

A new method for the determination of the platinum group elements in sedimentary materials

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Introduction

The platinum group elements (PGEs: Ru; Rh; Pd; Os; Ir; Pt) are of high commercial value and usually extracted from rich precious metal deposits, but little is known about their general distribution in sedimentary systems. Anomalously high concentrations of the PGEs (particularly Ir) have been documented at many extinction levels (e.g. K/T boundary) in the stratigraphic record. Potential economic deposits of the PGEs have been identified in black shales, but the mechanisms by which such enrichments take place and the extent to which black shales contain anomalous levels of the PGEs are uncertain.

The two main problems for determination of the PGEs in sediments, are their low concentrations (usually less than 1 ng g^{-1}) and inhomogeneous distribution. Detailed analysis of elemental distribution in sedimentary successions, require an ability to analyse relatively small sample sizes, preferably $< 10 \text{ g}$. Existing analytical techniques for the determination of the PGEs, typically involve fire assay preconcentration of 25–150g aliquots. These existing techniques, are unable to deal with this special combination of requirements. However a new method (Totland, 1993) developed for the determination of PGEs in sediments, deal with these requirements and is subsequently reviewed in this paper, together with preliminary data for a suite of 1g river sediments.

Sample preparation

Samples (50g) undergoing PGE determination are dried, ground, sieved (250 mesh UK) and homogenised, before 1g subsamples are taken for analysis. The samples undergo a number of preparation stages (i) microwave dissolution by acid attack; (ii) filtration and alkali fusion of insoluble residues; (iii) ion-exchange separation of the PGEs from their matrix; and (iv) preconcentration and their determination by inductively coupled plasma-mass spectrometry (ICP-MS).

Microwave dissolution. 1g samples undergo acid attack, from a 30ml mixture of AristaR grade hydrochloric, hydrofluoric and nitric acids in closed microwave digestion vessels. A 'CEM 2000 microwave digestion system' is utilised for the dissolution. The vessels are allowed to naturally depressurize before opening, and the solutions are transferred to polytetrafluoroethylene (PTFE) beakers. Evaporation of the acidic mixture is allowed to proceed over a hotplate, until a crystalline paste forms. Two 10ml applications of AristaR hydrochloric acid is applied to the paste with subsequent evaporation, before the paste is finally dissolved in 0.5 mol dm^{-3} hydrochloric acid.

Filtration and alkali fusion. The dilute acidic solution is vacuum filtered using a cellulose nitrate membrane filter paper, and any remaining insoluble silicate residue transferred to a vitreous carbon crucible. The filter paper is dissolved with AristaR nitric acid and the acid evaporated off on a sand bath. The remaining residue is fused with a 1:1 sodium carbonate: sodium peroxide flux, over a reducing natural gas flame and once cool the fused material is dissolved in 0.5 mol dm^{-3} hydrochloric acid.

Ion-exchange separation. Ion-exchange columns are prepared, using a 'Bio-rad AG-50X' cation exchange resin and preconditioned with 0.5 mol dm^{-3} hydrochloric acid. After preconditioning, the filtrate is applied to the 45ml resin bed and elution is allowed to proceed, followed by the dissolved residue. Elution is allowed to continue using 0.5 mol dm^{-3} hydrochloric acid, and the eluted solution is collected from the column.

Preconcentration and analysis. The final solution is reduced to about 5ml on a sand bath and quantitatively transferred to a 10ml volumetric flask. Finally the solution is transferred to a sample vial, whereupon it is analysed by ICP-MS to determine the concentration of the PGEs present in the solution and thus determine their distribution in the original sample.

TABLE 1. RTZ stream sediment data (ng g^{-1}) for 1g samples obtained by ICP-MS following microwave digestion, alkali fusion and cation-exchange preconcentration

Sample	Ru	Rh	Pd	Ir
M1	1.92±0.98	2.90±2.96	12.1±7.7	0.50±0.65
M2	3.56±2.27	2.07±0.55	22.0±4.1	0.75±0.26
M3	7.77±3.80	3.74±0.68	45.4±9.6	1.82±1.15
M4	9.37±4.31	5.58±2.50	47.51±5.3	1.68±0.30
M5	12.8±3.8	4.88±1.54	63.22±2.5	1.96±0.35
W1	1.16±0.87	0.82±0.31	7.27±1.70	0.26±0.06
W2	2.31±1.28	0.35±0.34	7.50±3.34	0.23±0.06
W3	1.93±0.91	1.13±0.22	7.71±3.95	0.28±0.11
W4	3.51±2.33	1.35±0.57	15.2±4.9	0.58±0.17
W5	1.78±1.62	0.44±0.34	7.97±4.55	0.32±0.19

Conclusions

The results of the preliminary data serve to illustrate the sensitivity of this new method, but the accuracy of the results could not be satisfactorily evaluated, since values for all elements were below the quantitation limits of comparative studies employing Pb fire-assay with

ICP-AES, and NiS fire-assay with INAA.

References

- Totland, M.M. (1993) *Determination of the Platinum Group Elements in Geological Materials*, Unpublished PhD Thesis, Kingston University, 362 pp.