Analytical techniques for the determination of precious metals in geological and related materials

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1 Introduction

Determination of the precious metals in complex geological and allied materials has always been a fascinating field of analytical chemistry. Trace level occurrence, economic compulsions and the uncertainties in the world prices are the natural causes for the interest in their exploration and analysis. The renewed interest in the search for their deposits has led to improvements in the methodologies to determine the precious metals.

The members of the platinum group elements (PGE) *viz.*, platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os) and gold (Au) occur in nature as various mineral species chiefly as antimonides, arsenides, bismuthides, sulfides, tellurides and in the native state. The details of various minerals are described in Table 1.

The precious metals possess some unique geochemical characteristics. They are very refractory, having high boiling points and a strong affinity for iron[1] (siderophile) and for sulfur[2] (chalcophile). They are normally present in silicate rocks at very low levels[3] (Table 2). The precious metals often form discrete phases, such as alloys and therefore, unlike the rare-earth elements, they do not appear to partition themselves extensively between silicate phases. It is therefore a critical task to select a representative sample mass for analysis, since the presence or absence of one precious metal grain in the analyzed aliquot could have a significant effect on the analysis, particularly if small sample masses (< 5 g) are chosen. The onus therefore is on the analyst to establish that his/her data are not affected by large sample inhomogeneity errors.

The analytical chemistry of the noble metals has been reviewed extensively by Beamish and Van Loon,[4] Yi[5] and Barefoot.[6] Procedures can normally be divided into two stages. The first is the sample decomposition and preconcentration step in which these elements are separated from the host matrix. In

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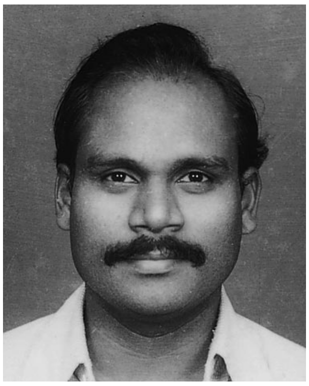

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this we have lead fire assay (Pb-FA), nickel sulfide fire assay (NiS-FA) and wet chemical attack using acid mixtures like hydrofluoric acid–*aqua regia* (AR), hydrobromic acid–bromine and cyanide leaching followed by solvent extraction and fusion with lithium borates, sodium hydroxide and sodium peroxide, *etc*., followed by a preconcentration step. The wet chlorination is another important decomposition procedure for the determination of precious metals.

The second is the measurement stage. In this we have various instrumental techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis (NAA).

2 Sample decomposition and preconcentration stage

Sample decomposition may involve three stages: (a) breaking open the matrix in which the precious metals are held; (b) solubilizing the gold and PGE minerals; and (c) complexing and or collecting the freed precious metals.

The two dry assay procedures *viz.*, Pb-FA and NiS-FA, after separation from the slag, result in buttons of manageable proportions amenable for easy manipulation. The other decomposition methods *viz.*, multi acid decomposition, fusion, *etc.*, accomplish only the first two steps necessitating another mechanism for ‘preconcentration’.

In the first instance fire assay techniques are discussed. The technique of fire assay, which still forms an important aspect of modern determinations of these elements, involves fusing together a sample and flux at a temperature of about 1000 °C. The resultant melt separates into two immiscible phases. The lighter glassy slag contains the aluminosilicates and base metals and is discarded, whereas the more dense ‘collector’ phase, usually composed of molten lead or nickel sulfide ‘button’, sinks to the bottom. The noble metals are strongly partitioned into this collector phase from which they may be subsequently separated for analysis.

2.1 Lead fire assay[7,8]

In this method all the precious metals are extracted from the sample by a reductive fusion and collected in a lead button. The fluxes used comprise sodium carbonate, borax, litharge and a reducing agent such as flour or charcoal. The exact composition of the flux depends on the nature of the sample. Sulfide and arsenide bearing samples have to be roasted at 600–800 °C to oxidize and to volatilize the sulfur and arsenic in order to prevent the formation of a matte (base metal sulfide) during fusion which would otherwise retain the precious metals. If the sample contains appreciable amounts of lead and sulfur then, instead of roasting, potassium nitrate would be added to the flux to oxidize the sulfide. Chromite samples are difficult to fuse and require increased amounts of sodium carbonate and borax along with silica and calcium fluoride. The sign of a successful operation is a highly fluid melt indicating the complete solubilization of the PGE and gold in the molten lead. Silver is normally added to the flux as powder or as a solution to collect the gold and the PGE. The ratio of Ag : Au + PGE is about 20 : 1. The molten lead and slag are poured into iron moulds and allowed to solidify. The slag is removed from the lead button by tapping and the lead button is then cupelled by placing it in a cupel made of bone ash or MgO and heating it to about 960 °C in an oxidative atmosphere. Most of the molten lead is absorbed (as PbO) by the cupel or is volatilized leaving a silver prill which contains Au, Pt, Pd and Rh. Osmium is completely lost during cupellation as volatile oxide and ruthenium and iridium are partially lost as oxides into the cupel. When estimation of gold is not required the PGE are collected by gold instead of silver. Most analytical methods proceed from the silver or gold prill stage, either determining the elements by NAA after appropriate radiochemical separations[8] or in a solution obtained thereafter by AAS, ICP-AES, ICP-MS, *etc.*

In general terms Pb-FA suits the determination of Au, Pt, Pd and Rh.[9] Hall and Pelchat[10] reported an improved Pb-FA method to determine Au, Pt and Pd. A suite of CRMs, lake

Table 1 Chemistry of the common minerals of gold and platinum group elements

Gold—
Free or native metal is the major source

Other Minerals are (a) calverite, Au, Te_2; (b) petzite, $(Ag, Au)_2$, Te; (c) sylvanite Au, Ag, Te_4
Certain sulfide and arsenide minerals also contain appreciable amounts of gold.

