Development of rapid techniques based on selective dissolution for the determination of the precious metals in geological samples

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Development of rapid techniques based on selective dissolution for the determination of the precious metals in geological samples

A thesis submitted for the Degree of Doctor of Philosophy

Charles John Buttress Gowing

BSc. (Hons.) University of Sheffield, 1987

Department of Earth Sciences

The Open University

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Abstract.

The development of a rapid analytical technique for the determination of the platinum-group elements (PGE) and gold in geological samples is described. The technique is based on selective aqua regia acid leach followed by a selective extraction (using diphenylthiourea and 1,2-dichloroethane) to separate the PGE and Au as a group from concomitant matrix elements. Organic extracts and aqueous raffinates were analysed by graphite furnace atomic absorption spectrometry, for which a comprehensive assessment of matrix interference effects was undertaken. Direct analysis of the aqua regia acid leachates by inductively coupled plasma-mass spectrometry (ICP-MS) was also evaluated. A number of other techniques were used to evaluate recoveries following acid attack, including x-ray fluorescence spectrometry and instrumental neutron activation analysis of solid residues and beta-autoradiography of thin sections to characterise PGE mineral solubility.

The results of these investigations identified optimum conditions for aqua regia extraction (20 ml of normal (3:1) aqua regia for a 10 g sample, stirring for two hours at room temperature) and that quantitative recoveries can be expected for Au and semi-quantitative for Pd with lower, but variable recoveries for Pt, Rh, Ru and Os and very low recovery of Ir. The solvent extraction procedure was effective in selectively extracting Au and Rh but was not quantitative in the extraction of Pt, Pd and Ru, the extraction of which appeared to be influenced by the sample matrix.

Further studies on the solubility in aqua regia of individual PGE minerals indicated that the main control of aqua regia extraction efficiency was sample mineralogy. The aqua regia leach procedure was applied to a range of samples that had been independently analysed by NiS fire assay as well as appropriate reference materials. This extraction procedure, with direct analysis of leachates by ICP-MS, was also used as the primary technique for characterising the homogeneity of two new chromitite reference materials, CHR-Pt+ and CHR-Bkg.

Charles Gowing, PhD Thesis, 1993.

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Chapter 1.
Introduction.

1.1 The precious metals.

The precious metals are the platinum-group elements (PGE) (ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt)) together with gold (Au). The PGE elements are found in the same group (VIII A) of the periodic table, and as such, they have similar chemistry, which is reflected in the fact that they are often found together in the natural environment. They are often termed noble metals due to their relatively high resistance to attack by chemical reagents (Van Loon, 1984).

1.1.1 The uses of the precious metals.

Much research has been stimulated by the high monetary value of these metals coupled with political uncertainties in the major producing countries, South Africa and the former Soviet Union. Indeed their scarcity and consequent high value has led them to be used as investment media, as coinage metal and in jewellery. They are used as alloys in dentistry and in the electrical industry, where it is important that electrical contact is free from film formation. The precious metals are also relatively inert chemically and, as such, have found use as corrosion resistant materials and as catalysts (in both the chemical industry and, with increasing importance, in catalytic converters in the automotive industry). A list of some of the various uses to which the precious metals have been put is presented Table 1.1.

1.1.2 Modes of occurrence of the precious metals.

This section describes the different modes of occurrence of the PGE in the geological environment. These different modes of occurrence have relevance to the potential co-extraction by aqua regia of matrix and other trace elements with the PGE (see Chapter

4) and to the relationship between analytical recovery of the PGE and sample composition (Chapter 7).

Table 1.1. Some of the uses of the platinum-group elements and gold. A number in the table under an element signifies that element has been used for the particular application and the number refers to one of the following references: 1: Vines (1941); 2: Trotman-Dickenson (1973); 3: Sen Gupta (1973); 4: Kallmann (1984); 5: Bem and Ryan (1985); 6: Mertie (1969); 7: Seeverens et al. (1983); 8: Naldrett and Duke (1980); 9: Griffith (1967); 0: Use of the metal in these applications is known, but no reference has been found.

Application	general	Pt	Pd	Ir	Rh	Ru	Au	Os
Alloys-hardener				2	2	2		2
Anodes		1	0	1	1,9			
Bearings for clocks and watches				9				9
Biological staining						1		1,9
Bookbinding Leaf		1	1				0	
Burner Nozels		1		1				
Catalysts-dehydrogenation		1	1,2			1		
Catalysts-hydrogenation		1	1,2		1			
Catalysts-petroleum	3,8	2,6	5,6					
Catalysts-specific						2		
Catalytic convertor (automobile)	8	7	7,5					
Ceramics	3							
Chemical lining		6	6	6	6	6		6
Coinage	3	9		9			0	
Construction-sheaths & lining			2					
Corrosion resistance		1,2	1	1,2,9	1		1	
Crucibles		1		1	1			
Dentistry	3,4,8	1,2,6	1,2,6	1,9		1,9	4	
Electronics and electrical industry	3,4,8	1,2,6	1,6	1,6	1,2	1,6	1,4	1
Electroplating		1	1		1,2			
Engineering-chemical		2						
Engineering-electrical		2						
Fertilisers	3							
Finger print detection						1		1
Fuses		1	1	1			1	
Glass	8	6			6			
High temperature		2						
Investment	3,4							
Jewellery	8	1,2,6	1,2,6	1,6	1,6	1,6	1	
Laboratory		2	0				0	
Laser crystals	3							
Light filters		1			1			
Magnets		2						
Medals		1	1	1	1	1	0	
Medical	3,8	2,6	6				7	
Metal-to-glass seals		1						
Organic oxidation						9		9
Pen nibs		1		1,9		1	0	1,9
Photography	8	1	1					
Record styli				9				9
Thermionic cathodes (with Ni)		1						
Thermocouples		1,2	1		1,2,9		1	

The PGE are primarily siderophile, tending to associate with transition metals Fe, Ni and Co in iron meteorites and, presumably, the Earth's core. In the range of oxygen and sulphur fugacities prevalent in the crust and upper mantle, however, the PGE commonly exhibit chalcophile behaviour. The precious metals are present only at trace levels in natural geological samples, average abundancies of the precious metals in the crust and some rock types are detailed in Table 1.2 along with the average type C1 chondrite concentrations. Mafic and ultramafic igneous rocks are the most PGE-rich of the common crustal rocks (Naldrett and Duke, 1980).

Table 1.2. Average abundance of precious metals in the crust and certain rocks (concentrations in ppb[1]), from O'Leary and Meier (1984). * Average type C1 chondrite abundance data from Naldrett and Duke (1980).

	crust	ultramafic rock	basalt	granite	chondrite*
Os	0.4	-	-	-	514
Ir	0.4	-	-	-	540
Ru	0.4	-	-	-	690
Rh	0.4	-	-	-	200
Pt	2	20	20	8	1020
Pd	4	20	20	2	545
Au	4	5	4	4	152

- no data reported.

Twenty years ago, little was known about the modes of occurrence of the precious metals (Robért et al., 1971). However, since then, it has been reported that precious metals could occur as discrete minerals, in solid solution and as inclusions within sulphides, silicates and spinels (Hall and Bonham-Carter, 1988) and in solid solution within chromite (Grimaldi and Schnepfe, 1969). Au is often associated with the PGE but also occurs independently since, although there are substantial similarities in the chemical properties of the PGE (Marczenko et al., 1984) significant differences are found between the chemistries of Au and the PGE. These differences lead to different formation phenomena during the primary magmatic crystallisation.

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[1] The units for element concentrations in samples used in this thesis are parts per billion (ppb, ng/g) and parts per million (ppm, µg/g).

Wright and Fleischer (1965) reported that the PGE were present as trace constituents in most mineral types, and most importantly in sulphides, selenides, tellurides and arsenides. Crocket (1979) identified the major features of PGE geochemistry as (a) their strong siderophile character, attested to by the occurrence of many metallic alloys among the platinum-group minerals and the high proportion of metallic bonding character of many of the platinum-group element minerals (PGM), (b) their common association with sulphides in ultramafic rocks and (c) their very low concentrations associated with sulphide-poor silicate rocks and rock-forming minerals.

1.1.2.1 PGE/matrix association.

The close association of the PGE with certain rock-forming minerals has been studied by a number of workers. The presence of the PGE within matrix mineral phases has been explained by incorporation during magmatic cooling. Gijbels et al. (1974) reported that the PGE passed into chromite which crystallises early from the magma and, upon cooling, 25% of the PGE present passed into neighbouring silicates by post-depositional equilibrium. Crocket (1979) reported that there were higher PGE contents in chromite-rich rocks than chromite-poor rocks and little was known about the relative importance of silicate minerals as PGE-carriers, though there was some data to indicate that Ir may be concentrated in olivine.

Due to the similarity in their atomic radii, PGE can occur as interstitial solid solutions (as atomic replacements) of elements in ore minerals and even in some rock-forming minerals. For example, Mertie (1969, p. 14) reported the existence of Pt-bearing Ni-Cu, Cu and Cu-Co sulphides related to basic or ultrabasic rocks and Wright and Fleischer (1965) reported that these elements could occur in solid solution with each other and can replace Fe, Ni and Cu in minerals (e.g. chromite, cassiterite, olivine and hornblende) and rocks (e.g. dunite, serpentinite, peridotite and pyroxenite). Agiorgitis and Wolf (1984) suggested substitution of Ir and Os for Cr in the chromite lattice.

Although Au, Pd and Ir are concentrated by lherzolite minerals (i.e. spinel > clinopyroxene > orthopyroxene > olivine > garnet), Mitchell and Keays (1981) reported that 60-80% of the PGE occurred in a sulphide-rich intergranular component. Scoates and Eckstrand (1986) reported associations of Ir, Rh, Pt, Pd and to a lesser extent, Au with sporadic concentrations of disseminated sulphide minerals. Chyi and Crocket (1976) reported that Pd concentrated into pentlandite ($(Ni, Fe)_9S_8$) and Pt and Ir concentrated into chalcopyrite ($CuFeS_2$).

Table 1.3. Average contents of Au, Ir, Pt and Pd in certain rock types, from Oshin and Crocket (1982).

	Au	Ir	Pt	Pd
olivine chromitite	0.28	30.0	1.5	0.33
dunite	1.3	2.4	28.0	21.0
pyroxenite	1.4	0.24	17.0	29.0
gabbro	1.7	0.017	4.5	3.0

Concentrations in ppb.

Oshin and Crocket (1982) reported average noble metal concentrations for olivine chromitite, dunite, pyroxenite and gabbro (Table 1.3). It can be seen from the data in Table 1.3 that each of the four elements considered has preference for one rock type (e.g. Ir in olivine chromitite; Pd in pyroxenite), there may thus be fractionation of elements during magma genesis and cooling. Amossé et al. (1990) reported elemental fractionation to the extent that Pt, Pd and Rh were dissolved in base metal sulphides whereas Ir, Ru and Os were incorporated during early crystallisation of ultrabasic cumulates. This fractionation could be explained by Pt, Pd and Rh being more soluble in silicate magma than Os and Ir, which generally form alloys, and Ru, which mostly forms laurite (Barnes et al., 1985).

The cause of fractionation is not of direct relevance to the current work, rather the fact that fractionation occurs may be used in the development of partial dissolution techniques for precious metal element determination or in the explanation of variable recoveries (see Chapter 7).

1.1.2.2 PGE minerals.

Whether or not chromite concentrates the PGE through a solid solution mechanism is uncertain, but in some instances high PGE levels have resulted from inclusions of platinum-group minerals, PGE-rich arsenides and sulphides, within the chromite (Crocket, 1979). Crocket et al. (1976) reported that only a fraction of Ir (40%), Pd (35%), Pt (~10%) and Au (~5%) were associated with oxide and sulphide minerals, the remainder of the precious metals were present as discrete minerals.

Zientek et al. (1990) reported that as well as being in solid solution with base metal sulphides, Pt and Pd formed discrete sulphides, tellurides, arsenides, antimonides and bismuthides as well as alloys with Fe, Sn, Hg and Au. Dillon-Leitch et al. (1986) reported that rare PGM occurring in silicates were confined to sheared and carbonatised rocks, often associated with sulphide veins. Constantinides et al. (1980) observed no Pt, Pd or Rh minerals and reported that Os- and Ir-bearing laurite ($(Ru, Os, Ir)S_2$) and Ir- and Ru-bearing erlichmanite ($(Os, Ir, Ru)S_2$) were completely enclosed within chromite grains. This observation was repeated by Ohnenstetter et al. (1986) who found only one grain of laurite outside the chromite from about 100 specimens.

Vermaak and Hendricks (1976) reported that five of the most common PGM, sperrylite ($PtAs_2$), cooperite (PtS), braggite ($(Pt,Ni)_{6-x}Pd_{2+x}S_8$), laurite (RuS_2) and Pt-Fe alloy (Pt_3Fe), were most often associated with pyrite, pyrrhotite, pentlandite and chalcopyrite. Sperrylite was found as euhedral crystals enclosed by pyrrhotite and partially enclosed by pentlandite (Vermaak and Hendricks, 1976) and deeply embayed crystals in chalcopyrite (Kingston and El-Dosuky, 1982). Cooperite and braggite are usually found as simple intergrowths at or near a pentlandite-silicate contact (Kingston and El-Dosuky, 1982). Vermaak and Hendricks (1976) reported that 90% of the laurite in their samples was present at the sulphide-silicate boundary and that the PGE showed a general site preference at the contact between base metal sulphides and matrix phases. The site preferences for a silicate ore were: within base metal sulphides (16.2%), within matrix minerals (12.6%) and at the contact (71.2%) and for a chromite ore were: within base metal sulphides (13.9%), within matrix minerals (32.1%) and at the contact (54.0%) (Vermaak and Hendricks, 1976).

Often, the PGE occur as natural alloys which have as wide a range in composition as their crystallography permits. For example, native Pt usually contains the other five PGE in variable proportions, osmiridium (Ir,Os) often contains traces of Ru, Rh and/or Pt, sub-micron grains of one alloy may be present inside another and alloys are commonly attached or intergrown with chromite, which sometimes contain minute inclusions of base metal minerals (Mertie, 1969, p. 11). Feather (1976) reported the occurrence of Ir, Os and Ru as Os-rich alloy cores enclosed by Ir- and Pt-rich rims, occasionally with exsolution lamellae of Pt-Fe alloys. Kingston and El-Dosuky (1982) reported observations of myrmekitic Pt-Fe alloys in pyrrhotite.

