistically evaluated. It was concluded that three points were analytically representative.

Calibration

Figure 1 shows the calibration curves obtained after ratioing the intensity of the isotope of interest to the intensity of ^{61}Ni, the blank intensities having been discounted. For Os and Pt, only data for ^{189}Os and ^{194}Pt are shown, but ^{188}Os and ^{195}Pt were also measured. Results for both isotopes in reference samples being very close together, they were averaged. Error bars shown represent the standard deviation (1s). Calibration graphs shown in Figure 1 show good linearity, but it can be observed that for most elements, the button with 4.77 μg g⁻¹ gave a high relative standard deviation, reaching 28% for rhodium. Some other points also show relatively high standard deviations that may be related to the presence of local heterogeneities in the PGE concentration within the NiS buttons. For example, Urban et al. (1995) showed that different PGE-containing phases may form during a nickel sulfide fire assay procedure. Using electron microprobe analysis and back scattered electron images, they identified a matrix of Ni_3S_2 containing small amounts of Rh, Ru and Ir, with inclusions of a sulfide of Ni, Ru, Rh and alloys containing all PGE except Pd (for which no data were presented, using sodium tetraborate as flux), plus nickel in different proportions. There is some difficulty in generalizing the results obtained by Urban et al. (1995) because they used a greater concentration of PGE to obtain their NiS buttons. Calculations with their data indicate that their buttons could contain as much as 2.16 mg g⁻¹ of each PGE. This is up to 10⁴ times higher than the concentration of PGE in buttons prepared in the present work. Even so, it shows that any heterogeneities within the buttons may affect analysis by laser ablation. This was already suggested by Paukert and Rubeska (1993), when they showed that palladium, at a concentration of ≈1% m/m in a 2 g NiS button, could form randomly scattered spots of alloys or sulfides with nickel and other PGE. However, the relatively large size of the craters (≈ 200 μm) formed during the laser ablation in this work helped to minimise any problems associated with the presence of heterogeneities, since the individual phases or local concentrations of the PGE, shown by Urban et al. (1995) and Paukert and Rubeska (1993), are much smaller in size.