Platinum group elements—
Free or native platinum and inter-metallic alloys of PGE occur in significant proportions.[114,115] Other important minerals of PGE are:

	Ru	Rh	Pd	Os	Ir	Pt
(a) Antimonides			Sudburyite (Pd, Sb) Stibiopalladinite (Pd_3Sb)			Stumpflite (Pt, Sb) Geversite ($PtSb_2$)
(b) Arsenides		Holling worthite (Rh, As, S)			Irsarite (IrAsS)	Sperrylite ($PtAs_2$)
(c) Bismuthides			Frodite (Pd, Bi_2)			Insiswaite (Pt, Bi_2)
(d) Sulfides	Laurite (Ru, S_2)		Vysotskite (Pd, Pt)S	Erlichmanite (Os, S_2)		Braggite (Pt, Pd)S Cooperite (Pt, S)
(e) Tellurides			Merenskyite (Pd, Te_2) Michenerite (PdBiTe)			Moncheite (Pt, Te_2)
(f) Alloys	Ruthenosmiridium (Ir, Os, Ru)			Iridosmium $Os_{80}Ir_{20}$	Osmiridium $Ir_{80}Os_{20}$	Isoferroplatinum (Pt_3, Fe) Tulameenite (Pt_2CuFe) Platiniridium ($Ir_{50}Pt_{50}$)

sediments and humus materials has been investigated. Practical detection limits of 2, 0.1 and 0.5 ppb for Au, Pt and Pd were reported, respectively. Further improvements in the detection limits of Pd have been suggested by purifying the flux components.

2.2 Nickel sulfide fire assay[11,12]

The effectiveness of NiS as a collector for precious metals has been known since the initial work of R. V. D. Robert at the National Institute of Metallurgy, South Africa. In this preferred assay technique for the collection of all the precious metals, the cupellation stage is absent thereby minimizing their losses.

The sample and flux mixture consisting of sodium carbonate, borax, nickel (as metal or as oxide or carbonate) and sulfur is fused at 1000 °C for 1.5 to 2 h. The NiS formed during the fusion collects the gold and PGE. The crushed NiS button, after separation from matrix, is treated with hot concentrated HCl and the insoluble precious metal sulfides along with the dissolved precious metals are then collected on tellurium. The tellurium co-precipitation step effectively collects all the PGE sulfides avoiding the H_2S passing step at this stage. The black precipitate is filtered off and analysed either directly by NAA or dissolved in *aqua regia* or HCl + hydrogen peroxide and analysed by ICP or AAS.

The advantages of this method are:

(a) All the PGE are collected including Os, Ir and Ru.

(b) Fewer modifications in the flux compositions are required for varying sample types.

(c) Preliminary removal of nickel and sulfur in the sample is not required.

(d) Large sample sizes can be handled since the flux to sample ratio is smaller.

(e) The NiS button may also be used directly for laser ablation studies.

On the other hand the disadvantages of the NiS fire assay are:

(a) The relatively high cost.

(b) The large quantity of hydrogen sulfide gas evolved during the treatment of the NiS button with hydrochloric acid requires an efficient fume and gas extracting system.

(c) When dealing with low grade samples the PGE impurities in the relatively large weights of reagents used overshadow the analyte concentrations themselves. Of particular interest is the PGE impurity in the nickel salts. Nickel manufactured by the carbonyl process is preferred for the purpose.

Comparison of the two assay procedures for the precious metal determination in SARM-7, CHR-Pt+ and 12 other samples from different ore types of the Keivitsa mafic layered intrusion in Northern Finland comprising quartz carbonate rock, hornblendite and peridotite were reported. Quantitative recoveries for Au, Pt and Pd were seen in Pb-FA while all the PGE except gold were recovered quantitatively by NiS-FA.[13] The effect of collector mass on the recovery of PGE and gold in a platinum ore grade sample and a komatiite sample which contained < 10 ng g^{-1} of PGE were investigated in detail by Frimpong *et al.*[14] They concluded that recoveries are more dependent on the sample type and PGE content rather than the collector mass. Asif and Parry[15,16] and other workers[17,18] have used the mini fusion technique involving buttons of around 0.5 to 1 g mass for the quantitative recovery of precious metals.

Formation of different phases based on the flux composition and the distribution of different PGE in discrete NiS mineral phases has been the subject of a study by Urban *et al.*[19] The NiS button has also been used by Silvester and Eggins[20] for a detailed investigation for the direct determination of PGE and gold by the laser ablation technique.

Table 2 Elemental abundance of PGE and Au

Element	Range in unmineralized samples[3]/ng g^{-1}
Platinum	1–10
Palladium	0.1–3
Rhodium	< 0.5
Ruthenium	< 1
Iridium	0.3–5
Osmium	< 0.1
Gold	0.1–10

2.3 Chlorination

The technique involves conversion of precious metals into respective sodium salts by heating (at 580 °C) with sodium chloride in a current of chlorine.[21,22] Analytes occurring as native metals, natural alloys or sulfide minerals are attacked. Separation of the precious metal chlorides is effected by water or weak acid dissolution and the insoluble and non-chlorinated matrix is separated by filtration. For chlorination resistant minerals, such as silicates, microwave digestion is adopted.[23]

The advantages of the method are very low blanks and the large sample masses that can be analysed. The technique (using Carius tube) has found wide application in Os/Re geochemistry.[24,25]

2.4 Wet chemical attack

In this technique, which forms an important and widely followed method for precious metal determinations, mixtures of HCl, $HClO_4$, HNO_3, HBr, Br_2, H_2O_2 *etc.*, are used. Serious problems, however, beset the multi-acid digestion procedures. Some of the reasons for this are particle size,[26] varying sample matrix and incomplete wetting[27] as well as the different experimental conditions used. Therefore an important prerequisite for obtaining reproducible data by the wet chemical attack is to ensure a uniform sample mesh size of 200–250 otherwise discrete noble metal minerals may be completely occluded within the grains of the host matrix and may not be effectively dissolved by acid attack. Roasting at 600 °C for an hour to volatilize sulfur and oxidize organic matter is preferable to effect complete dissolution of the noble metals.

For the sake of convenience the available methods can be discussed under two headings.