1.1.2.3 Occurrence of Au minerals.

There are 26 known Au minerals, 10 of which are alloys, 9 are tellurides and 7 are sulphides and selenosulphides and 18 unpublished/unnamed compounds. Despite this number of minerals, natural Au usually occurs as alloys with Ag and/or Cu. Pure Au is very rare in nature (Harris, 1990) and the other minerals have only been recorded from 1 or 2 localities in the world (Bowles, pers. comm.). Of increasing importance in the analysis of geological materials is the presence of invisible gold. Invisible Au is that which occurs either as sub-microscopic inclusions or as a solid solution within the host minerals, or simply Au that is chemically bound to matrix minerals (Harris, 1990). Cathelineau et al. (1988) suggested that chemically bound Au may occur by the coprecipitation of Au with Fe, As and S during arsenopyrite crystallisation.

Zhenru Zhang et al. (1987) reported the presence of microscopic Au in pyrite, stibinite and arsenopyrite and that the Au^+ ion could occupy a crystallographic site by replacing Fe^{2+}. Mironov and Geletiy (1979) reported that Au could isomorphically replace Cu in chalcopyrite. Cabri et al. (1989) reported a study of arsenopyrite with structurally bound Au (which rendered the mineral refractory to metallurgical treatment by cyanidation). The most common host minerals for Au are pyrite and arsenopyrite, followed by galena, sphalerite, chalcopyrite and pyrrhotite (Harris, 1990).

1.1.3 The precious metals in the Unst ophiolite complex, Shetland.

Much of the work described in this thesis was carried out using chromitite samples collected from the Unst Ophiolite Complex, Shetland (Prichard, 1985). One of the advantages of using such material was that samples from this ophiolite complex have been the subject of very thorough mineralogical examination (Prichard et al., 1989). In particular, the mineralogy of samples from the Cliff and Harold's Grave have been well described,[2] indeed samples from these two localities provide much of the data presented by Prichard et al. (1989). Both Cliff and Harold's Grave are disused chromite quarries, where chromite-rich lenses were enclosed by a dunite envelope in harzburgite 1 km from the junction between the harzburgite and the overlying dunite (Prichard et al., 1989).

The predominant PGM are alloys (with other PGE and base metals) arsenides, antimonides and sulphides. The range of PGM observed in samples from Cliff are summarised in Table 1.4. Prichard et al. (1989) also reported textural relationships observed between PGM and matrix grains. They identified 3 settings for PGM: (i)

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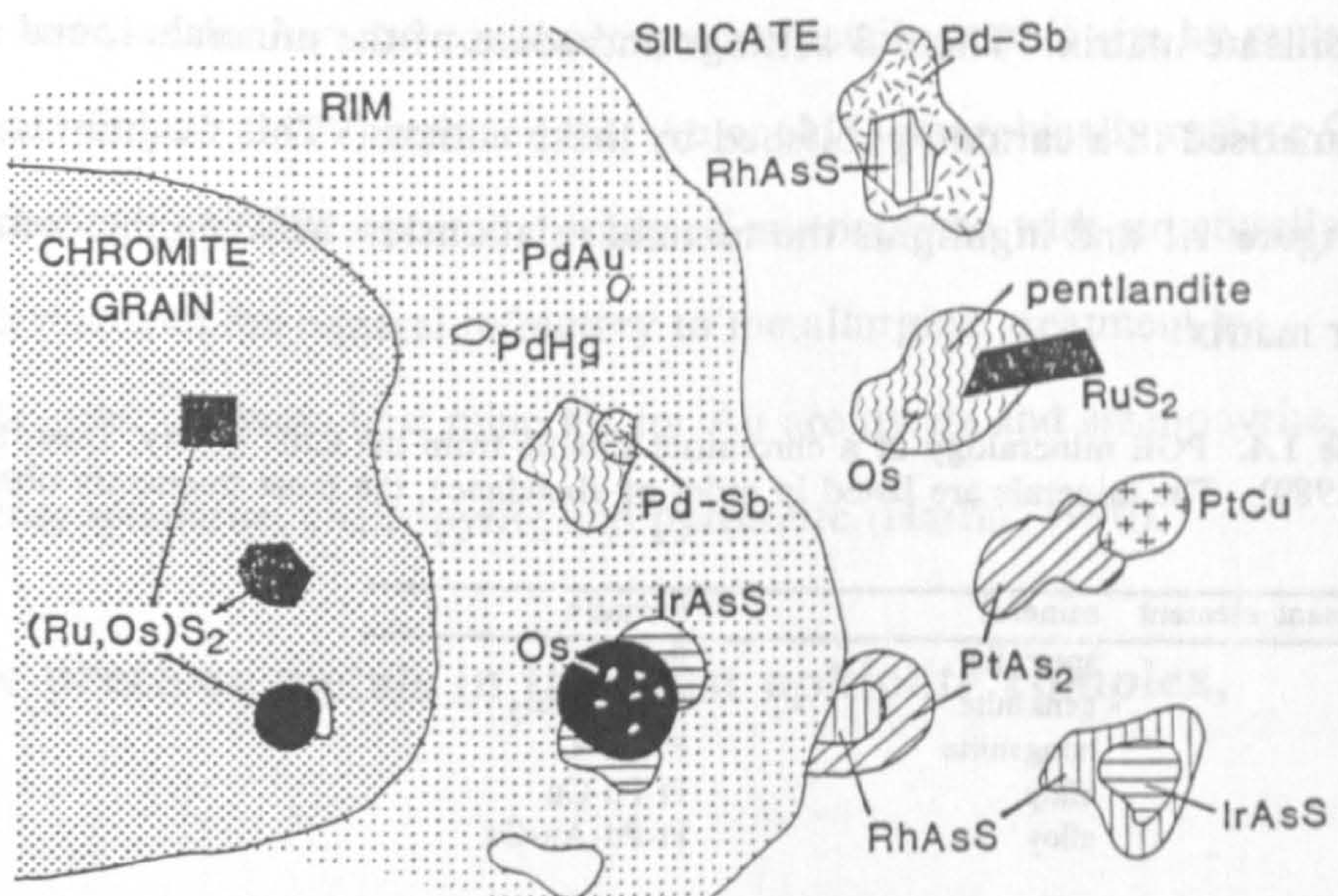
[2] Material from the Cliff quarry was used to produce the Open University in-house reference material, OU-CX, and a trial sample used in this thesis, CHR-C (Chapter 4; Gowing and Potts, 1991), and the candidate reference material CHR-Pt+ (Chapter 8; Potts et al., 1992).

within chromite grains; (ii) within a narrow rim around the chromite grains; (iii) within the silicate matrix. These 3 settings and some of the minerals found at the sites are summarised in a cartoon published by these authors. This diagram is reproduced here as Figure 1.1 and highlights the textural relationship between the common PGM and their matrix.

Table 1.4. PGE mineralogy of a chromitite sample from the Cliff quarry, Unst, Shetland (Prichard et al., 1989). The minerals are listed in order of abundance, the most frequently observed is listed first.

dominant element	mineral	formula
Pt	sperrylite	$PtAs_2$
	genkinite	$(Pt,Pd)_4Sb_3$
	hongshiite	PtCuAs
	alloy	Pt-Pd-Cu
	alloy	Pt-Pd-Au-Cu
Pd	mertieite	$(Pd,Cu)_8(Sb,As)_3$
	stibiopalladinite	$(Pd,Cu)_5(Sb,As)_2$
	potarite	PdHg
	alloy	Au-Pd
Rh	hollingworthite	(Rh,Pt,Pd)AsS
	unidentified	Rh(Sb,S)
	unidentified	(Rh,Ni)Sb
Ir	irarsite	(Ir,Ru,Rh,Pt)AsS
	unidentified	Ir(Sb,S)
Ru	laurite	$(Ru,Os,Ir)S_2$
	ruthenian pentlandite	$(Ni,Fe,Ru)_9S_8$
Os	native metal	Os
	iridosmine	Os,Ir

Figure 1.1. Schematic diagram of the PGM and their textural position in relation to chromite grains. From Prichard et al. (1989), Figure 12. Not to scale, grains are typically 5-20 μm in diameter.



Os-bearing laurite (RuS_2) was observed enclosed within chromite grains, irarsite (IrAsS) was located within or close to the chromite rims, sometimes enclosed by hollingworthite (RhAsS), which itself can be enclosed by sperrylite ($PtAs_2$) or palladium antimonides. Even from this simple cartoon, it can be seen that the mineralogy and textural relations of these samples is very complex. The textural relationships described by Prichard et al. (1989) and summarised in Figure 1.1 is often referred to in subsequent chapters (Chapters 4, 8 and, particularly,7).

1.2 Criteria for a complete analytical technique.

Angino and Billings (1972) proposed five criteria for an analytical method for the analysis of trace elements all of which are particularly important for the analysis of the precious metals: a method should be (i) simple in operation; (ii) sufficiently sensitive that chemical preconcentration is unnecessary; (iii) relatively interference-free – or adequate methods should be available for their correction; (iv) rapid – to allow large number of samples to be run; (v) precise and accurate.

Kallmann (1987) added to this that a method should be tailored to the sample matrix in which the platinum-group minerals occur, the individual PGE concentrations and the desired sensitivity and precision. This author continued to stress the importance of speed, cost effectiveness and personnel requirements in the application of a method to the industrial workplace. The precious metals industry places greater emphasis on precision and accuracy than most other industries owing, to the high value of the materials in question and, with the pressing need to maximise the profitability of industrial processes, speed of analysis was also becoming a major concern (Everett, 1982).

With reference to the criteria proposed by Angino and Billings (1972), it can be said that, in principle, an acid attack is more simple than a fire assay preconcentration, the button from which may require secondary acid dissolution (Chapter 2). The development of sensitive analytical instrumentation (e.g. inductively coupled plasma-mass spectrometry (ICP-MS)) has either met, or at least gone some way towards meeting, the sensitivity criteria, but the nature of the precious metals is such that a preconcentration step is almost invariably necessary prior to determination (Section 1.1.2).

The inclusion of solvent extraction in the aqua regia dissolution method here described served to eliminate the sources of many of the analytical interferences encountered (the use of matrix modification to overcome analytical interferences in graphite furnace atomic absorption spectrometry (GFAAS) is described in Chapter 6).

The simplicity of the aqua regia method makes it potentially applicable to large batches of samples, such that sample throughput rate could ultimately be determined by the analytical finish technique. The high sensitivity analytical technique, GFAAS, is restricted to the determination of one analyte at a time, however, multielement techniques (e.g. ICP-MS) have increased significantly the potential sample throughput when determination of more than one element is required.

Precision and accuracy are dependent upon both sample and instrumental characteristics. Analysis of homogenous samples of relatively uniform composition combined with use of analytical instrumentation of proven reproducibility and calibration characteristics should give results that are both precise and accurate. Analysis of reference materials by a particular method can be used confirm both these parameters.

1.2.1 The importance of sample homogeneity.

The first step in the analysis of a geological material is to select a sub-sample that adequately represents the whole sample. Indeed, Clifton et al. (1969) wrote that, for a sample to be meaningful, it must accurately represent a larger entity, a deposit or a part of the deposit. Bergeron (1990) mentioned that the selection of the analytical method is not only dependent upon its type but also on the representivity of the samples for analysis. Hoffman et al. (1956) stated that scattered results were characteristic of analyses performed on samples in which the constituent sought was not intimately dispersed throughout the sample. The choice of sub-sample and homogeneity will be further discussed in Chapter 4.

While considering the importance of the accuracy of results in any field of analysis, Van Loon (1985) lamented the lack of generally available certified reference materials with certified concentrations of the PGE. The dearth of reference materials will be approached in Chapter 8 in which details are given of the preparation and characterisation of 2 candidate reference materials.

1.3 Overview of work presented in this thesis.

This thesis is subdivided into three parts. Chapters 1-3 include introduction and background information relevent to subsequent chapters. Chapters 4-6 describe the development of a method based upon aqua regia dissolution with a selective solvent extraction and graphite furnace atomic absorption spectrometry. The final chapters include the investigations that were undertaken to characterise this method and conclusions.

In the course of this work, 2 candidate reference materials have been prepared. The aqua regia dissolution method (sans solvent extraction) was used to characterise the homogeneity of these 2 materials. This characterisation is described in Chapter 8, together with a thorough statistical assessment of the data.

1.3.1 Introductory chapters.

The present chapter has introduced some concepts of general applicability to the thesis. Knowledge of the geological settings of the PGE and Au is important in understanding some of the difficulties and limitations experienced during the course of this work.

Previous methods used for the preconcentration and separation of the precious metals have been discussed in Chapter 2. A detailed appraisal of fire assay techniques has been presented in recognition of the universal use of this technique as the method of choice for decomposition of samples prior to the determination of the precious metals. An understanding of the benefits and restrictions of such methods is useful when bringing into context the development and characterisation of the aqua regia dissolution method investigated in this work.

A number of analytical techniques that have been applied to the analysis of both solutions and solid materials for the determination of the precious metals have been reviewed in Chapter 3. Emphasis was placed on AAS as this method attracted the greatest proportion of work here (Chapter 6).

1.3.2 Method development.

Optimisation of the aqua regia dissolution method is described and its quantification detailed in Chapter 4.

A selective solvent extraction method was applied to the aqua regia leachates to remove interferent elements from analyte solutions and potentially to preconcentrate further the precious metals. The development and application of this solvent extraction procedure is described in Chapter 5.

Extensive work was carried out on the the development of thermal programmes and the characterisation of interferences encountered in GFAAS. This work is described in Chapter 6, together with an assessment of the applicability of this technique to the analysis of organic extracts.

1.3.3 Characterisation of the method.

It is recognised that the aqua regia dissolution method has a number of limitations. Limitations due to characteristics of sample mineralogy have not often been considered in previous discussions and appraisal of analytical methodologies. Attempts made to characterise some of the problems encountered in the method development are described in Chapter 7.

Chapter 2.
Preconcentration of the precious metals.

2.1 Introduction.

The PGE and gold are by their very nature rare and usually occur at concentrations in the ppb to sub-ppb (pg/g) range in geological samples (Brügmann et al., 1990). At these concentrations they are too low for direct determination by most existing techniques (Hoffman et al., 1978). Large sample weights are normally required to ensure that a representative sample is analysed for a number of reasons including: (i) the precious metals are present in low concentrations in most ores (Bowditch, 1973); (ii) the precious metals are inhomogeneously distributed in the form of discrete minerals (Asif and Parry, 1990) and possibly in solid solution in rock-forming minerals, chromites and sulphides (Hoffman et al., 1978); (iii) homogeneity is a function of sample size (St. Louis, 1987).

Any technique for the analysis of geological samples for these elements, therefore, will require preliminary treatment with the dual aims of separating the analyte elements from the matrix elements, which may cause interferences in subsequent analytical procedures, and collecting them from a large sample mass into a more concentrated usable form for analysis. For geochemical samples, this has traditionally been accomplished by application of a fire assay procedure, but other methods, including the use of aqua regia, have also been applied.