Another aspect which is seldom considered, is the procedure used to cool the NiS button. In the classical method, the hot melt is poured into a cold iron mould. Some authors prefer to leave the melt to solidify in the clay crucible, after taking it from the hot furnace
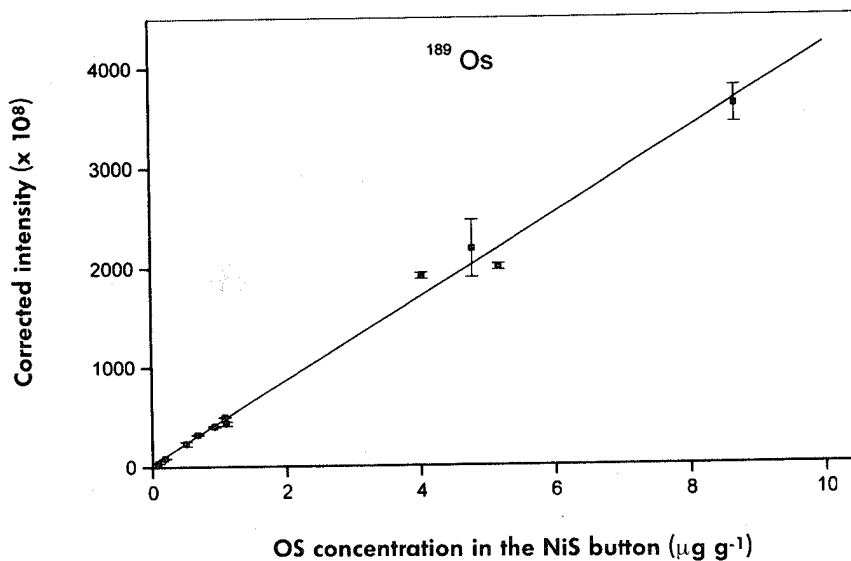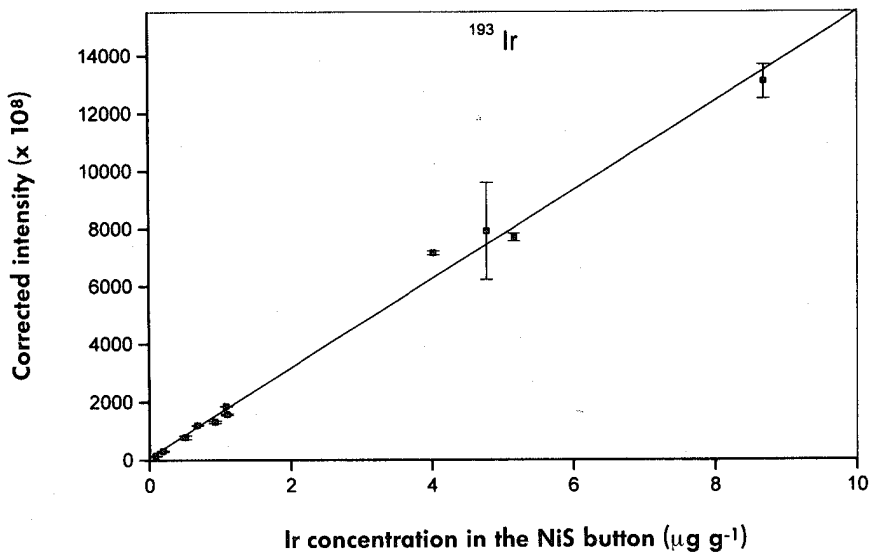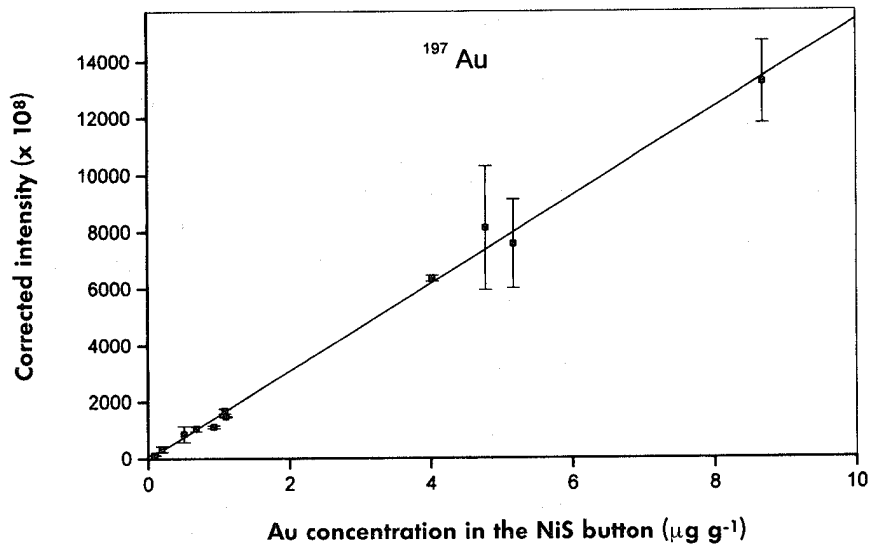
Figure 1. Corrected intensity of the signal of the PGE and Au, obtained during the calibration of the LA-ICP-MS, using NiS buttons prepared by fire assay of quartz doped with PGE standard solution. The corrected intensity was obtained by ratioing the signal obtained for the isotope of interest against the signal of ^{61}Ni and subtracting the same ratio obtained on a blank button.
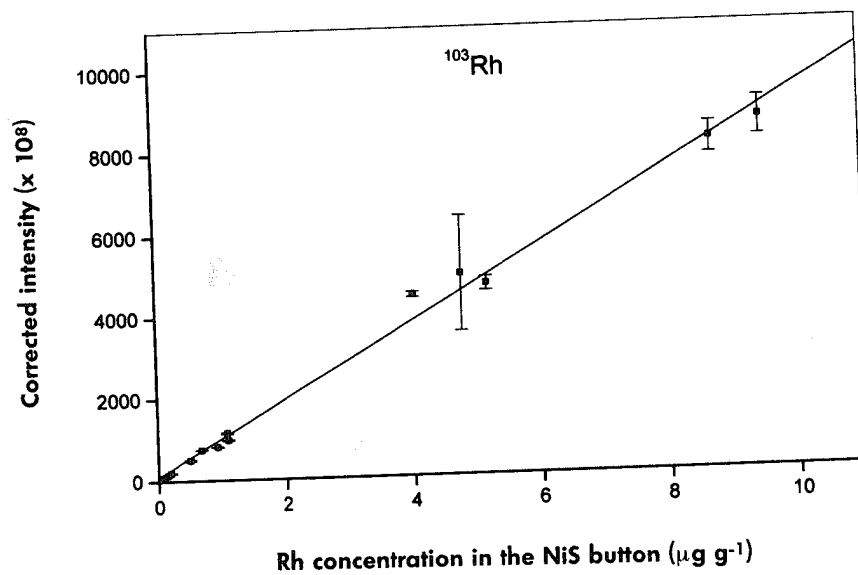