2.4.1 Gold. Two oxidizing acid leaches are in use for the extraction of gold from rocks and sediments: AR (HCl + HNO_3; 3 + 1) and bromine–hydrobromic acid mixture (0.5% bromine in 9 M HBr). AR, a medium often used for the dissolution of sulfides, has been reported to be quite efficient for the solubilization of gold in geological materials.[28,29] Addition of HF along with AR and Br_2–HBr has also been employed by some workers[30,31] to effect complete dissolution of gold in siliceous materials. However, in the case of iron/sulfide ores an initial attack of the sample with HCl is necessary as this would dissolve any iron oxide coating on gold bearing particles and allow contact of such particles with AR in the second step. Strong and Murray-Smith[32] demonstrated the importance of incorporating this step (heating in 6 M HCl) in some iron and sulfide ores and observed that recoveries of gold rose from 12% to 100%. Digestion is carried out on a sample weight of about 10 g with heating to hasten the dissolution.

The simplicity of either attack (AR or Br_2–HBr) renders the method amenable to greater output.[33] Recently some workers[34,35] also reported methods suitable for batch analysis utilizing fusion techniques for variety of sample types.

After the gold is solubilized its separation from matrix elements is achieved by solvent extraction into methyl isobutyl ketone (MIBK),[36,37] co-precipitation on tellurium[38] or mercury[39] to avoid interferences at the measurement stage and to effect preconcentration. Using a 2 g sample Balaram *et al.*[30] reported a rapid multi-acid digestion procedure utilizing mixtures of AR, Br_2, HF, $HClO_4$ and H_2O_2 which is amenable for batch analysis. The report deals with gold, Pt, Pd and Ag in a suite of 12 CRMs.

Cyanide leaching of gold has been used commercially for many years,[40] more for rocks containing metallic gold at 'ppm' rather than 'ppb' levels. In this technique if gold is to be extracted into MIBK prior to instrumental analysis, it must first be oxidized from the mono- to the trivalent state with Br_2–HBr or potassium permanganate.[41]

Reddi *et al.*[33] reported a method where gold was extracted from a 20 g sample with HCl and HBr–Br_2 mixture at room temperature with agitation. The solubilized gold metal was then coprecipitated on tellurium and measured by flame AAS. Results compared well with those obtained by Pb-FA. The method particularly suits placer samples.

Hall *et al.*[27] reviewed the various current methods used for the estimation of gold in geological materials. In their view, major sources of error at the 10 g weight or greater are believed to be due to non-wetting of the samples, inefficient mixing during digestion and also due to the protection of gold by unattacked gangue. Moreover, the proportion of gold leached by AR is dependent upon the sample matrix. Therefore, several workers suggested that addition of HF along with AR and, intimate, prolonged contact between the grains of the sample and the acid mixture is necessary for complete solubilization of gold. Further, when the mineralogy of the sample is unknown, and particularly if the presence of chromite is suspected, the use of a fire assay decomposition procedure is preferred to a wet chemical procedure.

2.4.2 Platinum group elements (PGE). Sample preparation by means of acid digestion has been studied and used extensively. Extraction of PGE by acids have proved to be a more rapid and economical alternative to fire assay. Often, acid extractions do not result in complete recovery of the PGE. Usually, additional preconcentration steps are needed prior to the determination of the analytes after acid treatment.

The results for a variety of samples have not always been quantitative and have depended upon the type of samples as well as the experimental conditions. Dissolution of PGE in AR may be limited because some proportion of the elements may be embedded within refractory chromite and/or silicate minerals. In addition, PGE may occur as alloys or compounds which are insoluble in AR. Further, the ratio of sample weight to the volume of acid is also a significant factor in acid dissolution techniques.

Different methods such as digestion with multiple acids in open vessels,[30] autoclave decompositions,[42] microwave digestions[43] and fusion with lithium borates, sodium hydroxide and sodium peroxide[44] prior to the determination of selected PGE have been reported. The details of studies by various workers are furnished in Table 3.[45–53]

It is evident from Table 3 that the choice of sample decomposition method depends on the particular elements to be determined and the sample matrix. Further, separation by co-precipitation, ion-exchange or extraction to preconcentrate the analytes may lower detection limits and remove or reduce interelement interferences to a tolerable level.

Thus it may be deduced that wet chemical attack has the following advantages: (a) low cost; (b) low blanks; (c) amenability for batch analysis; and (d) it is ideal for semi-quantitative data generation for exploratory work.

The drawbacks are: (a) limitations in handling large sample weights contributing to nonhomogeneity problems (nugget effect); (b) partial dissolution of PGE and gold when they occur as alloys or compounds in which case a fusion step is required; (c) does not attack refractory minerals such as chromite, *etc.*; and (d) not comprehensive for a wide range of sample types as against fire assay techniques.

3 Instrumental/measurement stage

The solution obtained after the digestion/dissolution or pre-concentration stage is presented to an analytical instrument for the measurement of the analytes. More often the choice of the analytical technique depends on the availability and the level of occurrence of the precious metals.

3.1 Atomic absorption spectrometry (AAS)

3.1.1 Flame AAS.[54–56] The flame version (air–acetylene or nitrous oxide–acetylene) of the AAS has found few applications in the precious metal determinations except possibly gold. The reason lies in the poor sensitivity of the technique and the level of analyte concentrations sought. The flame types used and the interferences encountered in the estimation of gold and PGE are described in Table 4 and the detection limits in Table 5. Evidently these elements normally require some separation and preconcentration prior to their determination.[57,58] Beamish and Van Loon[59] discussed the usage of this technique for the analysis of Pt, Pd and Au in ores and concentrates. Hall and Bonham-Carter[58] discussed the flame AAS and its attributes in

Table 3 Sample decomposition for the determination of PGE (selected samples)