Fire assay techniques are reviewed in detail to permit comparison with aqua regia digestion and to highlight their limitations as well as their advantages in sample decomposition. Aqua regia digestion is also fully reviewed as it is the basis of the work herein described. Other methods of sample decomposition are also reviewed, although they are less often used than either fire assay and acid digestion. Because there is often a need to further separate the precious metals from matrix elements, secondary preconcentration techniques are also reviewed in detail. No one technique is used consistently as the definitive separation technique and it is important to understand how they work before they can be used efficiently.

2.2 Fire assay preconcentration.

The aim of the fire assay is to separate the precious metals as intermetallic compounds soluble in mineral acids or to convert them into a physical state more suitable for decomposition by mineral acids or oxidising fusions (Beamish, 1966, p. 24). Fire assay also serves to produce a sample for analysis with a relatively simple matrix compared to the starting material (Van Loon, 1977). This is accomplished by intimately mixing the powdered sample with a suitable flux and carrier and fusing at a high temperature. The matrix of the sample dissolves in the flux and the precious metals form an alloy or matte with the finely dispersed droplets of the carrier. The collector then separates from the silicic slag and collects in the bottom of the assay crucible forming an alloy or matte button. On cooling, the resultant button and slag can then be physically parted, the slag discarded or reworked as required and the button retained for analysis or further treatment as required prior to analysis.

2.2.1 Classical lead fire assay.

The benefit of using lead as the collector for gold in fire assay has been realised since times of the Holy Roman Empire (Van Loon, 1984) and cuniform tablets indicate that the Babylonians used fire assay in the 14th Century B.C. (Kallmann, 1984). Beamish and Van Loon (1972, p. 70) stated that for almost a century following the discovery of the PGE, the only effective general method for the determination of these metals in ores involved a collection in molten lead from fused media of suitable composition. Furthermore, there can be little doubt that this method suggested itself through the similarity in properties of the PGE and gold for which the assay-metallurgical method had been an ancient procedure.

Kallmann (1984) pointed out that the applicability of fire assay to the PGE is limited to the extent that their physical properties differ from those of Ag and Au to which the original forms of fire assay were applied. Moreover, Beamish (1966, p. 162) was surprised at the success of fire assay for some of the PGE considering that the use of lead fire assay for the PGE has grown out of an irrational assumption that they are as 'noble' as gold, when it is known that the PGE form oxides on heating in a Bunsen flame. Although the fire assay presented a reducing atmosphere such that oxide formation should not have presented a problem, the subsequent oxidative removal of lead from the button may have resulted in the loss of some the PGE.

Despite the above reservations of Kallmann and Beamish, lead fire assay is potentially applicable to almost all geological samples although some expertise is required to undertake the procedure successfully. For example, Beamish and Van Loon (1972, p. 71) stated that the classical fire assay would reveal commercially valuable values for all ores and concentrates although quantitative success would depend upon the assayer's experience and wisdom in the choice of technical conditions.

2.2.1.1 Lead fire assay procedure.

In the lead fire assay procedure, the flux components, sodium carbonate, lithage (PbO) and borax ($Na_2[B_4O_5(OH)_4].8H_2O$), provide a medium for the formation of metal borates and silicates thus exposing the noble metals to the extractive action of lead (Beamish, 1966, p. 167).

Lead fire assay is described in detail by Haffty et al. (1977) and Moloughney (1986). Kallmann (1987) neatly summarised the theory and practice of lead fire-assay. An assay ton (32.667 g), or a multiple or fraction thereof, is taken for analysis and mixed with a suitable flux containing a large proportion of PbO and various proportions of compounds such as sodium carbonate, potassium carbonate, borax, silica, potassium nitrate, and organic substances such as starch or flour. The ratio of the various components depends on whether the sample (a) contains an excess of basic components, in which case more silica is added, (b) contains an excess of acidic components (additional carbonate or borax is then required), (c) is high in copper (more PbO is then used), (d) tends to oxidise the flux components, requiring addition of organic reducing substances. Often excess Ag (or Au if determination of this element is not required) will also be added to a fire assay fusion mixture to prevent mechanical losses of the PGE during the fire assay steps and to assist manipulation of the subsequent 'prill' (see below).

Optimum conditions, as indicated by the fluidity of the melt and the weight of the lead button desired, are ensured by a judicious balancing of the weights of sample and the various flux reagents. The PGE, together with Ag and Au, are collected in the resultant lead button. The matrix elements react with the flux components to form a slag which is subsequently discarded, unless additionally reworked for the recovery of trace amounts of the precious metals.

When the lead button weighs more than 60 g or is known or is suspected to contain base metals, it should be transferred to a fire clay dish called a scorifier. More lead and a little silica are added and the mixture is melted in an oxidising atmosphere for 30 min at about 900°C (scorification). Much of the lead then oxidises to form a glassy slag which further extracts impurities. The lead button is next placed on a preheated cupel made from bone ash or magnesite. On heating in a muffle furnace at a temperature of about 800-850°C in an oxidising environment (cupellation), the resultant lead oxide is absorbed into the cupel or is volatilised, leaving a metallic residue, called a prill, of Ag (or Au) containing the PGE.

Although some PGE form an alloy with lead in the same way as Au, others are collected in the lead by purely mechanical process (Artem'ev and Stepanov, 1982). It is essential, therefore, not only to develop in detail the fire assay procedure but also to adhere to this procedure to permit the physical collection as well as the chemical collection of the elements.

2.2.1.2 Collection of the precious metals by lead.

Lead fire assay relies on two phenomena, firstly that the PGE will dissolve in the molten lead forming an alloy and secondly that those which do not dissolve will settle to the bottom of the crucible owing to their high density and so become incorporated with the lead. For example, Beamish (1966, p. 166) stated that it was not unlikely that all the iridium and iridosmine, (when the latter was present) were recovered by the fall of these high density metals through the low viscosity liquid in the latter stages of fusion.

More recently, the collection of Ir, Ru and Os by lead has been confirmed. Artem'ev and Stepanov (1982) have shown from autoradiograms of the upper surface of the lead button and slices through a remelted spiked lead sample that the distribution of Ir is comparatively uniform whereas that of Ru and Os is non-uniform. These authors offered two explanations for the latter observation, either Ru and Os did not interact with lead or that they did dissolve in the lead but precipitated during cooling. The first of these explanations, despite contradicting the alloy theory, lends weight to the dense metal settling theory, and the second relies on a combination of both theories. Bowditch (1973) summarised that Ir, Os and Ru have only limited solubility in lead and are largely collected in the lead because of their high density.

The precious metals were not always collected quantitatively by a single fusion, Bowditch (1973) reported that it was often necessary to perform a second fusion of the glassy slag. Kallmann (1987) went so far as to say that lead is not that good a collector owing to the high melting points of the PGE and their inability to form alloys with the added Ag or Au suitable for subsequent chemical treatment.

Beamish (1966, p. 163) considered the influence of the PGE mineralogy on the lead fire assay procedure; because the form of the PGE in the original sample matrix was unknown, the collection of lead may have been ineffective for certain ores. This author suggested (p. 163, 230) that prior wet treatments could be used to convert PGE to constituents such as relatively simple chlorides that were known to respond to the usual fire assay lead collection. Diamantatos (1977) found that a preliminary leach with HCl and NH_4Cl eliminated Cu from the sample prior to fire assay as this element caused problems in subsequent preconcentration. Beamish (1966, p. 165) reported, however, that prior acid treatment did not significantly increase the recovery of the precious metals from South African floatation concentrates and proved to be tedious. The influence of the character of the platinum-group minerals is studied in more detail in Chapter 7, where evidence is presented to show that not all natural platinum-group minerals are in fact soluble in acids.

2.2.1.3 Loss of precious metals during lead fire assay.

The literature does not present a unified approach to the applicability of lead fire assay for the PGE, moreover, many authors have chronicled evidence of non-quantitative collection of noble metals by lead. Although lead fire assay has been used with repeated success for Au, Pt and Pd, the other PGE (Rh, Ru, Ir and Os) have different physical and chemical properties such that classical assay schemes are not particularly suitable for their determination (Kallmann, 1984). Beamish and Van Loon (1972, p. 70) reported that results of investigations made to determine the effectiveness of lead as a collector were in approximate agreement and showed that lead collection was effective for ppm concentrations of such metals as Au, Pt, Pd, Ru, Os and perhaps for Rh.

Kallmann (1987), however, specified that the lead collecting system was suitable for isolating Au and Ag, less so for isolating Pt and Pd and only to a very limited extent for isolating Rh, Ru, Ir and Os. Van Loon (1977) maintained that, in general, Au, Pt, Pd and Rh are readily collected by lead and that collection of Ru, Ir and Os is more seriously affected by flux composition and assay conditions.

Generally, most reports in the literature show that any losses of the PGE reported in the literature will occur during cupellation or subsequent treatment of the lead button. However, in consideration of a standard production method for Au determination, Werbicki (1982) draws attention to four sources of precious metal losses: cupel absorption; volatilisation losses; incomplete parting of the button; parting losses.

It has been reported (Beamish and Van Loon, 1972, p. 70) that the presence of Cu or Ni causes some dissolution of Ir and Rh in the parting acid used to dissolve prills from a fire assay procedure adapted for Russian copper-nickel ores, mattes and concentrates containing large amounts of Se, Te, As and Sb. Bergeron (1990) also reported that a Ni concentration above 4% interfered with the lead preconcentration of samples causing the Pt concentration to be underestimated. Samchuk and Latysh (1982) found that all the Pd and up to 90% of the Pt dissolved from the Ag prill into 2:1 HNO_3, the remaining Pt along with the Au was insoluble.

Bumstead (1984) reported that despite a loss of gold to the slag (about 2%) and to the cupel (about 1%), lead fire assay has been adopted for exploration work using rock chip and drill hole samples. Robért et al. (1971) found that during cupellation of the lead button some Ir and Ru and virtually all the Os were usually lost. Bowditch (1973) reported cupellation losses of all the Os, 50% of the Ru and 20% of the Ir, the precise percentage loss depending upon the cupellation conditions.

Inaccurate analyses of samples treated by fire assay may also arise from difficulties in the subsequent treatment of the assay button. Potts (1987, p. 489) reported that part of the difficulty of ensuring complete dissolution of the prill appeared to be the resistance to acid of the intermetallic Rh-Ir-Ru alloys which could form in the prill. Kallmann (1987) also detailed losses during the HNO_3 parting of the prill of Pd and Rh, and even of Pt if the Ag content of the sample was high enough.

2.2.1.4 Limitations to lead fire assay.

As well as incomplete collection of some of the elements, scorification and cupellation losses and problems encountered with treatment of the lead button, there are some more fundamental technical limitations to lead fire assay. It is a relatively expensive technique in terms of both equipment and chemical reagents required, although these costs can be offset by commercial laboratories offering a large sample throughout. Fire assay requires the services of a highly skilled assayer, because no two samples for analysis will ever require exactly the same conditions for assay, for example Gil'bert and Shabanova (1990) reported one industrial plant that used 35 different charges for assay preconcentration of raw materials and intermediate products. The equipment is bulky and the actual procedure is relatively 'dirty', thus a large amount of valuable laboratory space is occupied and unavailable for other uses. Because of the large quantities of chemicals used, there is a risk of contamination, although this can be compensated for with the judicious use of blanks (Van Loon, 1977).

Because the presence of some elements causes problems in the fire assay procedure, it is often necessary to preanalyse the samples for S, As, PbS, Cr, Ni and Cu (Hall and Bonham-Carter, 1988). Sulphides and arsenides can be removed by roasting the sample at 600-800°C prior to assay to prevent formation of a matte which would retain the PGE. If appreciable amounts of S are present, then instead of roasting, nitre (KNO_3) is added to the flux to oxidise the sulphide. Chromite can be accommodated in the assay by roasting with Na_2O_2 and SiO_2 prior to fusion with a flux that has been reduced in Na_2CO_3 and SiO_2. Similarly Cu and Ni can be accommodated by increasing the PbO in the flux or by prior leaching.

Although lead fire assay is widely used and is capable of giving quantitative recoveries for well-characterised sample types, care must be taken in the general application of this technique, particularly to samples of unknown composition. It has been stated many times that the fire assay with lead as the collector may fail to reveal platinum metal values quantitatively, or may even fail to indicate their presence (Beamish, 1966, p. 230). Faye and Inman (1961) considered that despite being successful for Au and Ag, lead fire assay was not entirely satisfactory for the PGE for the reasons referred to above.

2.2.2 Alternative collectors in fire assay.

Because lead fire assay cannot be applied quantitatively to all the precious metals, the use of other collectors of the precious metals has been considered, specifically tin, iron-nickel-copper alloys, sulphide matte and nickel sulphide.

2.2.2.1 Other metal collectors.

To be suitable for this purpose, the collector must readily alloy with the the precious metals, be reduced easily from one of its compounds to the metallic state at a comparatively low temperature, form a button that can be clearly separated from the slag and can be readily separated from the precious metals in subsequent operations (Faye and Inman, 1961).

Tin as a collector in fire assay.

Beamish (1966, p. 25) recorded that fusions with tin had been used successfully as an intermediate step in the acid dissolution of Ru, Rh, Ir, Pd and Pt. Further to this, Faye and Inman (1961), Beamish (1966, p. 236), Jones et al. (1971), Van Loon (1984) and Herring et al. (1987) suggested the use of tin as a collector in the analysis of Cu-Ni mattes, precious metal concentrates, meteorites and iridosmine. The precious metals were collected in tin after fusion of the sample with a mixture of tin oxide, sodium carbonate, silica, borax and flour at 1200°C. Faye and Inman (1961) proved the success of tin as a collector in the determination of Pt and Pd and proposed its use for Rh, Ir, Ru and possibly Os. Subsequently, Jones et al. (1971) and Artem'ev and Stepanov (1982) claimed that tin was a more efficient collector than lead and that it retained the bulk of the Os.

Moloughney and Faye (1976) favoured the versatility of tin over lead, although a substantial fraction of Rh dissolved during parting of a tin button. This loss may have resulted from alloy formation between Sn and Rh which promoted dissolution of the Rh in the subsequent parting. Palmer and Watterson (1971) reported losses to the slag of Au (6.9%, 15.3%), Ir (4.8%, 11.6%), Ru (7.4%) and Os (5.1%, 11.6%) from sample masses 1 g and 2 g, respectively.

Iron-nickel-copper alloys as collectors in fire assay.