Figure 1 (continued). Corrected intensity of the signal of the PGE and Au, obtained during the calibration of the LA-ICP-MS, using NiS buttons prepared by fire assay of quartz doped with PGE standard solution. The corrected intensity was obtained by ratioing the signal obtained for the isotope of interest against the signal of [61]Ni and subtracting the same ratio obtained on a blank button.
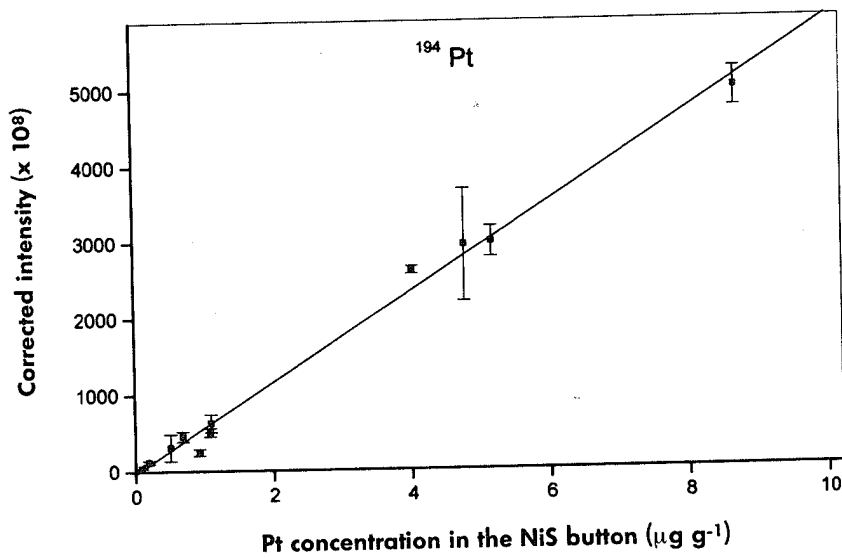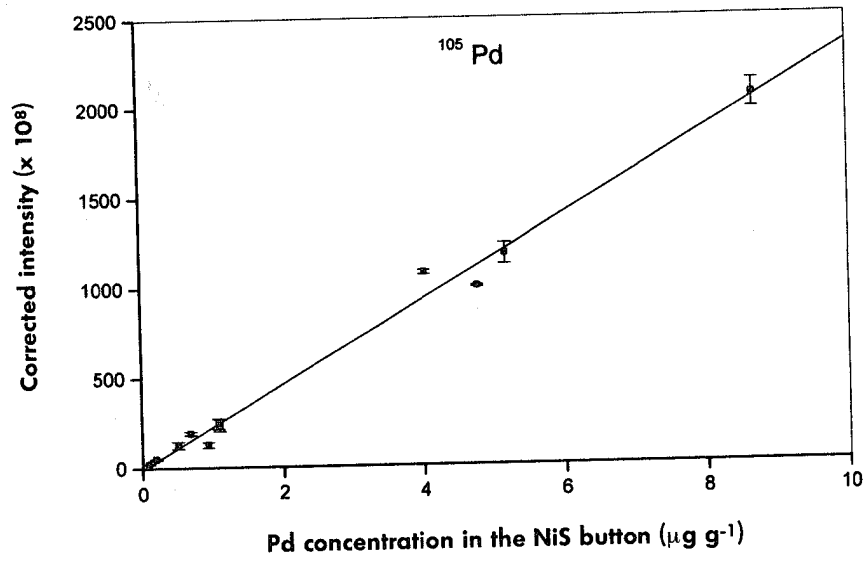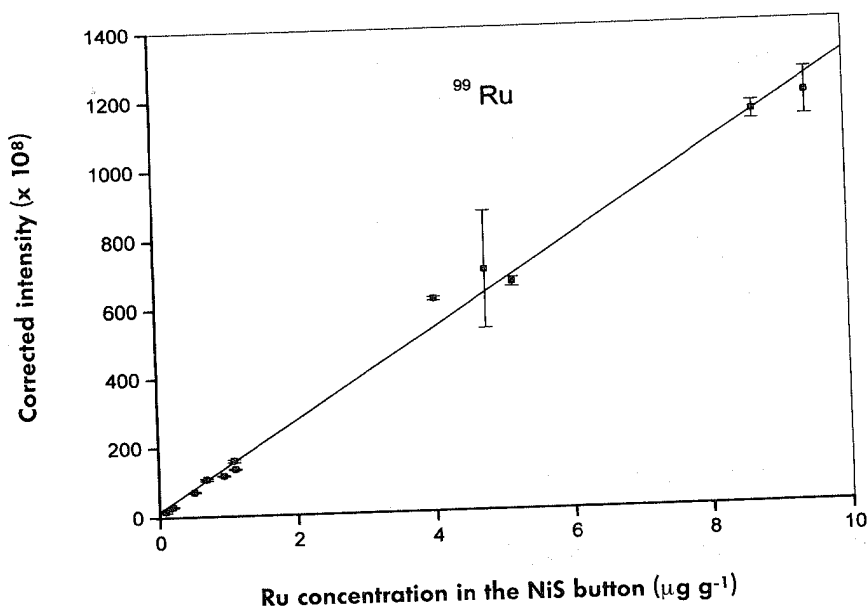
Figure 1 (continued). Corrected intensity of the signal of the PGE and Au, obtained during the calibration of the LA-ICP-MS, using NiS buttons prepared by fire assay of quartz doped with PGE standard solution. The corrected intensity was obtained by ratioing the signal obtained for the isotope of interest against the signal of [61]Ni and subtracting the same ratio obtained on a blank button.