Reagents	Separated by	Determined by	Reference
HBr–Br_2 (Pt, Pd)	Co-precipitation	Spectrophotometry	Thompson, 1967[45]
HBr–Br_2 (Pt)	Extraction	FAAS	Stanton and Ramankutti, 1977[46]
Aqua regia (AR) (Pt, Pd)	Co-precipitation	GFAAS	Fryer and Kerrich,1978[47]
HF–AR (Pt, Pd, Rh)	Co-precipitation	GFAAS	Sighinolfi *et al.*, 1984[38]
AR (Pt, Pd)	Ion exchange	GFAAS	Branch and Hutchison, 1986[48]
$LiBO_2$–$Li_2B_4O_7$/AR (Pt, Pd)	Ion exchange	ICPAES	Chung and Barnes, 1988[49]
HNO_3–HF–$HClO_4$/AR (Pt, Pd)	Extraction	GFAAS	Brooks and Lee 1988[50]
HF–AR/Na_2O_2[a] (Pt, Pd, Rh, Ir, Ru)	Ion exchange or co-precipitation	GFAAS	Sen Gupta, 1989[51]
HNO_3–HCl–$HClO_4$/AR (Pd)	Extraction	GFAAS	Wilson *et al.*, 1989[52]
Sodium peroxide	Co-precipitation	RNAA	Nogueira and Figueiredo, 1995[34]
HNO_3–HCl–HF–$HClO_4$ (Pt, Pd, Ir, Rh, Au)	Direct estimation	ICP-MS	Totland *et al.*, 1995[43]
Sodium peroxide fusion (Pt, Pd, Ru, Ir)	Tellurium co-precipitation	ICP-MS	Enzweiler *et al.*, 1995[35]
AR, Br_2–HF, $HClO_4$, H_2O_2 (Pt, Pd, Au)	Direct estimation	ICP-MS	Balaram *et al.*, 1997[30]
HF–HNO_3–HCl (Pt,Pd,Rh,Ru,Ir)	Ion exchange	ICP-MS	Jarvis *et al.*, 1997[53]
Sodium peroxide fusion (Pt, Pd, Ru, Rh, Ir, Au)	Se/Te carrier	ICP-MS	Amosse, 1998[44]

[a] The designation HF–AR/Na_2O_2 means that the sample is first digested with HF–AR and the insoluble residue remaining after digestion is fused with Na_2O_2.

relation to other techniques in the estimation of Pt, Pd and Au. Recently Hoang *et al.*[60] reported a modified flame AAS method for the determination of gold in ores. Zhang *et al.* used the technique for the estimation of precious metals with dithiozone chelate forming resin[61] and gold–Orange G chelate forming resin.[62]

It is evident from Table 4 that the necessity of using suppressing agents and the poor sensitivity of Pt, Ir, Ru and Os limits the applicability of flame AAS only to the estimation of precious metals in concentrates.

3.1.2 Graphite furnace AAS.[63,64] A variant of the AAS technique, graphite furnace AAS, offers the unique advantage of enhanced sensitivity over the flame version. The residence time of individual atoms in the optical path is approximately 1–2 s for the graphite furnace technique while in the flame atomization it is of the order of milliseconds. The detection limits are thus lowered by at least one to two orders of magnitude depending on the element and sample volume. Thus GFAAS competes favourably in terms of detection limits with other sensitive techniques such as NAA and ICP-MS in precious metal determinations.

The major disadvantages, however, are its inherently lower productivity and more severe interferences. Matrix modification, background correction using a continuum source (*e.g.*, deuterium lamp) or Zeeman and standard addition, *etc.*, are useful in overcoming some of the interferences. For PGE mutual interferences appear to be more common especially at high concentrations where no specific modifiers are suggested.[65,31] However for gold, 10 μL of 1000 mg L^{-1} of iridium is used as a modifier.[65]

Simultaneous multi-element instruments overcome the problem of lower productivity to some extent. In a study Sen Gupta[31] analyzed the precious metals in two groups *viz.*, Ru, Rh, Pt and Ir in one firing and Au, Pd and Ag in another. Using polarized Zeeman correction, three Canadian CRMs and four new Canadian candidate reference materials were studied. Recently Kubrakova *et al.*[66] has used this technique in conjunction with microwave decomposition followed by slurry nebulization for the determination of low levels of PGEs. Belskii *et al.*[67] and Schuster and Schwarzer[68] have also used this technique for precious metal analysis.

Various operating parameters for the determination of precious metals by GFAAS are furnished in Table 6.

3.2 Inductively coupled plasma atomic emission spectrometry (ICP-AES)

Optical emission spectroscopy, with argon plasma as the excitation source (ICP-AES), has gained world wide acceptance as a versatile analytical technique for geological samples. The technique is characterized by low background emission hence superior detection limits, high temperature (~ 10 000 K) leading to few chemical interferences and wide linear response range (5–6 orders of magnitude).

The ICP-AES in conjunction with Pb-FA and AR dissolution of the silver prill has been recognized as a widely applied technique for the determination of Au, Pt and Pd in geological samples. With precautions like adding scandium as internal standard to minimize the effect of the variations in acid concentrations, adding uniform amounts of magnesium to standards and analyte solutions to reduce the effect of magnesium contamination (from Mg adhering to the silver prill) the method is quite effective.[58] When all the PGE are to be estimated NiS-FA and tellurium co-precipitation (Te-Coppt) are employed.

However the limited use of ICP-AES in precious metal analysis, as evinced by the fewer publications, is mainly due to the large sample to volume ratio required (typically, 20 g in 3

Table 5 Comparison of detection limits for PGE and Au (Average of literature and manufacturer's suggested values)

	Limit of determination in ideal solutions[26]/ng mL^{-1a}				
Element	FAAS	GFAAS[b]	ICP-AES	ICP-MS	INAA[c]
Pt	210	0.6	110	2	5
Pd	45	0.3	88	1	2
Rh	15	0.3	88	2	0.1
Ru	900	0.6	60	8	5.0
Ir	1500	1.5	54	4	0.1
Os	300	6.0	0.7	2	1
Au	30	0.03	34	1	0.5

[a] Ideal solution detection limit is an estimate of the 6σ detection limit of single element solutions. [b] Based on 100 μL injection volume. [c] By NiS–INAA (ref. 95).