Several workers, including Kavanagh and Beamish (1960), Beamish (1966, p. 234) and Kallmann (1984) described the use of an iron-nickel-copper alloy as the PGE collector. The base metals were reduced in a mixture of carbon, sodium carbonate, borax and ore at 1450°C. Ideally the ore would contain sufficient quantities of Fe, Ni and Cu, but these base metals could be added to the mixture as oxides if required (Beamish, 1966, p. 234). The inclusion of Ni metal in the carrier is advantageous since it is a selective and persistent carrier of Pt and Pd. Furthermore, since the Ni is preferentially reduced, there is a practically complete transference of Ni to the button. Beamish and Van Loon (1972, p. 72) added strength to the theory of this technique by correlating the regular natural occurrence of PGE with Cu, Ni and Fe, saying that it seemed probable that these metals could serve as collectors in a fire assay. The disintegration of the base metal silicates and the noble metals would occur simultaneously and their juxtaposition would thus encourage the efficiency of collection. The success of this technique is exemplified by the fact that fusion permits dissolution of even such resistant alloys as Tasmanian iridosmines (Beamish and Van Loon, 1972, p. 73). However, Beamish (1966, p. 235) stated that the benefits of this alloy fusion would be lost in use for sulphide ores because the constituents of the charge would produce a matte and the subsequent roasting would volatilise Ru and Os.

Brügmann et al. (1990) fused samples with an (80:20) iron-nickel alloy and a basalt powder (as carrier and flux) at 1360°C in an inert atmosphere of nitrogen, carbon dioxide and carbon monoxide (to obtain a stable metal phase and prevent the loss of Os). Danilova et al. (1982) used a Cu-Ni carrier for the PGE in fire assay of copper-nickel sulphide ores and their processing products making use of the major-element content of the original sample to contribute to the assay charge.

2.2.2.2 Collection by matte or speiss.

Because of the chalcophilic nature of the PGE, some workers suggested the use of a sulphide matte (or an arsenide or antimonide speiss) for the collection of the PGE. Beamish (1966, p. 165) stated that As and Sb speisses are good collectors for Os, Ir and Ru, but less effective for Pt and Pd; if a flux contains As as well as the usual fusion mixture and fusion is carried out in the presence of an iron nail, the fused mixture solidifies into distinct layers and the addition of Fe filings prevents slag losses of the PGE. Beamish and Van Loon (1972, p. 65) recorded that in cupellations of an artificial matte, up to 4% As could be tolerated without loss of Au, but with 6% Sb losses of Au approached 6%. The presence of S caused little difficulty in the assay for Au.

Beamish (1966, p. 164) reported early attempts at using an iron sulphide matte collector to extract the PGE. Kallmann (1984) and Herring et al. (1987) recorded the use of nickel sulphide and copper sulphide mattes. The use of nickel sulphide as a collector will be considered in detail in Section 2.2.3. Kallmann (1986) detailed the use of copper sulphide fire assay in the analysis of industrial sweeps, having noted that the presence of increasing amounts of Cu in nickel sulphide fire assay markedly improved the collection of Au. Indeed, Kallmann (1984) has reported complete collection of Au and Ag as well as the PGE with copper sulphide as a collector, whereas using nickel sulphide as the collector resulted in incomplete collection of Au and Ag, although Hall and Bonham-Carter (1988) reported that the presence of CuS in a NiS button caused dissolution problems (Section 2.2.3.1).

In some samples, the precious metals are associated in nature with Te and can be collected from aqueous solution by coprecipitation with Te (Section 2.3.2.1). For these reasons, and because Te is also chalcophilic, Shazali et al. (1988) investigated a tellurium sulphide fire assay collection scheme for the precious metals with partial success. These workers found that chromitite samples were difficult to fuse and that the button did not separate easily. Quantitative collection of Os (100%) and Ru (98%) occurred, although the collection of Ir (89%), Pt (84%), Pd (80%), Rh (71%) and Au (51%) was less satisfactory.

Yuan Lin et al. (1988) used antimony as a collector for Au. The use of Sb permits a lower fusion temperature (950°C) than that of lead fire assay. Their results showed that Au enrichment is superior or equal to that achieved with lead fire assay collection.

2.2.3 Nickel sulphide fire assay.

In the early 1970s Beamish and Van Loon (1972, p. 73) were to write: "despite the availability of new collectors for the noble metals the classical lead collector remains clearly superior for the determination of Pt, Pd, Au and perhaps Rh. The device of cupellation to remove lead selectively requires very little attention and it is a reasonably rapid process compared to the methods required for the removal of Cu, Ni, Fe or Sn." Although at the time, this statement was self evident, substantial changes arose from work of Robért et al. (1971). From their studies of efficiencies of alternative collectors, Robért et al. (1971) had developed a different method of collecting the PGE that would overcome many of the deficiencies of the lead collection scheme and would become regarded as the standard method for the collection of all the PGE.

Of the collectors that were tested to replace lead, nickel sulphide was found to be the best and most selective. Bowditch (1973) wrote that a good collection of all platinoids and Au was obtained, and refractory minerals such as osmiridium were decomposed enabling accurate determination of both Os and Ir. Having developed the technique, Robért et al. (1971) concluded that apart from the possible incomplete collection of Pt and Au, the nickel sulphide procedure offered a precise and accurate method for the concentration and isolation of the noble metals in samples of ores, concentrates and mattes. Herring et al. (1987) also praised the value of this method saying that the nickel sulphide extraction procedure offered the best overall method for the separation and preconcentration of the PGE particularly where a re-extraction of the slag was used to improve recoveries.

2.2.3.1 Nickel sulphide fire assay procedure.

Robért et al. (1971) and Hoffman et al. (1978) detailed the use and application of nickel sulphide fire assay. The principles of nickel sulphide fire assay are similar to those of lead fire assay but a different flux is used. 20-50 g of the sample is mixed with a flux containing borax (or lithium tetraborate), sodium carbonate, sodium hydroxide and 16 g nickel powder (nickel carbonate or oxide was used in the initial work but the metal has lower blank levels) and 12.5 g sulphur. The mixture is heated gradually to 1000-1100°C, the flux dissolves the sample and, at the same time, nickel and sulphur combine to form nickel sulphide which forms a fine mist within the molten flux. The precious metals then pass into the nickel sulphide as it rains down through the molten flux. The whole mixture is then transferred to an iron mould to cool. The nickel matte separates cleanly from the slag, which is discarded, forming a button, the ideal weight of which should be 25-30 g (Robért et al., 1971).

The nickel sulphide button is weighed and crushed to a powder, which is then weighed to establish any grinding losses. This powder is then heated with concentrated hydrochloric acid to dissolve the nickel sulphide. The insoluble residue of precious metal sulphides is then filtered off. This precious metals residue is then dissolved in acids prior to determination by spectrometry. Alternatively, the insoluble precious metal sulphide residue can be analysed directly by INAA without the need for dissolution (e.g. Asif and Parry, 1989; 1990).

As well as offering a more complete preconcentration for a broader range of the precious metals, this procedure has other advantages. A smaller flux to sample ratio is used compared to the lead fire assay procedure and fusion occurs at a lower temperature. A more varied range of sample types can be accommodated with no change in the flux composition, except for chromitites when more flux is required. Samples high in nickel and sulphur can be analysed without the pretreatment necessary if lead fire assay were used (Robért et al., 1971). Hall and Bonham-Carter (1988) explained that it is often routine practice for some laboratories to analyse a small aliquot of the sample for Ni, Cu, Cr and S and to adjust the flux accordingly. If the sample is Cu-rich, then a lower mass of sample is taken to prevent the formation of copper sulphide which would collect the PGE and cause dissolution problems. Cr could only be accommodated by increasing borax and soda by 50% and combining two assay beads from samples half the usual preferred mass or by substituting lithium tetraborate for borax (sodium tetraborate). These authors also stated that a high Zn content leads to poor fusion and low recoveries. Also silica must be added to more basic samples to promote successful slag formation and prevent corrosion of the assay crucible (Potts, 1987, p. 491).

Despite this requirement for preanalysis outlined above the nickel sulphide fire assay has proved to be superior to the lead fire assay for a number of reasons (Hall and Bonham-Carter, 1988). Nickel sulphide fire assay is applicable to all the PGE and requires fewer modifications of the flux composition for changes in sample type. The preliminary removal of Ni is unnecessary, although this element should be predetermined in Ni-rich samples, and a smaller flux to sample ratio is required so larger samples can be accommodated. The technique is, however, more time consuming and expensive.

2.2.3.2 Limitations of nickel sulphide fire assay.

Despite substantial advantages over lead fire assay, the nickel sulphide preconcentration procedure does suffer from some limitations. Potts (1987, p. 491) reported some of the drawbacks of this procedure, pointing out that despite Au and all the PGE being quantitatively recovered, the procedure was more complicated than for lead fire assay. Physical methods, such as scorification and cupellation, for removal of the button matrix cannot be used, indeed an acid attack is required to separate the PGE from the button. Niskavaara and Kontas (1990) reported that reagent blank contamination created a problem at ultratrace levels when large amounts of flux reagents were used. The nickel powder, carbonate or oxide used in the fusion mixture must be of high purity.[1] Shazali et al. (1988) found that some commercially available nickel products, even the purer varieties, contained substantial amounts of noble metals rendering them unsuitable for use in nickel sulphide fire assay. Robért et al. (1971) reported an incident where reagent grade NiO contained individual noble metals in the range 0.3-2.7 ppm and was thus unsuitable for use. Asif and Parry (1989) have been

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[1] Nickel compounds used as laboratory reagents are likely to contain trace concentrations of the PGE, which are found in nickel ores from which such reagents are refined

successful in developing the nickel sulphide fire assay procedure using a lower mass of nickel so that blank levels of the PGE associated to the nickel could be minimalised and a more rapid dissolution of the button can be affected to lessen the likelihood of PGE dissolution losses.

Incomplete collection of the precious metals.

Incomplete collection of some or all of the precious metals has been chronicled by a number of authors. For example, Hoffman et al. (1978) reported fusion losses for Pd (1-6%), Pt (2-6%), Ir (1-4%), Os (1-5%), Ru (1-5%), and Au (4-7%, with an additional dissolution loss of 1% for seven of the eight sample types investigated), Rh was not determined. Palmer and Watterson (1971) report losses to slag of Au (1.1-8.3%), Ir (0.3-7.8%), Ru (0.6-3.0%) and Os (1.9-6.5%) with sample masses up to 4 assay tons (117 g).

Shazali et al. (1987) showed that although the loss of PGE during fusion was insignificant, Au was largely reduced by sulphur to the free metal during fusion passing into the slag and being partially retained by the wall of the crucible. These authors claimed that nickel sulphide was not a very suitable collector for Au, but the results were semi-quantitative. Robért et al. (1971) conceded that in comparison to lead fire assay, nickel sulphide fire assay was slower and the Au recovery was 10-20% less efficient.

Robért and Van Wyk (1975) found that incomplete collection could be overcome to a large extent by grinding the slag and reassaying, a second fusion was especially necessary for chromitite samples in which up to 10% of the total Pt and Pd were found in the second button as against 1.5-3.5% in non-chromitite samples, but this was time consuming and multiplies any contamination problems.

Shazali et al. (1987) analysed the black residue that remained after the parting of the nickel sulphide button and found that it consisted largely of nickel sulphides with Cr, cobalt sulphides, antimony sulphides and arsenic sulphides as well as the sub-µg amounts of the precious metals. These authors argued that although some of these elements may have come from the reagents (e.g. bromide from HCl) others including Cr, Sb, As and Co may have originated from the sample and that the presence of Cr could indicate that there was incomplete dissolution of chromite during the fire assay. These analyses were accomplished by INAA (Section 4.2.1), hence the elements reported, there may be other elements that are not detectable by this method also present.

Parting dissolution losses of the precious metals

Losses of the precious metals by incomplete collection during nickel sulphide fire assay is compounded by the possibility that further losses can occur at the button dissolution stage. For example, Hoffman et al. (1978) reported a dissolution loss of 1% of Au for seven of the eight sample types investigated in addition to the the fusion losses encountered. Asif and Parry (1989) reported mean recoveries of 80-83% for the PGE and only 76% for Au in their work in developing procedures for nickel sulphide fire assay using a 1 g button, claiming that approximately 20% of each of the elements is lost during the dissolution stage of the bead.

In the analysis of three different sample types (one silicate, SARM 7, and two Sudanese chromitite samples), Shazali et al. (1987) reported dissolution losses for Rh (3.3%, 33%, 20%, in the three samples respectively), Pd (2.7%, —, —), Os (0.3%, —, —), Pt (0.7%, —, —), Ir (0.7%, 20%, 4%), Au (18%, 40%, 19%) and Ru (0.7%, 12.5%, —) and suggested that the effect of dissolution by HCl on different buttons was inconsistent: less than 1.5% of the PGE from a spiked granite sample was passed into the filtrate after dissolution, but 5-15% of the Au passed into solution. Kallmann and

Maul (1983) reported no precious metal losses, even during heating of the fusion mixture.

Using radiotracer techniques, Palmer and Watterson (1971) reported dissolution losses of Au (1.5-2%), Ir (0-3.2%), Ru (0.1-5.1%) and Os (0-1.9%, and one result of 18.6%). Incidentally they also found that the losses of these elements during tin button dissolution were much greater than for nickel sulphide button dissolution and they considered that this could be explained by the formation of tin alloys which were more soluble than the noble metals alone, whereas during the nickel sulphide collection, the noble metals were probably present in the button as sulphides which were insoluble in HCl.

Robért and Van Wyk (1975) discovered that the presence of 1-5% tin in the fusion mixture has a detrimental effect on the recovery of Pt, Pd, and Rh (8-23%, 13-67% and 0-13% loss respectively) and that there were some interferences on Au (0-10% loss). They argued that this may have been explained by a small amount of tin sulphide entering the button, promoting dissolution of the precious metals in the parting acid. A Cu concentration of more than 7% causes problems in the subsequent analysis of the final solution but does not cause loss of precious metals. The addition of about 5% by weight of As, Se or Te resulted in 40-70% of these elements entering the button thus preventing dissolution of the parted residue and the subsequent analysis. But the authors continued to say that Sn, As, Se and Te were usually only present in trace concentrations in precious metal ores and at these low concentrations the interference effects were negligible.

Concentrations of the precious metals that pass into solution during parting of the button can be recovered by co-precipitation with Te and combination of the precipitate with the insoluble residue prior to further treatment (Shazali et al., 1987). However, Shazali et al. (1987) found that the average result for Au in SARM 7 was 9% lower than the recommended value.

2.2.4 Modifications to established fire assay procedures.

Many workers have attempted modifications of the classical lead fire assay technique because of its limitations to the complete analysis of all the precious metals, and further modifications of the nickel sulphide fire assay technique because of the incomplete recovery of Au and Pt.