Table 3.
Results obtained for CCRMP PGE reference samples by direct analysis of NiS buttons by LA-ICP-MS. Uncertainties shown for results are for n=3 (ng g^{-1})

	Ru	Rh	Pd	Os	Ir	Pt	Au
UMT-1							
Button 1	10.9 ± 0.9	14.7 ± 1.0	118 ± 16	8.6 ± 0.2	10.6 ± 0.6	161 ± 14	51 ± 3
Button 2	13.6 ± 0.7	13.8 ± 0.6	116 ± 8	8.8 ± 0.3	11.0 ± 0.4	168 ± 8	44 ± 13
Button 3	11.9 ± 0.4	12.9 ± 0.7	106 ± 7	7.7 ± 0.8	9.3 ± 0.7	104 ± 21	49 ± 18
Average	12.1 ± 1.4	13.8 ± 0.9	113 ± 6	8.4 ± 0.6	10.3 ± 0.9	144 ± 35	48 ± 3
Recommended	10.9 ± 1.5	9.5 ± 1.1	106 ± 3	(8)	8.8 ± 0.6	129 ± 5	48 ± 2
WPR-1							
Button 1	22.7 ± 0.3	18.1 ± 0.9	200 ± 28	16.5 ± 1.0	15.2 ± 0.8	250 ± 28	29 ± 9
Button 2	13.2 ± 0.3	11.7 ± 0.2	140 ± 9	10.0 ± 0.5	9.6 ± 0.3	157 ± 3	22.8 ± 0.4
Button 3	15.5 ± 1.2	13.7 ± 0.4	169 ± 23	11.2 ± 0.6	10.5 ± 0.1	186 ± 8	33.0 ± 0.8
Average	17.1 ± 5.0	14.6 ± 3.5	170 ± 30	12.6 ± 3.5	11.7 ± 3.0	198 ± 48	28 ± 5
Recommended	22 ± 4	13.4 ± 0.9	235 ± 9	(13)	13.5 ± 1.8	285 ± 12	42 ± 3
WMG-1							
Button 1	37.0 ± 3.1	64 ± 15	437 ± 149	31.0 ± 1.8	58 ± 5	728 ± 198	101 ± 26
Button 2	35.4 ± 1.3	50 ± 5	395 ± 50	29.4 ± 0.7	53 ± 4	756 ± 52	96 ± 28
Recommended	35 ± 5	26 ± 2	382 ± 13	(24)	46 ± 4	731 ± 35	110 ± 11

Recommended values are from CANMET certificate. Uncertainties shown are at the 95% confidence level. Values in brackets are provisional. Uncertainties for analysed values are 1s = one standard deviation.