Table 6 Operating parameters for GFAAS[a]

Element	Wavelength/nm	Ashing temp./°C	Atomization temp./°C
Au	242.8	1000	2500
Pt	266.0	1800	2700
Pd	244.8	1400	2600
Rh	343.5	1400	2600
Ru	349.9	1400	2700
Ir	208.9	1400	2700
Os	290.9	1400	2700

[a] Literature values for the operating parameters vary depending on the instrument, method of preconcentration, *etc.* (for example see Zereini *et al.*, 1994;[64] Hall, 1990;[80] Torgov *et al.*, 1996[42])

Table 4 Precious metal determination by flame AAS[9]

Element	Flame type	Detection limit[9]/ ng mL^{-1}	Wavelength/ nm	Interferences
Pt	Air–acetylene (lean flame)	100	265.9	Complex cationic interferences (suppressed by 1% lanthanum)
Pd	Air–acetylene (lean flame)	20	244.8	Several cationic interferences; 1% lanthanum suppresses these effects
Rh	Air–acetylene (lean flame)	10	343.5	Complex cationic interferences (suppressed by 1% lanthanum); 3% sodium sulfate suppresses anionic interferences
Ru	N_2O–acetylene (reducing)	100	349.9	No significant cationic interferences in dilute solutions
Ir	Air–acetylene (reducing)	600	208.9	Diverse interferences. Minimal cationic interferences
Os	N_2O–acetylene (reducing)	100	290.9	Minimal cationic interferences in dilute solutions
Au	Air–acetylene (lean flame)	20	242.8	Minimal cationic interferences

ml) to achieve a detection limit of 1,2,10 ppb for Au, Pd and Pt, respectively. This leaves no room for repeat analysis and the accuracy in diluting to such low volumes is difficult to achieve.

Schramel and co-workers have used the technique for the determination of gold in soil by dithiol–cotton fibre column separation[69] and its reliability and measurement uncertainty in environment samples.[70]

The technique has also been utilized for the determination of Au, Pt and Pd after preconcentration separation by porous resin containing imidazoline group[71] and for the determination of Pd and Rh in high purity alloys.[72]

The operating parameters and possible interferences applicable to ICP-AES in precious metal analysis are given in Table 7.

3.3 Inductively coupled plasma mass spectrometry (ICP-MS)

The ICP-MS technique combines advantages of the high temperature plasma source with the highly sensitive detection capabilities of the mass spectrometer. In this technique the mass spectrometer receives ions from the plasma tail flame after a two-stage vacuum reduction interface. With wide linear dynamic range, essentially simultaneous multi-element analytical capability due to rapid scanning facility and a fair degree of tolerance to interference free measurement of analytical signal the ICP-MS today is a widely used analytical tool for trace metal analysis. A particular benefit of this technique is the possibility of isotope dilution calibration strategies which account for the few interferences and loss of analytes at the preparation stage.

Date *et al.*[73] led the way in assessing the potential of ICP-MS for the estimation of precious metals and later various other workers for different types of samples. Among them Hall, Jackson, Jarvis, *etc.*, have pioneered the technique in precious metal analysis. Newer sample introduction methods such as laser ablation, electrothermal vaporization, slurry nebulization, *etc.*, have widened the applicability of the technique.

The NiS-FA followed by ICP-MS, after dissolution of the button in concentrated HCl and co-precipitation on tellurium, is the most widely accepted method for precious metal determinations. Compared to NAA, with similar detection capabilities, the NiS-FA/ICP-MS offers the advantage of eliminating the 5–7 d delay (for counting). Table 8 describes the details of selected studies in precious metal analysis.[74–94]

Table 7 Operating parameters for the determination of precious metals by ICP-AES[116]

Element	Emission line	Wave-length/nm	Detection limits[116]/ng mL^{-1}	Interference and spectral lines/nm	
Pt	II	214.423	30	Al I	214.54
				Fe II	214.44
					214.52
Pd	I	340.458	44	Fe I	340.44
				V II	340.44
				Ti II	340.50
				W I	340.53
Rh	I	343.489	60	V II	343.54
Ru	II	240.272	30	Fe II	240.26
	I	349.894	111		
Ir	II	224.268	27	Cu II	224.26
				Fe II	224.18
				Ni I	224.29
Os	II	225.585	0.36	Fe II	225.58
				Fe I	225.59
				Ni I	225.59
				Cr II	225.60
Au	I	242.795	17	Fe II	242.83
				Mn II	242.78
				Mn I	242.80
				V I	242.83
				V II	242.73
				W II	242.75
		197.819	38	Al I	197.84

The details of the isotopes, detection limits and potential interferences are furnished in Table 9.

3.4 Neutron activation analysis (NAA)

Neutron activation analysis is also one of the preferred techniques for precious metal analysis. The two variants of NAA *viz.*, instrumental NAA and radiochemical NAA scores over other techniques due to their sensitivity, accuracy and freedom from contamination.

3.4.1 Instrumental neutron activation analysis (INAA).

Gold. In this technique direct analysis of a sample is carried out after irradiation thus avoiding any separation or preconcentration. A popular application[58] of the technique, *i.e.*, determination of Au, involves neutron irradiation of the encapsulated sample, a delay period of 5–7 d (half life = 64.8 h) and measurement of the ^{198}Au nuclide at 412 keV. This method is simple and sensitive reaching a detection limit of 5 ppb for a 10 g sample. Iridium of the PGE can also be determined by this method. However, irradiation facilities should be available for handling such large sample masses. With less sample weights, on the other hand, nugget effect becomes a major problem.

Possible sources of error are due to: (a) nugget effect; (b) inefficient control of neutron flux; (c) high europium concentration in the sample (411.1 keV Eu interferes on 411.8 keV Au peak[95]); and (d) variations in the sample/standard position relative to the detector.

PGE. For PGE a chemical separation prior to irradiation is necessary to obtain better sensitivities and or eliminate interferences. Today most INAA results are derived after NiS fusion, which accomplishes separation of the analytes from the matrix. Due to lower background, better detection limits are obtained. The assay procedure also eliminates the problem of non-homogeneity in analyte distribution, direct interference of calcium on Pt[95] and, more importantly, fission product production of Pd and Ru from any uranium in the sample.