Adriaenssens and Verbeek (1973) used 6 M HNO_3 for dissolution of Ag and Pd from a partially cupelled lead button, followed by addition of HCl to precipitate the Ag as silver chloride and to form aqua regia which subsequently effected dissolution of the Pt and Au. Kolosova et al. (1984) used a similar procedure, reporting dissolution of Pt (30-70%), Pd (80-90%), Rh (90-99%) and Au (10-15%) with the HNO_3 and complete dissolution of these four elements after attack of the residue with aqua regia. Ir and Ru were hardly dissolved at all in either of these solutions, requiring alkali fusion to effect dissolution. Rakovskii et al. (1982) also reported analyses of Pt and Pd in solutions generated by an initial partial attack by HNO_3 followed by aqua regia attack of the residue after evaporation to dryness. The same concentration of Pd was determined after analysis of either the HNO_3 or the aqua regia signifying total dissolution of Pd into HNO_3. Pt values were, however, 10% low when determined in the aqua regia and 33% low when determined in a portion of the HNO_3 prior to evaporation, suggesting partial dissolution in the HNO_3.

Diamantatos (1977) reported the need for a wet analytical method for dissolution of the lead button because the time-honoured smelting method (cupellation) resulted in large losses of Ru, Os and Ir and usually in relatively small losses of Pt, Pd, Rh and Au. Moloughney (1980) reported the use of HNO_3 to remove the lead from the button without the scorification and cupellation steps usually associated with the classical procedure. Instead of dissolving the residue, the author recovered the precious metals from solution by reduction with $SnCl_2$ and coprecipitation with Te (97-105% efficient for Pd; 96-97% for Pt) (Section 2.3.2.1). This procedure has special implications for analysis of materials rich in Cu and Ni, which usually require many scorifications to free the button from these two elements, reducing the precision in the final analysis.

Diamantatos (1986) reported direct parting of the lead button with perchloric acid ($HClO_4$), dilution and subsequent precipitation of the precious metals, stating that this method was more precise through the elimination of cupellation and more satisfactory than previously recorded variations of classical assay, examples of which are outlined above. Indeed, this author stated that scorification and partial cupellation were not recommended techniques for accurate noble metal determinations, and that this method was superior to nickel sulphide fire assay which has unsatisfactory collection of Au and perhaps Pt.

Hall and Bonham-Carter (1988) stated that the establishment of a universal decomposition procedure capable of quantitative recovery of Pt, Pd and Au, regardless of mineralogical composition or occurrence (sulphide, silicate or chromite) had yet to be achieved. Both nickel sulphide and lead fire assay required fine balancing of flux components and experimental conditions for accurate, trouble-free analyses; skill and experience were required in both the fusion and cupellation procedures because the various temperatures used and the rate of heating and cooling play critical roles.

2.3 Other methods of initial sample decomposition.

Because of the limitations of fire assay preconcentration detailed above, various other methods have been developed to effect the decomposition of samples to release their precious metal content. None, however, have commanded the extensive use enjoyed by the fire assay techniques. Although fire assay achieves separation and preconcentration during fusion, all the other methods documented require a two stage procedure, an initial decomposition followed by a secondary preconcentration (Section 2.5).

Sample decomposition procedures described in the literature include peroxide fusion, chlorination, distillation and acid digestion. The first three of these techniques will be summarised below, acid digestion will be described in Section 2.4.

2.3.1 Peroxide fusion.

Peroxide fusion is a commonly used alternative to fire assay techniques and involves mixing the sample with flux (peroxide) and heating to form a uniform melt rather than the separation of bead from slag as occurs in fire assay. The advantage of the fusion lies in its simplicity: the sample is dissolved in a peroxide flux at high temperature then, after cooling, the melt is dissolved in water or dilute HCl. It is suspected that a small amount of crucible material will always be dissolved in these melts (Potts, 1987, p. 54), although carbon crucibles can be used for alkali fusions – removing the possibility of contamination. Bozic et al. (1989) praised the speed and cost effectiveness of the technique for metallurgical samples.

The most common form of peroxide fusion uses sodium peroxide (Na_2O_2) as the reactant (Nadkarni and Morrison, 1974; Everett, 1982; Stockman, 1983). Sen Gupta (1989) and Amossé et al. (1986) reported the use of peroxide fusion, but only as a secondary decomposition step on the residue after incomplete acid digestion (Section 2.4). Everett (1982) reported that most of the precious metals were taken into solution with addition of HCl to the aqueous solution of the melt but that HBr had to be added to ensure dissolution of Rh. Stockman (1983) found it necessary to boil the dissolved melt to break the peroxide bonds prior to analysis. Precipitation of Ag as its chloride was a problem but <0.1% of the other precious metals were coprecipitated, and there was a small loss of Ru unless the Na_2O_2 was completely hydrolysed (Everett, 1982). Some authors have reported methods with addition of other reagents to aid fusion, particularly for samples with resistant matrices. Nadkarni and Morrison (1974) and Stockman (1983) used a proportion of sodium hydroxide. Amossé et al. (1986) used sodium potassium carbonate when determinations of the PGE were required in addition to Au.

Barium peroxide (BaO_2) fusion has been favoured by some Russian workers as a secondary decomposition step on the residue after incomplete acid digestion (Razina and Viktorova, 1970; Myasoedova et al., 1988). Razina and Viktorova (1970) utilised BaO_2 fusion because Rh remained in the residue after aqua regia attack had dissolved Au, Pd and Pt. Ba is separated from solution by filtration after precipitation with H_2SO_4.

2.3.2 Chlorination.

As an alternative to fusion techniques, a few authors have proposed roasting a sample in a stream of a corrosive gas, such as chlorine. Beamish (1966, p. 8) described 3 forms of chlorination: (a) direct chlorination in the presence of an alkali or alkaline earth metal chloride; (b) wet chlorination in a sealed tube containing HCl and a suitable oxidising agent; (c) dry chlorination where chlorine alone is passed over the sample in the absence of a salt. Chlorination is usually applied to metallurgical rather than geological samples, and has been proved particularly useful for Os and Ir, the inertness of which precludes the use of many other methods. For example, Dhara (1984) used wet chlorination for the dissolution of slimes and concentrates by constantly passing chlorine through a solution in order to keep Ir in its oxidised form (Ir(IV)) necessary for subsequent subsequent solvent extraction (Section 2.5.4).

Direct chlorination in a closed system accelerates decomposition and prevents losses of elements that form volatile compounds (Belyaev et al., 1985), indeed Beamish (1966, p. 15) reported that Os, the element most susceptible to volatilisation losses, is attacked most easily. Belyaev et al. (1985) reported complete decomposition of slimes, concentrates and products of copper-nickel sulphide ore processing. Van Loon (1984) reported that dry chlorination at elevated temperatures is very effective for corroding precious metal samples, although it is not often used because of the corrosive and poisonous nature of the gas. Barnes and Edwards (1982) reported a wet chlorination leach to dissolve Pt, Pd and Au with base metals; a second wet chlorination solubilised Rh, Ru, Os and Ir after peroxide fusion of the insoluble residue from the first digestion.

2.3.3 Distillation.

Distillation has been proposed as a simple method of concentrating the precious metals from samples. Payne (1960) reported two procedures for distillation of the precious metals from solution: passing chlorine through an alkaline solution of ruthenate or osmate, and, the preferred technique, oxidation of bromate from weakly acidic solution. Chuburkov et al. (1990) distilled Au, Os, Pt, Ir, Ru and Rh directly from sulphide ores, chromitites, harzburgites and iron-manganese nodules into flowing air as oxides or other volatile products, such as chlorides. The distillate was then collected in HNO_3 prior to analysis. Effectiveness of the method has been quoted as Au (98%), Os (92%), Pt (81%), Ir (72%), Ru (68%) and Rh (67%), no data were reported for Pd.

This method has the advantages of simplicity and high purification and concentration in a single step and is applicable to the analysis of rocks such as chromitites and schists that would otherwise be difficult by alternative techniques. If the mass of sample is greater than a few grammes or the concentration of the precious metals is greater than a few ppm, however, the yields decline sharply due to low vapour pressure of the precious metal species and reduced access of the reagent gas to the grains (Chuburkov et al., 1990).

2.4 Acid digestion.

One of the most commonly used methods for preparing geochemical samples prior to classical or instrumental solution analysis is acid digestion. Acid extractions introduce less extraneous material into the final solution than fusion with fluxes, thereby reducing the chances of contamination and interferences and are more suited to the batch analysis of large numbers of samples (Fletcher, 1981). In many geological applications, a total digestion of the sample is achieved with, for example, a mixture of HF (which releases silica as volatile SiF_4), $HClO_4$ (a powerful oxidising and dehydrating agent) and HNO_3 (to permit dissolution of elements that have low solubilities in the other acids).

When only a selection of the elements are required for analysis, a partial acid dissolution can be applied (Chao, 1984). Partial digestions are often used in geochemical exploration surveys as the concentration of metals in hydromorphic compounds (i.e. compounds that have formed as a result of secondary surface processes) and sulphides is enhanced relative to metals bound in unattacked silicate phases, thus making anomalies more pronounced.

The preparation of geological samples for determination of the precious metals by acid digestion has been reported but to a lesser extent than decomposition by fire assay. Dissolution of the fire assay button or prill by acids prior to analysis has been extensively used (Section 2.2), but direct acid attack of the initial sample offers some advantages in comparison to the fire assay procedure. For the dissolution of the precious metals, a total acid extraction may not be required and a partial extraction of these elements with lower concentrations of matrix elements would offer some advantages. Only a few mixtures of mineral acids have been used for the dissolution of these chemically resistant metals, previous work with these acids will be summarised below.

2.4.1 Partial digestion by aqua regia.

The core of the work carried out for this thesis has been concerned with the effects of sample digestion with aqua regia, particularly with reference to chromitite samples from ophiolite complexes in particular the Unst Ophiolite, Shetland, and the mineralogical constraints to total dissolution of these samples. A report of this work has been published in the scientific literature (Gowing and Potts, 1991).

The precious metals are relatively inert from a chemical point of view, consequentially they are insoluble in most mineral acids. The majority of publications concerning acid dissolution of the precious metals have used a mixture of HCl and HNO_3. Gold is soluble in a 3:1 mixture of HCl and HNO_3, this mixture being termed "aqua regia". The properties of aqua regia have been realised since the 8th Century (Geber, from Briner, 1916), and it is commonly used for the dissolution of gold in a wide range of materials, including geological samples (Beevers, 1967; Strong and Murray-Smith, 1974). Aqua regia digestion ensures the almost total solubilisation of Au in common geological samples (Terashima, 1988). Rivoldini and Haile (1989) included 1 ml of bromine with 80 ml aqua regia for dissolution of gold from ores and concentrates. Jain et al. (1987) added potassium bromate to aqua regia to improve Au recovery from geochemical soil samples.

Digestion with aqua regia is the most widely used oxidative decomposition procedure for geochemical exploration samples. An aqua regia digestion is more convenient than a total attack for routine work, as it is easy to perform, requires only the most simple equipment and no special precautions are necessary, unlike with HF and $HClO_4$

(Macalalad et al., 1988). Aqua regia digestion offers a preconcentration and separation of precious metals from matrix elements, because many phases or mineral sites containing lithologically important metals are not dissolved,resulting in a lower total dissolved solids content, thus providing a lower effective limit of determination in subsequent analysis (Chao, 1984).

2.4.1.1 The acid mixture.

Briner (1916) observed that when HCl and HNO_3 were placed in a glass tube in the ratio of 3:1, the contact layer quickly took a yellow/brown coloration. When the tube was subsequently sealed and immersed in hot water, there was a tumultuous release of gases, the liquid became excited and finally a second liquid phase assembled below the aqueous phase presenting the beautiful red coloration of nitrosyl chloride (NOCl). Briner and Durand (1912) had previously observed that HNO_3 and HCl in a closed vessel would give rise to a liquid phase, containing NOCl and Cl_2 coexisting in equilibrium with the aqueous phase,

i.e. $4\,H^+ + 3\,Cl^- + NO_3^- \longleftrightarrow NOCl + Cl_2 + 2\,H_2O$.

The ability of aqua regia to dissolve the precious metals lies in the creation a combination of powerful oxidants, Cl_2 and NOCl, and the presence of HCl ensures complexation of the precious metal ions thus stabilising the corrosion products (Westland, 1987). Latimer and Hildebrand (1940, p. 206) attributed this ability to an increase in the reduction potential of the metals in the presence of chloride,

e.g. $Au \longrightarrow Au^{3+} + 3\,e^-$ $E^\circ = -1.42$ V

$Au + 4\,Cl^- \longrightarrow AuCl_4^- + 3\,e^-$ $E^\circ = -1.00$ V.

The 3:1 proportion of the acids is the classical form of aqua regia but some workers have used slightly different proportions, with varied degrees of success, for example 6:1 (Grimaldi and Schnepfe, 1967), 4:1 (Grimaldi and Schnepfe, 1968), 10:3 (Terashima, 1988), 5:2 (Sighinolfi et al., 1984) and 1:1 (Shukun Xu et al., 1991). Hoke and Moore (1916) studied the effects of different dilutions of different HCl/HNO_3 mixtures (5:1 to 1:3) on the dissolution of Pt metal.

2.4.1.2 Aqua regia dissolution for the precious metals.

The dissolution procedure is relatively simple, although more complicated variants involving repeated acid attack steps by different combinations of acids do exist to ensure total dissolution of specific samples. For example, Strong and Murray-Smith (1974) used an initial attack by HCl to dissolve the iron oxide coatings on gold grains. The conventional procedure is as follows: an aliquot of freshly prepared aqua regia (10-100 ml) is added to a weighed sample of rock powder (0.1-30 g depending on the type of sample). This mixture is usually then left overnight and/or heated before the extract solution is either centrifuged or filtered from the leached residue, which is then discarded. The filtrate is then usually evaporated to dryness (Section 2.5) and taken up in HCl prior to spectrometric analysis.

As has been mentioned above, aqua regia has been successfully used for centuries for the dissolution of Au. However, the application of this dissolution technique to the PGE has only recently been realised, and has yet to be fully characterised. It is known that, in metallic form, only Pd and Pt and their alloys containing less than 10% Ir, Ru and Rh are completely soluble in aqua regia. Rh and Ir are only slightly soluble when finely divided, but are soluble if alloyed with a large excess of Pt. In metallic form Rh, Ir and Ru and their alloys are not soluble in aqua regia. Ru is not acted upon by aqua regia, except to a slight extent when alloyed with other metals. Os is thought to be volatile under the prevailing oxidising conditions (Smith, 1987; Powell, 1962). Previous studies involving the aqua regia dissolution of the PGE from geological samples are summarised below.

