

Recent Development in Simultaneous Multi-Element Determination of the Platinum Group Elements and Gold in Geological and Environmental Samples^{*}

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Abstract: In recent years, the modern methods of multi-element analysis of precious metals have attracted wide attention in scientific research and industry. The application and development in the decomposition of samples, separation and enrichment, and modern instrumental analysis of the platinum-group elements (PGEs) and gold in geological and environmental samples have been reviewed. Finally, the tendency of analysis of precious metals is also prospected.

Key words: platinum-group elements; gold; geological and environmental samples; simultaneous multi-element determination; review

1 Introduction

Due to their great importance in scientific research and economic development, determination of the platinum-group elements (PGEs) and gold has aroused considerable interest in many fields, such as geochemistry, environmental science, biology and material science (Rao and Reddi, 2000). In this paper, more attention has been paid to the analysis of trace precious metals in geological and environmental samples. The significance in determination of the PGEs and gold in geological and environmental samples can be described as follows: (1) to guide geochemical exploration; (2) to be used as a geochemical tracer; (3) to be a new isotope chronology method established on the basis of both ^{187}Re - ^{187}Os and ^{190}Pt - ^{188}Os isotope decay schemes in Earth and planetary sciences (Morgan et al., 2002); (4) to explore the impact of extraterrestrial materials in terms of unusual levels of PGEs (Xie Liewen et al., 2001).

However, accurate determination of PGEs and gold is very difficult due to their extremely low concentrations, heterogeneity ("nugget effect"), refractory phases, and large amounts of complex matrix elements. In recent years, with the development of modern instrumental techniques, determination of PGEs and gold has changed its orientation from mono-element analysis to simultaneous multi-element analysis. This paper has reviewed the significant research contributions in the fields of sample decomposition, preconcentration and instrumental techniques for PGEs and gold in geological and environmental samples.

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2 Decomposition

Natural samples, in general, need to be decomposed before determination, for the concentrations of precious metals are very low. Methods of sample decomposition include fire assay, alkali fusion and acid dissolution.

2.1 Fire assay

As a traditional and classical technique, fire assay can be used to decompose samples and separate PGEs and gold from base metals and silicates in samples. There are several collectors, such as NiS, Pb, Bi, Sn, Sb, of which NiS is the most important (Wu Ruilin et al., 1997). Summary of NiS fire assay is presented in Table 1.

Table 1. Fire assay

Sample	Element	Procedure	DL* (ng · g ⁻¹)	Ref.
Rocks, SARM-7, CHR-Pt + CHR-Bkg	Pt, Pd, Ru, Rh, Ir, Os, Au	Ni-FA; Te coprecip.; ICP-MS	0.09 (Ir) - 2.1 (Ru)	Juvonen et al., 1994
Rocks, ores, heavy mineral concentrations	Pt, Pd, Rh, Ru, Ir	Ni-FA; Te coprecip.; ICP-MS	—	Reddi et al., 1994
SARM-7, BF-4	Pt, Pd, Ru, Rh, Ir, Os, Au	Ni-FA; ICP-MS	—	Frimpong, et al., 1995
SU-1a	Pt, Pd, Re, Ru, Ir	Ni-FA; anion-exchange; ID-ICP-MS	—	Rehkamper et al., 1997
DZS-2, Cu-Ni ore, GPt-1, GPt-2, GPt-3, Gpt-4, GPt-5, GPt-6, GPt-7	Pt, Pd, Ru, Rh, Ir, Os	Ni-FA; Te coprecip.; ICP-MS	0.01 (Pt) - 0.2 (Ir)	Sun Yali et al., 1998
UMT-1, WMC-1, WPR-1, GPt-1, GPt-6, CHR-Bkg	Pt, Pd, Ru, Rh, Ir, Os, Au	Ni-FA; UV-laser ablation-ICP-MS	—	Jorge et al., 1998
GBW 07290 (GPt-3), GBW 07294 (GPt-7), GBW 07102 (DZΣ-2)	Pt, Pd, Ru, Rh, Ir, Os, Au	Ni-FA; Te coprecip.; ICP-MS	—	He Hongmiao, et al., 2001
Marine sediments (GSMS-2 and GSMS-3) and Mn nodules (GSPN-2 and GSPN-3)	Pt, Pd, Os, Ru and Ir	Ni-FA; Te coprecip.; NAA	0.003 (Ir) - 1.0 (Pt)	Li Xiaolin et al., 1996
UMT-1, WPR-1	Ru, Rh, Pd, Os, Ir, Pt, Au	Ni-FA; laser ablation-ICP-MS	0.2 (Os and Ir) - 7 (Pt)	Elisa et al., 1998
Rocks	Pt, Pd, Os, Ir	Ni-FA; NTIMS (Os); ID-ICP-MS (Pt, Pd, Ir)	—	Ravizza and Pyle, 1997

* Detection limits.