(Jackson et al. 1990, Paukert and Rubeska 1993, Frimpong et al. 1995). In this study, the crucibles were left in the furnace overnight, so the temperature of the melt decreased slowly. Unfortunately, nobody has yet shown that all procedures are equivalent, which may not be the case, especially where buttons of reduced mass are concerned.

Precision

Results obtained for UMT-1, WPR-1 and WMG-1 reference samples, respectively an ultramafic ore tailing, an altered peridotite and a mineralized gabbro, are shown in Table 3. The values listed for each button are the average of the analyses at three different positions.

Table 4.
Results obtained for other PGE reference materials by direct analysis of
NiS buttons by LA-ICP-MS. Uncertainties shown for results are for n=3 (ng g⁻¹)

	Ru	Rh	Pd	Os	Ir	Pt	Au
CHR-Bkg							
Button 1	63 ± 2	10.2 ± 0.5	60 ± 2	27.7 ± 1.1	35.8 ± 1.0	36 ± 1	5.6 ± 0.2
Button 2	57 ± 1	8.7 ± 0.5	47 ± 7	24.5 ± 0.6	33.0 ± 0.7	29 ± 13	12.7 ± 1.6
Proposed	67	9	70	27	28	50	28
GPt-4							
Button 1	4.4 ± 0.3	6.9 ± 0.1	90 ± 8	2.4 ± 0.2	8.0 ± 0.3	63 ± 2.4	3.0 ± 0.3
Button 2	3.3 ± 0.3	6.4 ± 0.3	95 ± 17	2.3 ± 0.3	7.8 ± 0.3	65 ± 4.0	45 ± 10
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							
Button 1	9.8 ± 1.0	26 ± 4	586 ± 66	13.3 ± 0.5	36 ± 3	449 ± 126	57 ± 33
Recommended	13 ± 1	22 ± 3	568 ± 51	15.6 ± 2.0	28 ± 7	440 ± 37	(45)

Proposed values for CHR-Bkg are from Potts *et al.* (1992).
Recommended values are from IGGE certificate; the confidence level of uncertainty is not specified.
Uncertainties for analysed values are 1s = one standard deviation.

Relative standard deviations of these measurements tend to be low to moderate (less than or approximately 10%) for almost all elements. The results obtained for Rh, Pd, Pt and Au in Button 1 and Au in Button 2, for reference sample WMG-1, are exceptions, which may be related to the presence of different PGE phases within the buttons. High standard deviations were also observed for Au in Buttons 2 and 3 for UMT-1. The averaged results for samples UMT-1 and WPR-1 are also shown in Table 3. There is a tendency for the relative standard deviations of WPR-1 results to be much higher then those obtained for UMT-1, which is a consequence of the greater range of results for the three buttons of WPR-1.

General good precision within buttons and between buttons was observed for results of reference samples CHR-Bkg, GPt4 and GPt-6, shown in Table 4.

Accuracy

A comparison between results (average ± 2σ) presented here and recommended values (Tables 3 and 4) was made either by taking into consideration the confidence interval of certificate values or by applying the t-test where only a provisional value was available for the reference material concentration. For reference sample UMT-1, our results fall within the confidence interval, excepting rhodium for all buttons and Ir and Pt in Button 2. When the same criteria are used to evaluate results for reference sample WPR-1,

good agreement was observed for the average of the three buttons, but not for the individual results of Buttons 2 and 3. The almost uniform lower results of Button 2 of WPR-1 shows that some problem occurred, but it is not clear if it was during the sub-sampling for the fire assay or at another stage of the analysis.

Results obtained for Rh in reference samples UMT-1 and WMG-1 are much higher than the certified values of this element. This was attributed to the presence of copper in the buttons, which in the plasma may combine with argon forming a $^{63}Cu^{40}Ar^+$ species, interfering with ^{103}Rh determination. Although special buttons were prepared containing copper but no PGE, to evaluate the magnitude of this interference, no signal at mass 103 was detected. Further studies need to be made to clarify this point.

Results obtained for Ru, Pd, Ir, Pt and Au for both buttons of reference sample WMG-1 fall within the 95% confidence interval of the reference value.