Herring et al. (1987) reported that Pt and Pd often gave near quantitative recoveries with aqua regia dissolution, although the recoveries of Ir, Rh and Ru were more variable. Firsova et al. (1965) recovered 96-98% of the Pt as well as 100% Au and Pd, 90-98% Rh and 2-50% Ir from an aqua regia leach of an Ural Pt slick ore. Grimaldi and Schnepfe (1967; 1968) obtained quantitative (94%) dissolution of Pd and Pt by aqua regia and also noted that the similar recoveries were obtained for samples of different grain sizes, although a greater proportion of the finer samples was dissolved. Grimaldi and Schnepfe (1967) suggested that apparent losses of Pd in the absence of Pt arose from a failure of aqua regia to dissolve strongly ignited products and the fact that these losses were not evident when Pt was present was due to the formation of a readily soluble Pd-Pt alloy. Grimaldi and Schnepfe (1968) suggested that low Pt and Pd recoveries in the presence of Rh and Ir may be due to the formation of alloys that were resistant to aqua regia attack after ignition of the Te precipitate (Section 2.5.1).

Palmer et al. (1971) reported extractions of Pt (98%), Pd (95-98%) and Rh (75-98%), the efficiency for Rh being the least for a chromite ore (see next Section, 2.4.1.3). These authors also noted that aqua regia extraction of an ore, a low-grade concentrate and a chromite ore resulted in a higher recovery of Pt than that obtained after a lead fire assay procedure; results for Pd, Rh and Au were comparable except for the chromite ore, in which case the aqua regia dissolution resulted in lower recoveries of Pd and Rh. However, Palmer et al. (1972), found that, with aqua regia digestion, there was higher recovery of Pt, comparable recovery of Au and lower recovery of Pd and Rh from chromite ore in comparison to lead and nickel sulphide fire assay. Niskavaara and Kontas (1990) found quantitative recovery of Au, Pd and Rh, but low results for Pt which were attributed to the presence of insoluble platinum minerals (Section 2.4.1.3). Having dispensed with nickel sulphide fire assay, Malhotra et al. (1983) reported total dissolution of all the precious metals by digestion with aqua regia followed by $HClO_4$.

Aqua regia is also a powerful solvent for sulphides and has been suggested as a reagent for sulphide selective attack for bedrock geochemistry (Fletcher, 1981).

2.4.1.3 Limitations to aqua regia dissolution for the precious metals.

From their work on the mode of occurrence of PGE in chromitite, Grimaldi and Schnepfe (1969) inferred that almost all the Rh and a proportion of the Pt was contained within the chromite lattice. This presents a problem as aqua regia is ineffective at breaking down certain resistant phases, most particularly chromite matrices. Consequently the total precious metal content of a sample may not be realised. For example, Belyaev et al. (1985) found that aqua regia was ineffective for the decomposition of 1-2 g portions of slimes, cakes and cinders over the course of 2-3 hours at temperatures up to 160°C; Ir, Rh, Ru and a small amount of Pt was found in the residue. Church et al. (1987) reported that aqua regia attacked and leached metals from mafic chain silicates and phyllosilicates (metals with coordination number of 6 or more), but did not leach appreciable metal from any other silicates.

The modes of occurrence of the precious metals have been detailed in Section 1.5 and due consideration must be made of limitations imposed by such factors on the efficiency of aqua regia digestion. Some workers (e.g. Sen Gupta, 1989) have used HF in conjunction with aqua regia to ensure total solubilisation of gold occluded within silica grains. Alvarado and Petrola (1989) used a 9:6:5 mixture of $HCl:HNO_3:HF$ in conjunction with microwave heating. Trancoso and Barros (1989) used a 5:1 mixture of aqua regia and HF. Moreover, the $HCl/HNO_3/HF$ mixture is one of the most preferred acid mixtures for dissolving silicate rocks.

Just as the application of aqua regia for the dissolution of gold has been extended to the dissolution of the PGE, so has the application of adding HF to the aqua regia to ensure more complete attack of the various minerals. Sighinolfi et al. (1984) found that because the precious metals were present in mineral phases such as sulphides and tellurides, which are soluble in aqua regia, a partial attack with aqua regia usually ensured an almost total solubilisation of Au, Pt, Pd and Rh, although Pt was not completely solubilised by aqua regia and required the addition of HF to the aqua regia residue to eliminate silica (Fryer and Kerrich, 1978). Sen Gupta and Gregoire (1989) digested silicate and iron-formation rocks and ores with an acid mixture containing equal proportions of aqua regia and HF. Eller et al. (1989) increased the power of aqua regia by adding 6.5 ml HF and 0.5 ml HNO_3 to 3 ml aqua regia after 15 minutes attack by aqua regia alone, then heating the whole mixture in a pressure bomb at 160°C.

Mineralogical limitations.

Not only can the PGE occur in the lattice of host minerals,these elements are also known to form discrete PGM present with various mineralogical associations (Canada: Cabri and Laflamme, 1976; South Africa: Feather, 1976; Mostert et al., 1982; USSR: Genkin and Evstigneeva, 1986; Shetland: Prichard et al., 1989). For example Tarkian and Prichard (1987) reported that an Os-rich laurite was entirely enclosed by chromite whereas an Os-free variety was located in the silicate matrix interstitial to the chromite.

Although Pd and Pt in the form of native metals or alloys containing less than about 10% Ir, Ru and Rh are soluble in aqua regia (Powell, 1962, p. 702), some of the most common PGM are extremely resistant to attack by aqua regia. Sperrylite ($PtAs_2$), cooperite (PtS) and braggite ((Pt, Pd, Ni)S) are insoluble in aqua regia unless they have been decomposed by roasting. Laurite ($(Ru,Os)S_2$) and osmiridium ((Os, Ir)) are insoluble in aqua regia even after roasting (Schoeller and Powell, 1955, p.325; Powell, 1962, p. 703). Although aqua regia was used to attack native Pt, Sen Gupta (1972) had to submit the residue to direct chlorination to attain total decomposition of the sample. This author also used direct chlorination to effect the decomposition of osmiridium and sperrylite.

Au is usually present as the native metal or simple minerals which are soluble in aqua regia; solubilisation of Au is thus not generally subject to such mineralogical constraints. However, any Au minerals completely enclosed in insoluble acid resistant grains such as quartz would not be brought into solution and the resulting determinations would be low. Fine grinding of the sample would help to overcome this mineralogical occlusion, but problems may then occur due to plating of Au onto the grinding equipment. It is necessary, therefore, to reach a compromise between sample preparation and experimental procedure in the development of an analytical technique to minimise the effects of these two sources of error (Lakin and Nakagawa, 1965).

2.4.1.4 Other applications of aqua regia dissolution.

Before the aqua regia digestion technique can be applied as a nominally selective extraction procedure for the precious metals, it is necessary to consider the effects of this acid on other elements likely to occur in natural geological samples. Aqua regia has been used not only for the dissolution of precious metal samples, but has also found application for a diverse range of geochemically important elements. For example, Niskavaara and Kontas (1990) used aqua regia to solubilise Ag, Se and Te as well as the precious metal elements mentioned above.

In their studies of a two stage oxalic acid-aqua regia partial digestion of geochemical samples, Church et al. (1987) found that more than 90% of the Fe, Mg and associated trace elements were leached from the olivine structure and 15% of the Fe, Ca and octahedral Mg were leached from diopside and hornblende structures. Biotite was almost completely dissolved but <10% K and octahedral Al were removed from muscovite; 25% of the Fe, Ca and octahedral Al and >75% of the Ti were removed from epidote. In the spinel group, magnetite was completely dissolved, 70% of the octahedral Mg and 30 % of the tetrahedral Al were removed from spinel, but chromite remained largely unattacked. These authors concluded that aqua regia would attack secondary minerals as well as sulphides, leaching many of the octahedrally coordinated lattice sites, but not the tetrahedrally coordinated lattice sites in silicates to a substantial extent.

Kuldvere (1989) studied the effects of six acids, individually and in combination, including aqua regia and reversed aqua regia (1:3 $HCl:HNO_3$) on the dissolution of As, Sb, Bi and Se. Both aqua regia and reversed aqua regia brought all four elements into solution quantitatively.

All primary sulphide minerals including pyrite, molybdenite and cinnabar are attacked efficiently by aqua regia thus providing an effective picture of primary mineralisation patterns. Bearing this in mind, Macalalad et al. (1988) have described a concise analytical scheme for Ag, As, Bi, Cd, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Te, Tl and Zn using an attack by aqua regia, doped with Br_2 to catalyse oxidation of sulphide at room temperature. The precision and accuracy attained for all 16 elements, proved to be adequate for geochemical exploration studies.

Lechotycki (1990) used 2:1 aqua regia to effect dissolution of Mo and V from soils. Rowbottom (1991) extracted Mo from soil and sewage sludge with aqua regia for pollution monitoring purposes. Both these authors noted that, although metals which form oxide, carbonate and sulphate were easily released by aqua regia, metals contained in the crystal lattices of unweathered primary minerals, particularly primary silicates, were not completely dissolved by aqua regia. It is thus usual to solubilise and recover only 60-90% of the element. This proportion could be increased, however, by the presence of more easily dissolved secondary minerals.

Bonilla (1932) identified the optimum physical conditions and proportions of HCl and

HNO_3 to effect the dissolution of Ni and Fe from metallurgical samples. The proportions of the acids were 3:40 for Ni and 7:20 for Fe with 30 and 12 minutes dissolution time, respectively. The maximum rate of corrosion was about 16x that observed with a 4:1 mixture, which had been used previously for the dissolution of the precious metals. Thus, the use of 3:1 aqua regia may result in an incomplete dissolution of Ni and Fe.

2.4.2 Partial digestion by other acids.

Although aqua regia has been used successfully to effect digestion of the precious metals, a few other acid mixtures have been used. There are many mineral and organic acid partial digestions used in exploration geochemistry studies, for example oxalic acid, dilute HCl and hydrogen peroxide/ascorbic acid (Church et al., 1987). The mixtures involving addition of another reagent to aqua regia have been considered above, other mixtures used for the dissolution of the precious metals, independent of aqua regia, will be summarised below.

2.4.2.1 Hydrobromic acid/bromine mixture.

Metallic Au and most Au-bearing minerals were soluble in acid solutions of bromine even at room temperature (Thompson et al., 1968). Lakin and Nakagawa (1965) recovered Au with greater than 99% efficiency using an extraction mixture of sodium bromate and HBr followed by solvent extraction into ethyl ether. The results from the HBr/Br_2 digestion were in good agreement for Au concentrations of 1 ppm or more (Van Sickle and Lakin, 1968) and Thompson et al. (1968) reported that the method could be adapted for use in the field. The HBr/Br_2 digestion has benefits over fire assay of simplicity, sensitivity and cost (Van Sickle and Lakin, 1968), but Thompson et al. (1968) warn that the method was not intended to replace fire assay, but should be used as a supplementary method or for exploration work where rapid results are necessary.

The HBr/Br_2 digestion technique has been used regularly for the solubilisation of Au following the simple procedure described by Lakin and Nakagawa (1965). More recently, though, the extraction mixture has been used in a more dilute form to permit good extraction into methyl isobutyl ketone (Benedetti et al., 1987). In a comparison of various techniques, Hall et al. (1989b) reported that the HBr/Br_2 mixture solubilised only 54-89% of the Au that was released by aqua regia. These authors claimed that this difference was due to incomplete dissolution of the Au by HBr/Br_2, particularly as Benedetti et al. (1987) indicated the ratio of volume of HBr/Br_2 to weight of sample taken was critical. Despite its obvious success in effecting the dissolution for Au, the HBr/Br_2 digestion technique has not found application to the decomposition of geological samples for the release of the PGE.

Hubert and Chao (1985) made use of the HBr/Br_2 system by adding it to a mixture of HF and aqua regia to further ensure the complete dissolution of Au, In, Te and Tl from rocks, soils and stream sediments. Their paper exemplifies the need to consider, just as with aqua regia, the effects of the any acid mixture on the sample as a whole before it can be used as a selective extractant.

2.4.2.2 Orthophosphoric acid/perchloric acid mixture.

Having dismissed roasting pretreatment as too time consuming, Vermeulen (1989) used an oxidative acid attack as a preliminary step prior to HBr/Br_2 digestion. Aqua regia was considered as the oxidative acid and quantitative extraction of Au was realised for certain rock types, but not when Au was occluded in silicates or refractory minerals. Instead a 3:2 mixture of orthophosphoric acid (H_3PO_4) and $HClO_4$ was used because of physical properties of the mixture and its success in dissolving refractory minerals. Hannaker and Hou Qing-Lie (1984) also used a mixture of $HClO_4$ and H_3PO_4 for the dissolution of geological materials because (a) H_3PO_4 had previously been used to dissolve chrome and iron ores, (b) alkaline fusion gives a high salt content which can cause light scattering in subsequent atomic absorption spectrometry and (c) the $HF:HClO_4:HNO_3$ mixture can result in incomplete dissolution and is time consuming.

2.4.2.3 Sulphuric acid mixtures.

Despite a mixture of HF/H_2SO_4 being established as one of the most effective methods of rock dissolution (Oshin and Crocket, 1982), Amossé et al. (1986) found that better detection limits for Pt, Pd, Rh and Au could be achieved using aqua regia rather than the HF/H_2SO_4 mixture. Yoshikuni (1991) overcame the problems of insoluble chromite matrix by effecting dissolution in a mixture of H_2SO_4, Li_2SO_4 and $Ce(SO_4)_2$, MnO_2 or KIO_4 prior to determination of Cr. Although these mixtures will not dissolve the precious metals, they could provide an effective means for liberating the precious metals from the matrix in an initial attack prior to aqua regia dissolution of the residue.

2.4.3 Roasting pretreatment.

As mentioned above, roasting prior to decomposition of a sample can have great benefit in the recovery of the precious metals. This extra step serves to (a) prevent vigorous reaction during the early stages of acid attack, with evolution of hydrogen sulphide (Palmer et al., 1971), (b) destroy any organic material in the sample (gold can be adsorbed by carbon in the residue of unroasted samples (Bumstead, 1984; Kontas et al., 1986)) and (c) decompose many sulphide and arsenide minerals, in particular sperrylite, braggite and cooperite (see Section 2.4.1.3). Vermeulen (1989) recognised the benefits of this form of sample pretreatment, but regarded roasting as time consuming, labour intensive and a health hazard if large amounts of sulphur were present. The effects of roasting on the efficiency of aqua regia digestion of samples and sperrylite will be documented in Chapter 7.