For NiS-FA, the mixture of sample and flux is fused at about 1000°C for 1 to 2 h. The NiS button is treated with acid, and then the insoluble precious metal sulfides are attacked by oxidizing acid.

To obtain a high recovery, the key factors of NiS fire assay are flux ingredients, temperature, time, and treatment of the fire button. As for flux ingredients, two parameters should be examined systematically: E, the ratio of the combined weights of sample + flux to the weight of the collector, and Sc, the percentage of sulfur in the collector (Paukert and Rubeska, 1993). McDonald et al. (1994) reported that larger recovery (94% - 98% vs. 84% - 92%) was obtained by adding more silica and borax to the usual flux compositions for Ni-FA, in their study of some South African kimberlites.

Usually, losses of precious metals occur at the stages of fire assay, button crushing and dissolution. Losses can be avoided when buttons are directly dissolved in heated screwed-capped Teflon bombs (Sun Min et al., 1993). A modified technique, namely a semi-open dissolution system after fusion, using reflux setup, allows Os to be almost completely recovered (Gros et al., 2002).

Compared with alkali fusion and acid digestion, the main advantages of Ni-FA are described as follows: (a) easy handling of large sample weights that can overcome nugget effects; (b) assurance of quantitative collection of all PGEs and gold; (c) direct determination with NiS button. The disadvantage of NiS-FA is the large reagent blank that is derived mainly from Ni (Oguri et al., 1999).

2.2 Alkali fusion

Alkali fusion of samples in small crucibles with Na_2O_2 and/or Li_2O_2 or combined with NaOH, provides an ideal means of sample decomposition. A number of reports are summarized in Table 2.

Table 2. Alkali fusion

Sample	Element	Procedure	DL* ($\text{ng} \cdot \text{g}^{-1}$)	Ref.
UMT-1, WMG-1, WPR-1, WGB-1, TDB-1, SARM-7	Pt, Pd, Rh, Ir	Na_2O_2 ; Te coprecip.; ID-ICP-MS	0.3 (Ir) - 2 (Pt)	Enzweiler et al., 1995
SARM-7, CHR-Pt+	Pt, Pd, Au, Ir	Na_2O_2 ; Te coprecip.; RNAA	0.1 (Au) - 2 (Pt)	Nogueira and Figueiredo, 1995
UMT-1, WMG-1, WMS-1, WPR-1, WGB-1	PGE, Au	Peroxide fusion; Te coprecip.	—	Amosse, 1998
WPR-1, WMS-1, a meteorite sample, K-T boundary samples from Stevns Klint, Denmark	Ru, Pt, Ir, Pd	Na_2O_2 ; anion-exchange; ID-ICP-MS	0.05 (^{193}Ir) - 0.50 (^{108}Pd)	Yi and Masuda, 1996
WGB-1, TDB-1, UMT-1, WPR-1, WMG-1, WMS-1	Pt, Pd, Ru, Rh, Au, Ir	Na_2O_2 ; Te coprecip.; ID-ICP-MS	0.020 (Ir) - 0.32 (Au)	Qi Liang and Hu Jing, 1999

* Detection limits.

Methods of aqua regia leaching and sodium peroxide sintering were compared; the data showed that alkali fusion is better because of the strong ability of decomposition (Nogueira and Figueiredo, 1995). It is important to select a kind of suitable crucibles. Many experiments have demonstrated that corundum crucible is the best choice (Qi Liang and Hu Jing, 1999).

It can be concluded that the positive aspects of alkali fusion are: (1) easily attacking refractory samples such as chromites and silicates; and (2) low cost. On the other hand, the negative aspects are: (1) limitation in handling large weights of samples; (2) large amounts of sodium salts, which results in high dissolved salt content in the solutions (Dai Xiaoxiong et al., 2001).