Hoffman *et al.*[12] pioneered the technique and obtained detection limits of 0.1, 5, 5, 3, 1, 0.1 and 2 ppb respectively for Au, Pt, Pd, Ru, Rh, Ir and Os. Interference of Au on Pt (Compton scattering) and, when Te-Coppt is used, choice of the less sensitive 208 keV to remove the interference of Te on Pt are some of the noteworthy points. The NiS/Te-Coppt method has also been studied by Shazali *et al.*[96]

3.4.2 Radiochemical neutron activation analysis (RNAA).

Neutron activation analysis with radiochemical separation is a precise and accurate method for precious metal determination in certain type of samples. Radiochemical separations have several advantages over other analytical techniques in particular the avoidance of contamination and the ability to add carrier to monitor and correct for losses. The main limitation of RNAA is the restriction on sample mass so as to limit the activity of irradiated samples that are then subjected to a radiochemical method. The nature of the sample, in particular the mineralogical considerations, strongly influence the precision and accuracy.

Individual separation and counting schemes are necessary for each of the precious metals. Rhodium, which has short-lived nuclides, is not determined by RNAA. Parry[97] and Artem'ev[98] in their review articles discussed in detail the various radiochemical separation procedures employed for the precious

Table 8 Published methods to determine precious metals in geological materials by ICP-MS (selected examples)

Sl No.	Matrix	Elements determined	Notes on the method	Reference
Lead fire assay—				
1	Sulfide (SU-1a), Ultramafic rock (UM-1)	Au, Pt, Pd	Analytes collected in Ag prill, dissolved in HNO_3/HCl. External calibration matched in Ag concentration	Hall and Bonham-Carter, 1988[58]
2	Hydrothermal fluids	Au, Pt and Pd	Evaporation and Pb-FA of the residue. External calibration	McKibben *et al.*, 1990[82]
3	Stream sediments, rocks, soils, heavy mineral concentrates	Au, Pt, Pd	Analytes collected in Ag prill, dissolved in HNO_3/HCl. External calibration matched in silver concentration	Simpson *et al.*, 1990[75]
4	Rocks, soils, sediments and humus samples	Au, Pt, Pd	Analytes collected in Ag prill, dissolved in 3 M HNO_3 + 2.5 M HCl. Synthetic calibration solutions in matching acid and silver concentrations	Hall and Pelchat, 1994[10]
NiS fire assay—				
1	Pyroxene (SARM-7, sulfide concentrate (PTC-1)	Au, Pt, Pd, Rh, Ru and Ir	NiS button dissolved in HCl–H_2S. Precious metal sulfides dissolved in HCl–H_2O_2. External calibration	Date *et al.*, 1987[73]
2	Pyroxene (SARM-7), sulfide concentrate (PTC-1), sulfide (SU-1a)	Au, Pt, Pd, Rh, Ru, Ir and Os	NiS fusion; NiS dissolved in HCl+Te-Coppt; Au/PGE dissolved under reflux with HNO_3–HCl. Internal standardization with Cd for Ru, Rh, Pd and Tl for Os, Ir, Pt, Au. Isobaric correction for NiAr, NiCl on Ru, Cu, Ar on Pd and TaO on Au	Jackson *et al.*, 1990[76]
3	Stream sediments, rocks, soils, heavy mineral concentrates	Au, Pt and Pd	NiS button dissolved in HCl–H_2S and precious metal sulfides dissolved in HCl–H_2O_2. External calibration	Simpson *et al.*, 1990[75]
4	Rocks, ores and heavy mineral concentrates	Pt, Pd, Rh, Ru and Ir	Cost effective NiS fusion. NiS dissolved in HCl/Te-Coppt. PGE sulfides in HCl–H_2O_2. Internal standardization with Tl for Pt and Ir and Tm for Rh, Ru and Pd. External calibration	Reddi *et al.*, 1994[74]
5	SARM-7, CHR-Pt+ CHR-bkg	Au, Pt, Pd, Rh, Ru, Ir, Os	NiS-FA compared against Pb-FA and AR leach. NiS button dissolved in HCl, Te-Coppt; for Pb-FA studies silver prill dissolved in AR. For AR leach 5 g sample + 10 ml AR	Juvonen *et al.*, 1994[13]
6	Slurry made out of standard solutions, automobile Pd catalysts	Pt, Rh, Ru, Os and Ir	Varying flux constituents. Phase distribution study by electron microprobe	Urban *et al.*, 1995[19]
7	Ore grade sample (SARM-7), komatiite (BF-4)	Au, Pt, Pd, Rh, Ru, Ir and Os	Effect of collector (NiS) mass and concentration of Ni, S, Cu and Zn in the sample on the recovery of precious metals	Frimpong *et al.*, 1995[14]
8	Komatiite (WITS-1), SARM-7, PCC-1	Au, Pt, Pd, Rh, Ru, Ir and Os	Low grade standard preparation using different techniques/laboratories	Tredoux and McDonald, 1996[77]
9	Many CRMs comprising ultra basic rock, chromitite, Cu–Ni ore, *etc.*	Pt, Pd, Rh, Ru, Ir and Os	NiS button dissolved in HCl/Te-Coppt. Os content calculated using isotope dilution. The objective of the study is to establish a low blank method for PGE and Os	Sun *et al.*, 1998[78]
Wet chemical/water/fluids/fusion—				
1	Water (surface, brines)	Au, Pt and Pd	Analytes adsorbed on activated charcoal; solubilized in AR after ashing. Isotope dilution for Pt, Pd	Hall, 1988[81]
2	Rocks and ores	Ru, Pd and Ir	HF–AR decomposition, residue fused with Na_2O_2 separation of the analytes by Te-Coppt. Isotope dilution	Sen Gupta and Gregoire, 1989[79]
3	Vegetation	Au, Pt and Pd	Ashing at 870 °C; HF–AR decomposition of the residue, Te-Coppt and dissolution in AR. External calibration	Hall *et al.*,1990[80]
4	Surface and ground waters	Au, Pt and Pd	Concentration by evaporation. External calibration	Wood and Vlassopoulos,1990[84]
5	Hydrothermal fluids	Au, Pt and Pd	Activated charcoal adsorption of the analytes; solubilized in AR after ashing. Isotope dilution for Pt and Pd	McKibben *et al.*, 1990[82]
6	Interstitial pore fluids	Au, Pt and Pd	Evaporation of the fluids; dissolution of the residue in HF–AR, Te-Coppt, isotope dilution for Pt and Pd	Parkinson *et al.*,1991[83]
7	SARM-7, PTA-1, PTC-1, PTM-1, SU-1a, GXR-1, GXR-4, chromatite (OU-CX)	Au, Pt, Pd, Rh, Ru, Os and Ir	AR leach followed by analysis of residue by energy despersive XRF and by INAA	Gowing and Potts, 1991[86]
8	Fresh waters	Au	MIBK extraction	Cidu *et al.*, 1994[85]
9	SARM-7, SU-1a, NBM-6b	Au, Pt, Pd, Rh, Ru and Ir	AR–microwave digestion. Filtered solution diluted (100 : 1) with HNO_3 and analysed by ICP-MS	Nowinski and Hodge, 1994[87]
10	Chromitite (2/77), SARM-7, SU-1a	Au, Pt, Pd, Rh, Ru and Ir	Microwave acid dissolution followed by fusion of the residue with Na_2O_2–Na_2CO_3 or pure Na_2O_2 dissolving the melt in pure HCl	Totland *et al.*, 1995[43]
11	Rocks, ores and other geological samples	Pt, Pd, Ru and Ir	Na_2O_2 fusion, separation of analytes by Te-Coppt. Isotope dilution	Enzweiler *et al.*, 1995[35]
12	Komatiite (WITS-1), SARM-7, PCC-1	Au, Pt, Pd, Rh, Ru, Ir and Os	Low grade ore standard preparation (WITS-1) using various methods	Tredoux and McDonald, 1996 [77]
13	Sulfide ores (CH-1, CH-3, ASK-3, PM-1, SARM-7)	Au, Pt and Pd	Multi-acid digestion involving AR/Br_2/HF/$HClO_4$, and H_2O_2 in Teflon vessels	Balaram *et al.*, 1997[30]
14	Synthetic multi-element solutions, (SARM-7, PTM-1, PTC-1)	Au, Pt, Pd, Rh, Ru and Ir	Different acid mixtures comprising HF, HNO_3, HCl, $HClO_4$ followed by Dowex 1-X8 based anion exchange separation	Jarvis *et al.*, 1997[88]
15	Geological and related materials	Au, Pt, Pd, Rh and Ir	High pressure microwave digestion with HF and AR; insolubles fused with Na_2O_2. Ion exchange separation of combined solutions	Coedo *et al.*, 1997[89]
16	SARM-7, PTC-1, PTM-1, GXR-1,GXR-4 and GAu-16, GAu-17, GAu-18	Au	Roasted sample treated with mixture of HCl and HNO_3 and the dried residue treated with $KMnO_4$ and HCl	Rao and Balaram, 1998[90]