Some procedures incorporate a roasting of the sample at 500-800°C prior to aqua regia attack (500°C: Niskavaara and Kontas, 1990; 600°C: Palmer et al., 1971, 1972; 700°C: Kontas et al. 1990; 750°C: Kontas et al., 1986). Strong and Murray-Smith (1974) and Parkes and Murray-Smith (1979) showed that 600°C was the optimum roasting temperature prior to dissolution of Au and Pd; below 550°C breakdown of sulphides may be incomplete, while above 650°C volatilisation of Au can occur, particularly if As is present. Sintering of certain clays can also occur above 650°C, which may result in the retention of Au, hence a reduction in the extraction efficiency recovery (Bumstead, 1984; Vermeulen, 1989).

Trancoso and Barros (1989) found that direct decomposition of sulphide ores, without a preliminary roasting, resulted in incomplete recovery of Au. Sighinolfi et al. (1984) reported that roasting a sample often favoured precious metal solubilisation in combined acids and removed S that if present in large amounts would reduce the efficiency of Te coprecipitation (Section 2.5.1). Ores rich in S and As are often roasted prior to tin fire assay to prevent the formation of a matte or speiss (Beamish and Van Loon, 1972, p. 71; Section 2.2.2.1), although care should be taken in this process to prevent the loss of volatile Au compounds.

Just as with aqua regia digestion, the sample mineralogy should be taken into consideration before indiscriminate use of roasting. For example Beamish (1966, p. 27) reported that, although Tasmanian iridosmines yield no traces of Os on high temperature treatment in air, certain alloys from Ethiopian placer deposits may readily yield OsO_4 on heating.

2.5 Secondary preconcentration methods.

In all the above techniques (peroxide fusion, chlorination, distillation (except those procedures described by Payne, 1960) and acid digestion), the procedure serves to decompose a solid sample leaving an aqueous solution containing most if not all the constituents of the original solid sample. As mentioned in the introduction (2.1), to achieve adequate sensitivity in the analysis of geological samples there is also a need to preconcentrate the PGE and Au prior to analysis, even taking into account the partial separation and preconcentration properties of the aqua regia digestion (Section 2.4.1) Various methods have been used to accomplish this, each successful in its own application. A secondary preconcentration step is often included even in addition to fire assay, once the button/bead has been taken into solution (e.g. Jackson et al., 1990).

The presence of HNO_3 will interfere with most classical as well as many instrumental methods of analysis and the use of HCl encourages the formation of chloro-complexes, with the advantage that in this form Os and Ru may resist distillation (Beamish, 1966, p. 364). Additionally, Cleare et al. (1979) reported that chloride was the only effective medium in which all the PGE in a concentrate could be brought into solution. Secondary separation procedures are relatively simple but, since samples must normally be analysed in chloride solution, repetitive evaporations to dryness after dissolution in HCl must usually be used as a first step after sample dissolution to remove oxides of nitrogen and to ensure complete conversion to precious metal chlorides. Care must be taken when redissolving residues that have been taken to near-dryness or dryness as Bumstead (1984) has identified incomplete re-solution as a potential source of loss of Au.

Recently, working on the principle that biological organisms have the potential ability to absorb selectively specific elements without preconcentrating the matrix, Mo Shengjun and Holcombe (1990; 1991) have preconcentrated Cu, Ni and Co on green algae from water samples. Such techniques are not available for the precious metals at present,and the more common forms of solution preconcentration are described below.

2.5.1 Coprecipitation.

A simple solution chemistry method for preconcentrating the precious metals is to remove them selectively from solution by precipitation with a suitable carrier. Beamish (1966, p. 69) documented that various reagents have been used to precipitate individual precious metals, for example hydroquinone (Au), dimethylglyoxime (Pd) and zinc (Pt), but other authors have considered a group precipitant for all the PGE and Au.

A few carriers have been tested but reductive coprecipitation with Te has proved to be the most successful. The most common procedure is to add an acidified portion of a solution of tellurite to an acidified sample solution, then to reduce the tellurite by adding an excess of $SnCl_2$ solution and boiling. A black precipitate of precious metal tellurides and tellurium metal forms, which is then filtered and washed until free of the filtrate containing the matrix elements. The precipitate is then analysed directly (Shazali et al., 1987) or dissolved in aqua regia to release the precious metals into a solution with much lower concentrations of interfering matrix elements (Fryer and Kerrich, 1978; Elson and Chatt, 1983; Stockman, 1983; Sighinolfi et al., 1984). Grimaldi and Schnepfe (1968) noted low recoveries of Pt and Pd if the precipitate is ignited before aqua regia dissolution, especially when Rh and Ir were present. These authors proposed that this may be caused by the formation of alloys or metals which are resistant to the action of aqua regia (Section 2.4.1.3).

Sighinolfi et al. (1984) argued that Te coprecipitation is superior to cupellation, fire assay and solvent extraction (Section 2.5.4) because (a) the number of handling stages is reduced, leading to a more rapid sample throughput, (b) the composition of the analyte is ideal for subsequent GFAAS analysis (Section 3.2.2), (c) in theory, almost complete separation of precious metals can be achieved from most of the rock matrix elements, thus reducing potential for interferences in subsequent analysis, (d) only a few milligrams of Te are required as Te is insoluble in water and HCl, and (e) Te is volatile and removed during thermal pretreatment prior to GFAAS analysis (Fryer and Kerrich, 1978), although increased Te in the analyte solution can reduce the atomisation rate for most metals which leads to a higher background. Sen Gupta (1989) used Te coprecipitation in preference to ion exchange (Section 2.5.2) to obtain adequate extraction efficiency from samples of large enough mass to ensure heterogeneity.

Fryer and Kerrich (1978) reported that this method provided quantitative recovery of Pt, Pd, Rh and Au. Shazali et al. (1987) reported high recovery of Rh, Ru and Ir, considering their low concentrations, but low recovery of Os. Stockman (1983) reported 90-100% recovery for Pd and Au but only 60% for Ir, failing to repeat the selectivity and quantitative yields, reported by Nadkarni and Morrison (1974) who used an ion exchange separation (Section 2.5.2). Elson and Chatt (1983) reported recoveries of Pd (102%), Rh (98%) and Ir (69%) and quantitative recovery of Pt. Sighinolfi et al. (1984) reported 90-96% recoveries of Au, Pt, Rh and Pd of, 80-92% in the presence of excess Fe, 78-93% in the presence of excess Ni and 84-95% from an artificial solution with a pyroxenite-type matrix. After parting a lead fire assay button with HNO_3 and coprecipitating the dissolved Pt and Pd with Te, Moloughney (1980) reported quantitative recoveries of Pt (96-98%) and Pd (97-105%).

Fryer and Kerrich (1978) stated that a single precipitation resulted in a significant magnitude of interfering species in the analyte which were not volatilised with the Te during thermal pretreatment but became adsorbed onto the atomisation furnace wall (Section 3.2.2). Sighinolfi et al. (1984) reported increased collection with a second precipitation of Au (11%), Pt (11%), Rh (5%) and Pd (4%) and suggested that some other trace elements, such as Hg, Bi and Cu, may form insoluble tellurides, being coprecipitated along with the precious metals. Elson and Chatt (1983) also reported low but significant collection of As, Sb (<12%), Re, Cu and Hg (<20%).

Amossé et al. (1986) used reductive coprecipitation with selenium to effect 90-100%

recovery of the PGE but had to use Te instead of Se to achieve quantitative recovery of Au. McHugh (1983) used hypophosphorous acid instead of $SnCl_2$ as the reductant for coprecipitation of Au with Te from water samples. Malhotra et al. (1983) used thiobarbituric acid for precipitation of Pt, Pd, Rh and Au prior to direct spectrochemical analysis of the precipitate. Jiucheng Li et al. (1989) used oxalic acid to precipitate dipicrylamine complexes of precious metals while passing high-frequency electrical or ultrasonic waves through NaCl leaches of soils. Pavlenko et al. (1980) coprecipitated Pt, Pd, Rh and Ir with a mixed collector of copper sulphide and 2-mercaptobenzothiazole from blister copper and vein ores, processing products of copper-nickel sulphide ores and rocks. Weiss and Fresco (1983) reported 97% efficient coprecipitation of Pd from extremely large (680-1660 L) sample volumes of seawater with bismuth sulphide.

Kontas et al. (1986; 1990) reported methods for reductive coprecipitation of Pd and Au with mercury, using $SnCl_2$ as the reductant. The final precipitate was an alloy which was subsequently dissolved in HCl-H_2O_2 or aqua regia. In this instance, the analyte elements are reduced to the elemental state together with a suitable collector. Niskavaara and Kontas (1990) argued that coprecipitation with Hg was better than Te because no heating is required to promote formation of the precipitate which was completely volatilised during thermal pretreatment of the analyte sample prior to AAS (Section 3.2.2). If the sample has a heavy matrix, however, the Hg coprecipitation may be incomplete. Kallmann (1987) reported that all the PGE could be precipitated with hypophosphite and a mercurous salt in slightly acid medium or with hydrazine hydrate or aluminium in an alkaline medium.

Of the various methods used previously, coprecipitation with Te has had the widest application and greatest success. Te has the additional benefits of being soluble in aqua regia, like the precious metals (Section 2.4.1) and volatile enough to be expelled during the thermal pretreatment stages of graphite furnace atomic absorption spectrometry. There are also selective coprecipitants specific for individual elements when their mutual separation and isolation is required.

2.5.2 Ion exchange.

Ion exchange is based on kinetic effects, specifically differences in the labile character of the precious metals to associate with cationic, anionic or complexing ligands attached to the ion exchange substrate. The separation process is based upon a reversible exchange of ions between a solid phase (resin) and a mobile phase (eluent). An ion exchange resin consists of a solid substrate, often based on styrene polymers, with functional groups attached to specific sites along the polymeric chain. Variations in the number and type of functional groups allows preparation of ion exchange resins with different selectivity properties. The resin is usually packed into a column and, after the sample has been loaded onto the top of the column, ions are eluted through the resin using a suitable solvent introduced at a controlled rate. A dynamic equilibrium is established between the analyte ions diffusing into the resin and the 'counter' ions leaving the functional groups.

There are three main types of this concentration and separation method, namely cation exchange, anion exchange and ion exchange by chelation. These three types of ion exchange are summarised by the following reactions:

Cation exchange: $M^{n+}{}_{(aq)}$ + resin.$(F^-H^+)_n$ <-> resin.$(F^-)_n.M^{n+}$ + n $H^+{}_{(aq)}$

Anion exchange: $M^{n-}{}_{(aq)}$ + resin.$(NR_3{}^+Cl^-)_n$ <-> resin.$(NR_3{}^+)_n.M^{n-}$ + n Cl^-
$_{(aq)}$

Chelation: $M^{n+}{}_{(aq)}$ + resin.$(L^-H^+)_n$ <-> resin.$(L^-)_n.M^{n+}$ + n $H^+{}_{(aq)}$

where M^{n+} is a metal cation (or complex cation), F^-H^+ is an acidic functional group (e.g. $-SO_3{}^-H^+$ for strongly acidic resins and $-COO^-H^+$ for weakly acidic resins), M^{n-} is a metal anion, (or complex anion) $NR_3{}^+Cl^-$ is an amine (primary, secondary or tertiary dependant upon the strength of ion retention required), L^-H^+ is the functional group containing chelating ligands and $_{(aq)}$ refers to the solvated species in solution in the aqueous eluent.

The ions are separated by their different affinities for a specific resin, the stronger the affinity the more strongly bound the ion becomes to the resin and the more solvent is required for elution. In the case of the PGE, these differences can be enhanced by varying the solution constituents (Al-Bazi and Chow, 1984), such that PGE complexes form ion pairs with large organic cations (Cleare et al., 1979). The selectivity of a particular resin for an analyte is dependant upon a number of factors: (a) the electroselectivity (e.g. doubly charged ions will be more strongly selected by ion exchange resins than singly charged ions, and selectivity decreases with increasing size of solvated ion); (b) the resin swelling factor (i.e. a smaller solvated ion will preferentially exchange with a larger one that causes physical strain within the resin, taking into account electroselective factors); (c) the potential for chemical interaction between ion and resin (i.e. chelation factors should be considered as well as the electrostatic interaction); (d) the pore size of the resin (i.e. the resin can be manufactured to exclude large ions); (e) the nature of any other ions present which may disturb expected solution conditions (Potts, 1987, p. 476).

2.5.2.1 Cation exchange.

The solution is loaded onto the column and the ions are eluted by acids. In weakly acidic solutions, base metals are retained and the PGE, owing to the strength of their chloride complexes, pass into the effluent. Although the chloro-complexes are usually the most convenient to use for ion exchange separation, Razina and Viktorova (1970), using Dowex 50-X2 resin, achieved the separation of Rh, Pt, Pd and Au from Fe, Cu and Ni from dilute aqua regia solutions, without the need of conversion to chlorides. Payne (1960) extolled the requirement of careful manipulation of acidity to avoid retention of PGE on the column as well as the base metals.

Grote and Kettrup (1987) used P-TD resin, the functional groups of which contained sulphur-bonded dehydrodithizone. The resin was found to be selective for some PGE and Au and could be regenerated. Myasoedova et al. (1988) utilised the high selectivity of noble metals in sorbents with heterocyclic amine groups. Using Poliorgs-IX, these authors found that benzimidazol groups were selective for PGE and Au (at percent concentrations) from solutions of Cu, Ni, Co, Te, As, Fe(III), Bi and Ti. Sen Gupta (1989) reported quantitative recovery of Ru, Rh, Pd, Ir, Pt and Au (Os was not determined), but found incomplete separation from Ti, Ca, Mg and Sr from actual silicate rock samples when using Dowex 50W-X8 resin. Srivastra and Rao (1990) utilised the strong chelating property of oximes, using a salicylaldoxime formaldehyde resin to separate Pd from Cu, Zn, Ni, Co, Cd, Mn, Pb and Fe with 99-100.5% efficiency.

2.5.2.2 Anion exchange.

Anion exchange differs from cation exchange in that after the weakly acidic solutions are loaded onto the ion exchange column, the precious metals, in the form of chloro-complexes, are retained on the resin and the base metals are eluted. The precious metals can then either be determined directly on the resin or, as is more often the case, are themselves eluted from the resin by a second solvent. Some anion exchange resins are so strong that they have to be ashed to recover the PGE (Razina and Viktorova, 1970). Watson and Moore (1984) found that the affinity of the PGE for Monivex resin so great that they could only be eluted with difficulty using large volumes of eluent, and even then not completely, although these authors reported that direct analysis of the resin as a slurry obviated this problem. The strength of interaction of PGE chloro-complexes with an anion exchange resin is highly dependent upon the charge of the complex, for example, compounds of the form MCl_n^{2-} are strongly sorbed, whereas those of the form MCl_n^{3-} are only weakly bound in static systems. However, in the case of Rh and Ru, the success of this approach is also dependent on the age of solution as chloro-complexes of these elements are labile to aquation (Al-Bazi and Chow, 1984).