2.3 Acid dissolution

Acid dissolution procedures are widely applied to rapid determination of PGEs and gold. Mixtures of HCl, HNO_3 , HF, HClO_4 , HBr, H_2O_2 , etc., are used in either open or closed vessels. There are three methods of acid digestion: (1) open acid digestion, which is not suitable for quantitative analysis (Nogueira and Figueiredo, 1995); (2) high-pressure digestion (e. g. Ely et al., 1999; Meisel et al., 2001); and (3) acid leaching combined with sodium peroxide fusion of the insoluble residues (Coedo et al., 1997). The details are listed in Table 3.

There has been ever increasing interest in the methods of Carius tube and high-pressure digestion, which is sometimes followed by alkali fusion of residues. Carius tube is airproof, which accounts for the quantitative data of PGE and complete isotope equilibrium.

Table 3. Acid digestion

Sample	Element	Procedure	DL* ($\text{ng} \cdot \text{g}^{-1}$)	Ref.
Rocks; WITS-1	Pt, Pd, Ir, Ru, Os	Carius tube with AR; solvent extraction (Os); anion-exchange; ID-ICP-MS	0.003 (Os and Ir) - 0.015 (Pt)	Pearson and Woodland, 2000
Ores, silicates, Fe-forming rocks	Au, Pt, Pd, Ir, Rh	High-pressure microwave digestion with HF and AR; insoluble residues fused with Na_2O_2 ; anion-exchange; FI-ICP-MS	0.15 (Rh) - 1.2 (Au)	Coedo et al., 1997
CHR-Bkg, WGB-1, TDB-1	Pt, Pd, Ir, Ru, Os, Re	High-pressure acid dissolution with HCl and HNO_3 ; anion-exchange; ID-ICP-MS	0.012 (Re and Os) - 0.77 (Pt)	Meisel et al., 2001
UMT-1, basalts	Ir, Ru, Rh, Pt, Pd	High-pressure acid dissolution with HF, HNO_3 , HCl; cation-exchange; USN-ICP-MS	in the $\text{fg} \cdot \text{g}^{-1}$ range	Ely et al., 1999
SARM-7, PTM-1, PTC-1	Au, Pt, Pd, Ir, Ru, Rh	HF, HNO_3 , HCl, HClO_4 ; anion-exchange; ICP-MS	—	Jarvis et al., 1997

* Detection limits.

The advantages of Carius tube and high-pressure digestion are: (1) the lowest reagent blank; (2) sufficient equilibrium of PGEs isotopes, especially for Os; and (3) tolerance to relatively high temperature (300°C) and high pressure which can hasten sample dissolution. In contrary, the drawbacks are: (1) high cost; (2) requirement of stainless steel jacket for security; and (3) little sample weight (e. g. Shirey and Walker, 1995; Du Andao et al., 2001).

3 Preconcentration techniques

In general, preconcentration is necessary prior to instrumental determination of PGEs and gold in geological and environmental samples. In the procedures, PGEs are concentrated from diluted solutions, and separated from major matrix elements and other minor elements, which would interfere with the subsequent analysis. Coprecipitation, ion exchange/adsorption, and solvent extraction are adopted commonly.

3.1 Coprecipitation

Coprecipitation is employed in many analytical procedures to recover the platinum-group elements and gold, especially in geological and environmental materials. Tellurium, is most frequently employed, combined with tin (II) chloride as a reductant. The key factors, governing the recoveries of PGEs and gold, are temperature, time, and acidity. In general, the recovery of Ir is lower than that of other precious metals. However, with the presence of KI in sample solution, the recovery of Ir will be obviously enhanced from 33% (without KI) to 97.5% (Amosse, 1998). High recoveries ($>90\%$) could be obtained under the optimum operation factors (Gros et al., 2002). It can be concluded that the advantages of Te coprecipitation are: (1) high recoveries (generally, $>90\%$) of all PGEs and gold, and (2) easy manipulation.