Table 8 continued over page—

Table 8 *Continued—*

Sl No.	Matrix	Elements determined	Notes on the method	Reference
17	WMS-1, WMG-1, WPR-1, WGB-1, UMT-1	Au, Pt, Pd, Rh, Ru and Ir	Peroxide fusion in zirconium crucibles and Se/Te as carriers	Amosse, 1998[44]
Alternative techniques—				
1	PTA-1, PTC-1,PTM-1, SARM-7	Au, Pt, Pd, Rh, Ru, Ir and Os	Slurry nebulization of samples (< 5 μm) with AR+ tetrasodium pyrophosphate as dispersive medium. Modified instrumental parameters, *e.g.*, increased forward power, nebulizer gas flow rate, 3 mm torch injector tube. Results (RSD 2–30%) tallied with published data	Totland *et al.*, 1993[91]
2	SARM-7, CHR-Pt+, chromitite (2/77)	Au, Pt, Pd, Rh, Ru, Ir and Os	Laser ablation of 1 g polished NiS button using Nd:YAG laser. Standardization against NiS buttons of CRMs and synthetic buttons obtained by doping high purity quartz. Good recovery for all except Pt (~ 30% low)	Jarvis *et al.*, 1995[92]
3	Natural waters, automobile catalysts and common commercial analytical reagents	Pt	Flow injection incorporating alumina micro-column coupled with ICP-MS for online preconcentration (factor of 600). LLD 4 ng L^{-1}	Hidalgo *et al.*, 1996[93]
4	UMT-1, WPR-1, WMG-1, GPt-1, GPt-6, CHR-BKg	Au, Pt, Pd, Ru, Rh, Ir and Os	UV laser ablation of the NiS button. Calibration using buttons prepared using doped quartz. Good agreement with certified values except Rh in UMT-1 and WMG-1 due to interference from Cu	Jorge *et al.*, 1998[94]

metal determination. Stone and Crocket[99] described a RNAA technique with tellurium co-precipitation for the determination of Pd, Pt, Ir, Au in sulfur depleted rocks.

McDonald *et al.*,[100] Nguyen[101] and other workers[15,17,102–108] have utilized the NAA technique for the precious metal analysis in different types of samples. The full details of the procedures are given in Table 10.

Various experimental details in the NAA analysis of precious metals are described in Table 11.

4 Conclusions

The wet chemical attack procedures comprising acid mixtures or fusion by strong alkalis have been widely applied for sample decomposition. Especially, the former has the ability to handle large sample masses. Incomplete attack[108] is the bane for multi-acid procedures except for Pt, Pd and Au in favourable matrices. The fusion methods place a restriction on the sample mass and increases salt content. An initial acid attack followed by fusion of the residue is a viable but more tedious method.

On the other hand the traditional assay procedures score over other methods by presenting a mass of manageable size wherein the precious metals are concentrated. The more practiced Pb-FA has been proved to be a good collector but the cupellation stage accounts for major losses except for Au, Pt and Pd. The nickel sulfide assay process, which does not involve a cupellation step, has been accepted to be a very good technique for the precious metals. Both fire assay procedures (Pb- and NiS-) in common usage require the judicious balancing of flux components and experimental conditions by the assayer. The dissolution of the NiS button in HCl accounts for a partial loss of precious metals, which are collected by the Te-Coppt procedure. The technique also ideally suits RNAA measurements due to the complete separation from matrix (including uranium).

