Ruthenium Recovery in Chromitites by NiS-fire Assay

L. Paul Bédard[1] and Sarah-Jane Barnes[2]
Sciences de la Terre, Université du Québec à Chicoutimi, Chicoutimi (Québec) G7H 2B1 Canada
e-mail: [1]pbedard@uqac.ca, [2]sjbarnes@uqac.ca

Chromitites are important hosts for PGE mineralizations and are notably difficult to analyze due to their refractory nature. In most cases, PGE not included inside the sulfides which are moderately easy to dissolve. Laurite (Ru, Os, Ir)S_2, when present is held inside chromite grains rendering it difficult to extract. Current laboratory protocols, such as Borthick & Naldrett (1984) and Asif & Parry (1990), dissolve sulfide properly but chromite grains are left in a worm-like sesquioxide texture (Borthick & Naldrett 1984) which indicate only partial dissolution. The final effect would be to lower Ru, Os and/or Ir value.

A series of tests were undertaken to find the flux mixture and ratio that would completely melt the chromite grains and allow a potential 100% recovery of all PGEs. The sample used to develop the new protocol is a piece of the UG-2 chromitite (Bushveld Complex) which is known to contain laurite. The first trial was a set of duplicate tests of commonly used published protocols : Asif & Parry (1990), Borthick & Naldrett (1984), Robert et al. (1971), and Zereini et al. (1994) which are condensed in Table 1.

None of these protocols showed a complete dissolution of chromite grains although partial attacks was observed. This inability to dissolve chromite is partly due to the low solubility of chromite ores in lithium borate (Cremer & Schlocker 1976). It has been proposed that sodium metaphosphate will have a higher solubility for chromite (Banerjee & Olsen 1978). A first series of tests were undertaken into which one the flux (lithium tetra-/meta- borate or sodium carbonate) was replaced by sodium metaphosphate. It are present in sulfides associated to chromite grains but

produced awful looking glassy slag (affectionately named toads) which foamed and dispersed the NiS droplets. Moreover some crucibles were partially dissolved, leaking inside the furnace and disaggregating the heating plates. A different strategy was undertaken. The best chromite dissolution was observed with the Borthick & Naldrett (1984) protocol, sodium metaphosphate was therefore added in amount of 5, 10, and 15 g to increase Cr solubility. It has been found that at 15 g of sodium metaphosphate, all chromites grains were dissolved but so did the crucibles, which renders this reagent ratio impractical. At 5 g, there were still some undissolved chromites grains in the glassy slag. At 10g, there was no more than one partially dissolved chromite grain by polished section of the glassy slag. Temperature of fusion in the preconcentration step is very important. At 1000°C chromite grains do not fully melt, but they are fully melted at 1200°C for 90 minutes.

The new protocol was tested on reference samples CHR-Pt+ which is a chromitite reference sample that have PGE results available (Potts et al. 1992). For all analytes except Rh and Pd, the modified protocol gives higher results suggesting a better recovery. Rhodium and Pd are within analytical errors of the conventional true value. PGEs values were obtained by dissolution of the NiS button in HCl and filtered (Robert et al. 1971) and sent for irradiation at École Polytechnique (Montréal) SLOWPOKE II nuclear reactor facilities for neutron activation analysis.

Table 1. *NiS PGE preconcentration reagents commonly used.*

Protocol	***Sample (g)***	***$NaCO_3$ (g)***	***$Li_2B_4O_7$ (g)***	***$Na_2B_4O_7$ (g)***	***CaF_2 (g)***	***NaOH (g)***	***Ni (g)***	***S (g)***	***SiO_2 (g)***	***T (°C)***	***Time (min.)***
Asif & Parry	25	25	50	0	0	25	0.5	0.35	5.0	1000	60
Borthick & Naldrett	15	15	30	0	0	0	5	3	3	1200	90
Robert et al.	15	30	0	60	0	0	16	10	10	1000	90
Zereini et al.	10	45	90	45	15	0	17	12.5	15	1000	90

It appears from petrography of the glassy slag and preliminary analytical results that a more complete dissolution of the chromitites ores and recovery of PGEs is possible by the addition of sodium metaphosphate. Currently used NiS preconcentration protocols do not fully attact all the chromites grains and might leave some of the laurite with its Ru in the glassy slag.

References

Asif, M. & Parry, S.J. 1990. Nickel sulphide fire assay for the collection of the platinum group elements and gold from chromitites using reduced bead size Mineralogy & Petrology v. 42 p. 321-326.

Banerjee, S. & Olsen, B.G.1978. Rapid analysis of chrome ores, chrome-magnesia and magnesia-chrome materials by XRF. Applied Spectroscopy, v. 32 p. 376-379.

Borthick, A.A. & Naldrett, A.J.1984. Neutron activation analysis for platinum group elements and gold in chromitites. Analytical letters v. 17(A4) p. 265-275.

Cremer, M. & Schlocker, J. 1976. Lithium borate decomposition of rocks, minerals, and ores. American Mineralogist, v. 61, p. 318-321.

Potts, P.J., Gowing, C.J.B. & Govindaraju, K. 1992. Preparation, homogeneity, evaluation and cooperative study of two new chromitite reference samples CHR-Pt+ and CHR-Bkg. Geostandards Newletter, v. 16, p. 81-108.

Robert, R.V.D., van Wyk, E. & Palmer, R. 1971 Concentration of the noble metals by a fire-assay technique using nickel-sulfide as the collector National Insitute of Metallurgy, South Africa, Report # 1371, p.1-16.

Zereini, F., Skerstupp, B. & Urban, H. 1994. Comparison between the use of sodium and lithium tetraborate in platinum-group element determination by nickel sulphide fire-assay. Geostandards Newsletter, v. 18 p. 105-109.

Table 2. *Preliminary results (μg/g) CHR-Pt+ chromitite reference sample.*

	Rh	***Pd***	***Au***	***Os***	***Ir***	***Ru***	***Pt***
Average of 7 determinations	4.18	78.53	5.66	2.17	7.55	9.71	73.02
RSD (%)	4	8	18	8	7	8	10
Conventional True Value	4.70	80.80	4.30	1.90	6.20	9.24	58.00
Standard deviation	0.72	13.15	0.75	1.30	0.83	2.00	6.69