3.2 Ion exchange/adsorption

Ion exchange resins and adsorbents are used as effective means of separating PGEs and gold from other elements. The recoveries of the precious metals by resins or adsorbents are listed in Table

4. The parameters, governing the recoveries of the PGEs, include acidity of media, electrovalence of PGEs complex, etc.

A procedure has been developed for samples containing precious metals greater than $1 \mu\text{g} \cdot \text{g}^{-1}$ (Shirey and Walker, 1995). Some modified procedures were reported to gain higher recoveries. For instance, two stages are involved in the routine procedure: chlorinating solutions and duplicating sorption onto a small anion exchange column (Dai Xiaoxiong et al., 2001). The resin retaining the PGEs is attacked in the HPA-S with concentrated HNO_3 (e. g. Coedo et al., 1997; Meisel et al., 2001).

A number of adsorbents have been reported such as fiber (Xu Liqiang and Cai Ximing, 1994), sulfhydryl cotton (Liu Shaofeng et al., 1994), polyurethane foam (Wildhagen and Krivan, 2002), and silica gel (Pu Qiaosheng et al., 1999).

Some disadvantages of ion exchange/adsorption are listed as follows: (1) ion exchange resin cannot separate Rh, due to its poor absorbability; (2) it is difficult to desorb quantitatively these analytes; (3) digestion resins or adsorbents need rigorous conditions (e. g. high pressure); and (4) handling is time-consuming.

Table 4. Recoveries of the platinum-group elements and gold on resins or adsorbents

Resin or sorbent	Element(s)	Recovery (%)	Ref.
Bio-Rad AG 1X8 anion resin	Pt, Pd, Ru, Ir	90 ± 10	Yi and Masuda, 1996
Dowex 1X8 anion resin	Pt, Pd, Ir, Rh, Ru, Au	50 - 100	Shirey and Walker, 1995
Dowex AG 50W-X8 cation resin	Pt, Pd, Ir, Rh, Ru, Au	87 - 100	Ely et al., 1999
Polystyrene sorbent SSPS	Pd(II), Pt(IV), Rh(III)	>95	Kovalev et al., 2000
Polystyrene based sorbent containing di-ethylenetriamine groups	Ru(IV), Pt(IV)	~85	Kubrakova et al., 1996

3.3 Solvent extraction

PGEs and Au in solutions can be separated from other elements by means of liquid-liquid or liquid-solid extractions, according to different distribution coefficients of PGEs and gold in two phases. A method for separation of stannous chloride complex anions of Pt(II), Pd(II), Rh(III) and Au(III) with liquid-liquid extraction of the n-propyl alcohol- $(\text{NH}_4)_2\text{SO}_4$ -water system, was reported (Gao Yuntao et al., 2001). The experimental results indicated that the method could extract these precious metals simultaneously and their extraction ratios were 98% - 100%. Several studies were reported for the separation of Pt(II), Pd(II) and Au(III) with liquid-solid extraction of the polyvinylpyrrolidone-salt-water system (Wu Lisheng and Gaoyuntao, 1998), and for enrichment of Pt and Rh as 2-mercaptobenzothiazole complexes by means of molten naphthalene extraction (Xiao Hongzhan and Liang Shuquan, 1994). Relatively, there are more reports about Re-Os determination with solvent extraction (Pearson and Woodland, 2000).

Solvent extraction, generally, is inferior to coprecipitation and ion exchange, because of the following two reasons: (1) large amounts of organic solvents which are always poisonous; and (2) low selectivity.

4 Instrumental determination of the PGEs and Au

With the rapid development of instrumental technology, it is possible to determine trace PGEs and Au simultaneously or sequentially. The detection limits of instrumental techniques for the PGEs and Au are described in Table 5 (Dong Shou'an, 2000).

Table 5. Available techniques for determination of the precious metals of different concentrations

Technique	Concentration range			
	$< \times 10^{-9}$	$\times 10^{-9}$	$\times 10^{-6}$	0.1%
FASS			Yes	Yes
GFASS	Yes	Yes		
ICP-AES			Yes	Yes
ICP-MS	Yes	Yes	Yes	
NAA	Yes	Yes	Yes	

4.1 Inductively coupled plasma mass spectrometry (ICP-MS)

The ICP-MS technique has become a popular approach to determination of PGEs and Au in geological and environmental samples owing to its following advantages: (1) simple spectra; (2) excellent detection limits generally $(0.001 - 0.1) \times 10^{-9}$; (3) wide linear dynamic range (five to six orders); (4) capability of simultaneous multi-element analyses due to rapid scanning facility; (5) a fair degree of tolerance to interference; (6) ability of measuring isotope ratios; and (7) possibility of isotope dilution calibration strategies that overcome the interference of losses of analytes at the preparation stages. The large quantities of references on PGEs and gold determination by ICP-MS showed that it is a favorite technique.