Osmium results were compared to provisional values using t-tests. For reference samples UMT-1 and WPR-1 our average values for Os show statistical agreement with reference values. Our results for Os in reference sample WMG-1 fall outside the 95% confidence level of the t-test.

In Table 4, results obtained for chromitite reference sample CHR-Bkg (Potts *et al.* 1992) are shown together

with GPt-4 and GPt-6 (Li and Tong 1995), both pyroxene-peridotites issued by IGGE (China). When t-tests were applied to results of Buttons 1 and 2 of CHR-BKg, statistical agreement with proposed values was observed for most data. The main exception was the results for gold, which were much lower than the suggested value.

Results for Ru, Rh and Ir obtained for reference sample GPt-4 in Button 1 and for Ir and Au in Button 2 are higher than the 95% confidence interval of recommended values. The high value obtained for gold in Button 2 (45 ng g⁻¹) suggests that a nugget effect may have occurred during sub-sampling for fire assay. From sample GPt-6, only one button was analysed; statistically good agreement was obtained with recommended values for all PGE and Au.

In this work, ^{61}Ni was used as an internal standard (Jarvis et al. 1995), and all measurements for PGE and Au were normalized to the signal of that isotope. This correction is intended to compensate for variations in the mass of material reaching the plasma, affected by the processes occurring during laser ablation and transport. According to Fryer et al. (1995), the fractionation factor of the isotopes of interest and the isotope used for correction should be similar. In the present work, the fractionation factors of PGE, Au and Ni were not evaluated, but the analysis of the raw intensity data showed that the PGE signal variation with time was not always directly related to the nickel signal. During analysis, an increase in the signal for nickel could sometimes be observed, with a simultaneous decrease in the signal for one or more of the platinum-group elements. This observation could be related to any heterogeneity of the ablated material.

A better internal correction would be achieved if enriched isotopes of PGE were used. Isotope dilution could then be used, with the advantage of a further improvement in both precision and accuracy, except for rhodium and gold which are monoisotopic.

Quantitation limits

Quantitation limits (10s) are shown in Table 5. These values were obtained by averaging values obtained for two different blank buttons, considering a sample mass of 10.0 g, and an average final mass of the nickel sulfide buttons of 1.3 g. In principle, these limits can be lowered since larger masses of sample may be used during the fire assay. The limits of Table 5

Table 5.
Quantitation limits (10s) on blank NiS buttons, prepared from 10 g of sample (test portion) and with an average mass for each NiS button of 1.3 g (ng g⁻¹)

Ru	Rh	Pd	Os	Ir	Pt	Au
5.0	1.0	3.3	1.3	0.7	8.3	1.7

were confirmed when the lower level reference samples TDB-1 and WGB-1 were prepared and analysed. Among the platinum-group elements, only palladium has recommended values in those samples above the quantitation limits. The values obtained for Pd in TDB-1 and WGB-1 were respectively 21.4 ± 0.3 ng g⁻¹ and 12.9 ± 1.5 ng g⁻¹ while the recommended values are 22.4 ± 1.4 ng g⁻¹ and 13.9 ± 0.3 ng g⁻¹. The recommended values for gold in these reference samples are higher than the quantitation limits listed in Table 5, but our results were much lower, a problem that was attributed to incomplete recoveries by the nickel sulfide during the fire assay procedure.

Conclusions

The results obtained by the direct analysis of nickel sulfide buttons of reduced mass using LA-ICP-MS show that this method may be used to determine the PGE content in low level mineralized samples, for which the quantitation limits are adequate. These limits could be further lowered by increasing the sample mass used in individual assays.

General analytical precision, determined both by repeated analysis of the same buttons and by analyzing different buttons of the same sample tends to be better then 10%. Some results showed much higher relative standard deviations, which may be related to local heterogeneity within the nickel sulfide buttons.

The analysis of the reference materials showed that, in most cases, good or excellent agreement with recommended or proposed values was achieved. Other less acceptable results are reminders of the difficulties associated with the analysis of PGE and Au.

The main advantages of using LA-ICP-MS for PGE analysis are the elimination of the dissolution of the NiS button and associated problems together with the faster analysis time. The buttons prepared to calibrate

the instrument may be used for many analytical cycles per button, and may be repolished, if necessary, to facilitate such repeated use.

Acknowledgements

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