Table 9 Isotopes generally used for analytical measurements, detection limits and potential interferences in ICP-MS[6,43]

Isotope	Abundance (%)	Detection limits[a]/ ng mL^{-1}	Potential interferences
^{101}Ru	17.0	0.22	^{84}SrOH, ^{61}Ni^{40}Ar, ^{64}Ni^{37}Cl
^{103}Rh	100	0.03	^{86}SrOH, ^{87}SrO, ^{63}Cu^{40}Ar
^{105}Pd	22.3	0.17	^{88}SrOH, ^{89}YO, ^{65}Cu^{40}Ar
^{189}Os	16.1	0.27	^{173}YbO
^{193}Ir	62.7	0.07	^{177}HfO
^{195}Pt	33.8	0.11	^{179}HfO, ^{178}HfOH
^{197}Au	100	0.06	^{181}TaO, ^{180}HfOH

[a] Detection limit calculated as the concentration equivalent to 3σ of the background signal in 1 M Aristar grade HCl.

Although most instrumental techniques today require separation of the analyte from matrix components, the inherent powers of detection of ICP-MS, NAA and GFAAS are such that the desirable determination limits for Au and PGE in rocks, soils and sediments are easily attained. Indeed, a limiting factor is the contamination contributed during the preparation steps from reagents. The NiS fire assay has the advantage of being an efficient means of collecting all the PGE and perhaps is more easily adapted to handle refractory matrices. Hence, with reduction in the size of the nickel buttons without sacrificing the accuracy and the resultant lowering of blank levels, the NiS method may be well suited for the PGE analysis. Another area of interest in the Pb-FA is the acid dissolution of the lead button without cupellation or scorification[109] to eliminate the cupellation losses and contamination.

A brief review of the currently used final measurement techniques reveal that ICP-AES offers relatively poor sensitivity for the heavy elements and therefore requires a high sample-to-volume ratio to achieve reasonable detection limits. The small sample volume precludes the second analysis and the high dissolved solid content of the solution is also a problem. Atomic absorption analysis is by far the most commonly used final measurement technique. However, the detection limits are higher than desirable for exploration work, and many types of material exhibit a chemical matrix dependence. When atomic absorption spectrometry is coupled with a graphite furnace atomisation cell (GFAAS), detection limits are improved significantly, but the sample throughput for the procedure remains low. The ICP-MS and NAA offer superior detection limits and are widely used presently all over the world for the estimation of gold and PGE. The elimination of the delay period prior to analysis, superior sensitivity and greater flexibility to manage interferences enjoyed by ICP-MS compared to NAA will probably ensure this technique a dominant role in this field when instrumentation becomes more widespread.

Finally, it is relevant to note that the reliability in precious metal data and the consequent bias is a point of concern. The implications arising out of such variations are discussed by McDonald.[110] Availability of well characterized CRMs of wide ranging analyte contents and their judicious use in routine analysis will help in reducing bias in reported values.[58]

Table 10 Published methods to determine precious metals in geological materials by neutron activation analysis (selected examples)

Sl No.	Matrix	Elements determined	Notes on the method	Reference
1	Ores, iron meteorites, chromites, soil and lunar rocks	Au, Ag, Pt, Ru, Os and Ir	NAA with micro fire assay involving NiS fusion with varying masses of fluxes	Kolesov and Sapozhnikov, 1995[17]
2	SARM-7, MA-1b	Au, Pt, Pd, Rh, Ru, Ir and Os	0.5–1 g NiS button, direct irradiation to eliminate losses during dissolution Au. Spiking technique to overcome the standardization of the button mass	Asif *et al.*, 1992[15]
3	SARM-7, CHR-Pt+	Au, Pt, Pd and Ir	Thermal neutron irradiation of 250 mg sample, chemical separation of the analytes by Te-Coppt utilizing AR leach and sodium peroxide sintering	Nogueira and Figueiredo, 1995[103]
4	Geological and other related materials	Au, Pt, Pd	Samples are irradiated for 10 h and allowed to decay for 24 h and then fused with Na_2O_2 in presence of added amounts of Au, Pt, Pd. Quantitative recoveries were obtained	Nguyen, 1994[101]
5	Marine sediments (GSMS-2 and GSMS-3) and Mn nodules (GSPN-2 and GSPN-3)	Pt, Pd, Os, Ru and Ir	NiS-FA; button dissolved in 6 M HCl and Te-Coppt. Irradiation of the precipitate. Very low detection limits ranging from 0.003 (Ir) to 1.0 (Pt) (ng mL^{-1})	Li *et al.*, 1996[104]
6	Iron meteorites, chondritic metals	Au, Rh, Ru, Pd, Os, Ir and Pt	Non-destructive determination of meteoritic metal samples. Interferences and neutron flux gradients among multiple samples discussed	Kong *et al.*, 1996[105]
7	Copper nickel sulfides	Pt, Pd, Rh, Ir, Os and Ru	Combination of scanning proton microprobe and NAA. Variable irradiation times. Very low detection limits reported	Li *et al.*, 1997[106]
8	South African kimberlites	Au, Pd, Rh, Ir, Ru and Os	NiS button crushed and extracted with 500 ml of HCl (37%). Insoluble PGE sulfides collected on filter paper and dried in desiccator before irradiation using thermal neutron flux. Different decay and counting times for different elements	McDonald *et al.*, 1994[100]
9	Proterozoic Dalma rocks of Eastern India	Au, Ir, Pt and Pd	Pb-FA preconcentration. USGS standards GSP-II for comparison. Pd and Pt were estimated by GF-AAS	Lahiri *et al.*, 1997[107]

Table 11 Experimental details for neutron activation analysis of precious metals[15,26]

Element	Isotope	$t_{1/2}$	Energy/keV
Ru	^{101}Ru	38.9 d	497.1
Rh	^{104m}Rh	4.41 min	51.4
Pd	^{109m}Pd	4.69 min	188.9
	^{109}Pd	13.5 h	88.3
Os	^{191}Os	14.6 d	129.4
Ir	^{192}Ir	74.2 d	468.1
Pt	^{199}Au	3.15 d	158.4
Au	^{198}Au	2.70 d	411.8

Preparation of series of CRMs, *viz.*, soil, sediment, shale, nodules, *etc.*,[111–113] and availability of other low grade precious metal containing CRMs would help in reducing the inconsistency in data.

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