One limiting factor is the low tolerance to high dissolved salts in sample solutions. Flow injection could overcome the problem to some extent (Cao Shuqin et al., 2000). Laser ablation (LA) is an alternative means of introduction for rapid determination. The LA-ICP-MS technique is applied to determination of the concentrations of Pt, Pd and Rh in urban road sediments (Motelica-Heino et al., 2001), and of Au and the platinum-group elements in geological silicates (Klemm and Bombach, 2001). However, there remain some problems in LA-ICP-MS, such as poor reproducibility and accuracy, the lack of suitable internal standard elements for the calibration of peak drift and matrix interference.

4.2 Neutron activation analysis (NAA)

NAA is also one of the preferred techniques for precious metal analysis in geological and environmental samples, owing to its high sensitivity, fine accuracy, and freedom from contamination (Li Xiaolin et al., 1996).

Among the precious metals, the most sensitive elements for NAA are Ir, Rh and Au (McDonald et al., 1994). Two techniques, namely ICP-MS and NAA, were employed to determine the PGEs in geological samples, and the data showed they are complimentary (Li Chunsheng et al., 2001). Hou Quanlin and Ma Peixue (1997) concluded that the interference of Au on Pt was serious for most rocks, yet the interference of U on Ru or Pd was negligible by NAA for most ultramafic rocks and sulfide ores.

Due to unhealthy and time-consuming of irradiation, the use of NAA tends to decline step by step.

4.3 Negative thermal ionization mass spectrometry (NTIMS)

Isotopic analysis by negative thermal ion mass spectrometry (NTIMS) has played a great role in determination of Re, Os and Pt for chronology (e. g. Peucker-Ehrenbrink and Blum, 1998; Sharma et al., 1999; Du Andao et al., 2001). Creaser et al. (1991) established a method of NTIMS for precise isotopic analysis of Os, Re and Ir and achieved an excellent result.

Compared with ICP-MS, the ratio of ionization is higher than that of ICP-MS, therefore, the sensitivity of NTIMS is, in general, higher than that of ICP-MS. Another advantage of NTIMS is no isobaric interference between Re and Os. Thus, separation of Os and Re is unnecessary.

4.4 Other techniques

Flame atomic absorption spectrometry (FAAS) is a useful tool to determine PGEs and gold at high levels, but is not suitable for those at the concentrations lower than $\text{ng} \cdot \text{g}^{-1}$. The use of FAAS for the PGEs analysis has been discussed in detail (Zhang Kai et al., 1997). Compared to FAAS, graphite flame atomic absorption spectrometry (GFAAS) has lower detection limits (Brzezicka and Baranowska, 2001). Osmium isotopes and silver, as tracers of anthropogenic metals in sediments, were determined by GFAAS and NTIMS, respectively (Ravizza and Bothne, 1996). The outstanding disadvantages of GFAAS are its poor productivity and severe interferences.

ICP-AES is characterized by high temperature ($\sim 10000 \text{ K}$), resulting in superior detection limits, low background emission, few chemical interferences and a wide linear response range (5 – 6 orders of magnitude). However, due to the requirement of a large sample weight to volume ratio, the application of the technique is limited.

5 Conclusions

As to sample decomposition, NiS fire assay is favorite for samples containing precious metals at $\text{ng} \cdot \text{g}^{-1}$ level. High-pressure digestion and Carius tube have been commonly applied to samples containing ultra-trace precious metals, which could promote greatly chronological research. As for pre-concentration, Te-coprecipitation is preferable. With regard to instrumental techniques, ICP-MS enjoys a leading role, due to high reliability, and NTIMS is a powerful tool for the analysis of Re, Os, and Pt.

Analyzing the development and application of simultaneous or sequential determination of multi-element PGEs and Au in the world, we can find out a basic formula for the whole determination procedure: a rapid, precise and accurate instrument determination method combined with complete sample decomposition and effective separation.

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