Anion exchange is most often used with the PGE to separate Rh and Ir from each other and from Pt and Pd when their mutual separation is required (Al-Bazi and Chow, 1984). Bruening et al. (1991) used anion exchange with thiamacrocycles (18 or 19 membered crown thiaethers, e.g. 1,4,7,10-tetrathia-18-crown-6) to exploit the difference in stabilities of the chloro-complexes of Pd and Au, with the additional advantage that the resin could be ashed to release the precious metals if elution was a problem. The lack of pH dependence of these macrocycles allowed the use of highly acidic media, so increasing the versatility of ion exchange. The authors did find, however, that an Fe(III) concentration greater than 1000 times the Au concentration caused a decrease in Au recovery by 20%.

Tikhomirova et al. (1991) used silica, modified with nitrogen-containing ligands, such as aliphatic mono- and polyamines, for ion exchange. This procedure required a complicated desorption procedure, so direct analysis of the sorbent phase was found to be necessary. McHugh (1986) used a combined method of ion exchange with AG-1-X8 resin and solvent extraction with MIBK for interference-free analysis of acidified water samples for Au. The preliminary ion exchange was simple enough to be accomplished in the field, so that a stabilised water sample could be taken to the laboratory for analysis. Shukun Xu et al. (1991) used Amberlite XAD-8 resin in an on-line flow-injection sorbent extraction to achieve a 97-108% efficiency for the recovery of Au.

2.5.2.3 Ion exchange by chelation.

The success of ion exchange is very dependant upon the retention capabilities of any particular resin. Most separation schemes use general purpose cation or anion exchange resins, however, a few resins have been synthesised which are selective for all the precious metals. For example, Srafion NMRR is specific for the noble metals as it binds only ions with d^8 electronic configuration which form square planar complexes. It also contains carbon-carbon double bonds which allow reduction of Pt(IV) and Ir(IV) to Pt(II) and Ir (I), respectively, which are then bound as square planar complexes (Nadkarni and Morrison, 1974). The effectiveness of Srafion NMRR is only apparent in weakly acidic (pH 1.3-1.4) conditions as metal ions and amino groups from the resin hydrolyse at pH>8, and the adsorption capacity of the resin decreases at very low pH; binding of the metal ions is performed by exchange with H^+ ions, so high concentration of H^+ ions reverses the reaction (Brügmann et al., 1990). Stockman (1983) found significant amounts of Cu, Cr, Fe and other species were retained on Srafion NMRR resin whose Compton background swamped Pd and Pt in direct INAA analysis of the resin. Brügmann et al. (1990) found low recoveries of Pd (73%), Au (76%), Os (78%), Ir (70%) and Ru (70%) were due to a loss of the elements during ion exchange.

2.5.2.4 Other separation methods based on ion characteristics.

He Xin-Cun (1991) used the differences in the kinetic properties of the PGE by ion floatation of anionic chloro-complexes, utilising the differences in their labile character. The technique is fast, simple and does not require expensive reagents and apparatus. Balcerzak (1988) developed a sensitive ion floation-spectrophotometric method for the determination of Os.

2.5.3 Chromatography.

Chromatography is similar in principal to ion exchange but utilises the differential solubilities of various elements in a particular eluent (mobile phase), rather than depending upon different ion retention. A sample solution containing both analyte and matrix elements is introduced to a column of inert filler (stationary phase). This sample aliquot is then eluted through the stationary phase by a particular solvent or mixture of solvents. The analyte elements and the matrix elements pass through the column at different rates, and the separated fractions are collected for analysis.

There have been few uses of chromatography for the separation of Rh, Ir, Pd and Pt from traces of base metals, and this technique tends to be most often used to separate the PGE from each other rather than as a group extractor (Beamish, 1966, p. 144). Razina and Viktorova (1970) used a very simple form of chromatography, paper partition chromatography, for the mutual separation of Pt, Pd, Rh and Au with 87-97% extraction efficiency, cutting up the paper chromatograms and washing off the element for determination. Agrinier (1962) reported separation of Au from a suite of matrix elements and PGE by paper chromatography after an aqua regia leach of roasted silicate rock samples, the results compared favourably to fire assay. Misra and Rajput (1990) reported the use of electrochromatographic separation of Pt(IV) from PGE and other metal ions. Alimarin et al. (1990) reported simultaneous determination of all six PGE in technological solutions of concentrates, alloys and catalysts.

Chromatography can combine the formation and separation of chelates, simplifying and accelerating sample preparation procedures. A combination of a preliminary group extraction with subsequent chromatographic treatment of the extracts permits maximum exploitation of high pressure liquid chromatography (HPLC) for multielement analysis and a significant lowering of detection limits (Basova et al., 1989). Alimarin et al. (1990) praised the effectiveness (96-101% mean recoveries for all the PGE), sensitivity and speed of HPLC as a solution to the problem of using a single sample for the determination of several PGE. Timberbaev et al. (1991) extolled the speed, throughput, repeatability and reproducibility of automated HPLC, determining the metals in the form of chelates.

Relatively concentrated acids have to be used as the mobile phase to prevent hydrolysis and disproportionation of the PGE, which would result in a broadening of the chromatographic zones and, because the volume of the mobile phase is sometimes large, a high degree of preconcentration cannot be achieved (Basova et al., 1990). Kinetic inertia of the initial aqua hydroxy- and acido-complexes and side effects from the introduction of a free reagent into the eluent cause contamination and increased background, limiting the number of determinable elements (Basova et al., 1989).

2.5.4 Solvent extraction.

The theory behind solvent extraction is similar to that purported for the use of ion exchange, but without the need for choosing and priming a resin and the lengthy processes of elution. The idea is to form selectively an uncharged complex of the analyte element which, upon shaking with an immiscible organic solvent, can pass from aqueous solution with high total ion concentration to organic solution with much lower total ion concentration or, preferably, containing just the analyte species,

i.e. Complex formation: $[MCl_6]^{n-}{}_{(aq)} + n\,L_{(aq)} \leftrightarrow [MCl_{6-n}L_n]_{(aq)} + n\,Cl^-$

Complex extraction: $[MCl_{6-n}L_n].mH_2O + m\,Solv \leftrightarrow [MCl_{6-n}L_n].mSolv + m\,H_2O$

where M is the analyte metal element, L is a specific releasing ligand, mH_2O represents aqueous solvation and mSolv represents organic solvation. The analyte element can then either be determined directly from the organic solution or back-extracted for determination in aqueous solution.

The extraction of precious metals from an aqueous solution into an immiscible organic solvent serves the two purposes. The analyte elements are both concentrated, enhancing sensitivity, and separated from potential interfering elements, enhancing selectivity (Freiser, 1984). An extra benefit is also realised as the resultant organic extract often yields enhanced sensitivity in atomic absorption spectrometry compared to aqueous solution (Samchuk et al., 1988), indeed solvent extraction methods have played an important role in the widespread acceptance of atomic absorption spectroscopy for noble metal determinations (Van Loon, 1977).

2.5.4.1 Complex formation.

The principle of solvent extraction for the precious metals is that the chloro-complexes in acidic aqueous solution are converted to more stable extractant-chloro-complexes, sometimes using an intermediary labilising agent to promote the formation of the second complex. These extractant-chloro-complexes are then extracted into a specific organic solvent to achieve separation from most of the matrix elements, which are themselves prevented from forming extractant-chloro-complexes by judicious use of an extractant selective to the precious metals. Formation of these complexes is accomplished by ion association (analogous to liquid ion exchange), solvation or chelation, the first two of these are in common practice in industry and the third is limited to analytical applications (Dhara, 1984). Vigorous shaking of the two phases serves to give essentially complete (>95%) extraction because mass transfer rates are much greater than chemical reaction rates and, in most analytical extraction procedures, conditions favouring extraction are sufficiently far from equilibrium (Freiser, 1984).

Because of the kinetic inertness of Pt complexes, fewer extracting agents are known for Pt than for either Pd or Au (Shkil' and Zolotov, 1988). To overcome this limitation, complexing agents can be added to the mixture to either mask foreign elements or labilise kinetically inert PGE complexes (Shkil' and Rukhadze, 1989). Rakovskii and Starozhitskaya (1974) made use of the variety of solution chemistries of the PGE and developed a scheme of successive isolation and determination of these elements based on the differences in reactivity of their chloride complexes.

Pechenyuk and Kuz'mich (1988) highlighted the need for careful consideration of the extraction conditions and selection of extractants and solvents, reporting that the interaction of different complexes of precious metals in solution can lead to incomplete recovery of an element or group of elements and that poor separation of a mixture had a negative effect on the accuracy and reproducibility of an analysis. For example, the heterogeneous hydrolysis of $RhCl_6^{3-}$ increases and $IrCl_6^{3-}$ decreases in the presence of $OsCl_6^{2-}$, while that of $OsCl_6^{2-}$ is drastically decreased in the presence of $PtCl_6^{2-}$, and the stability of $Ru_2OCl_{10}^{4-}$ increases in the presence of $IrCl_6^{2-}$ (all these chloro-complex anions are known to be present in HCl solution (Cleare et al., 1979)). These authors argued that the changes in complex character indicated that certain stable compounds were formed in solution with participation from both complexes and postulated that there was a degree of autocatalysis. For example, $[OsCl_6.IrCl_6]^{4-}$ was formed, then, upon precipitation of Os, the heterogeneous hydrolysis of $IrCl_6^{3-}$ was accelerated. Their data attested to the formation of compounds between coordinatively saturated low-spin complexes with central atoms in high and stable oxidation states, thus resulting in non-quantitative precipitation of Os, Ir and Ru and incomplete separation of Os from Ir, Pt and Rh.

2.5.4.2 Complex extraction.

The extraction of the complex into the organic solvent is accomplished by either (a) non-coordinating outer sphere mechanism with ionic or ion dipole binding between metal complex and solvent or (b) inner sphere coordination with the active species in the solvent system acting as nucleophiles and displacing a ligand from the metal complex. Ligand exchange of the type $MX_n + L \rightarrow MX_{n-1}L + X$ is, however, of limited use in precious metal separation because of the relatively slow substitution kinetics (with respect to the base metals), involving impractically long equilibrium times, in fact Pd (II) is the only precious metal species sufficiently labile to allow this to work (Cleare et al., 1979). Solvent extraction by solvation involves the transfer of a formally neutral species (ML) from aqueous to organic solution by solvation of the metal ion (Flett, 1982), i.e. $(ML).m\,H_2O_{(aq)} + n\,Solv_{(org)} \leftrightarrow ML(H_2O)_{m-n}(Solv)_{n\,(org)} + n\,H_2O_{(aq)}$

Solvent extraction separation procedures are based on due-consideration of the physico-chemical characteristics of the solution chemistry such as redox potentials, ligand exchange rates (both of which are dependent upon d-electron configuration), dissolved ionic complex species, reaction with extractants and extraction rates (Fuwa, 1987). Indeed, the selectivity of solvent extraction is achieved through the nature of the extractant/metal species interaction and to the prevailing chemistry of the aqueous phase (Flett, 1982). To separate binary or multi-component systems of the PGE, solvent extraction uses the differences in their kinetic behaviour (their labile character towards hydration) for the formation of extractable species as well as the strength of electrostatic interaction of their chloro-complexes with liquid ion exchangers. Hydrophobic anions, such as Br^-, I^-, SCN^-, $SnCl_3^-$ and $SnBr_3^-$, and neutral organic compounds, such as those containing N, P, S, As and/or Sb, can alter the lability of the PGE in the formation of extractable species (Al-Bazi and Chow, 1984) and are used to permit the successful extraction of PGE complexes (e.g. Senise and Levi, 1964; Mojski, 1980).

2.5.4.3 Solvent extraction for the precious metals.

In developing a scheme for the selective extraction of 18 of the most commonly geochemically analysed elements, Clark and Viets (1981) have shown the use of solvent extraction for geochemical exploration. Sandell (1959, p. 41) reported that extraction of a trace constituent by an immiscible organic solvent was frequently the ideal method for separating the constituent from large amounts of concomitant elements. Furthermore, selective solvent extraction schemes have been reported for the separation of the precious metals from one another (e.g. Al-Bazi and Chow, 1984) and for group extraction for all the PGE or precious metals (e.g. Seeverens et al., 1983).

Having had success in using solvent extraction for the separation of gold, Barnes and Edwards (1982) reported a method where the PGE were extracted sequentially from the total leach liquor. These authors said that the solvent extraction procedure offered greater selectivity and more complete removal of metal than precipitation methods through the use of multi-stage extraction. The varied use of extractants in industry is exemplified in the review by Fuwa (1987), three industrial refineries with large scale operations each used their own different solvent extraction technology.

There have been many extractants reported for the isolation of the precious metals for analytical applications, some are designed to extract selectively just one of these elements, some for more than one and some for a group extraction of all seven of the elements. Most of these references use chlorinated solvents such as chloroform ($CHCl_3$) and 1,2-dichloroethane (DCE) and a few use simple aromatic solvents such as benzene and toluene. The enormous variety of techniques, however, stems from the range of extractants studied for the separation of these elements. Faye and Inman (1961), Mojski (1980) and Hildago et al. (1991) reported the use of alkyl or aryl derivatives of phosphine. Khosla (1983), Shkil' and Zolotov (1988) and Gedye et al. (1989) reported the use of aniline derivatives. Diamantatos (1981), Rakovskii et al. (1984) and Němcová et al. (1990) reported the use of thiazine derivatives. Mueller and Lovett (1985), Taskaev et al. (1987) and Wilson et al. (1989) used dithiocarbamate derivatives. Zolotov et al. (1978), Rakovskii et al. (1974, 1984) and Vest et al. (1991) used derivatives of thiourea; the most successful as a group extractant has been N, N'-diphenyl thiourea (DPTU) (Zolotov et al., 1978; Seeverens et al., 1983).

Most of the above workers used a labilising agent to promote complex formation of the PGE, the most favoured was tin (II) chloride ($SnCl_2$). The $SnCl_2$ has the advantage of not only acting as a labilising agent but is also not carried over into the organic phase (Vest et al., 1991). For example, Rakovskii et al. (1974) reported that PGE extraction increased sharply with an increase in $SnCl_2$ concentration using thiophosphates, dithizonates and thiazolates as extractants. Mojski (1980) discussed the necessity of using $SnCl_2$ as a labilising agent prior to extraction of all the PGE with triphenyl phosphine (TPP, Ph_3P) into DCE.

2.6 Summary.

The finer points of conventional fire assay and the alternatives to this decomposition, separation and preconcentration procedure have been detailed above. Comparisons are drawn between the different methods of sample decomposition and secondary separation and preconcentration. The reasons why an aqua regia digestion followed by solvent extraction procedure was developed in this work are outlined below.

2.6.1 Initial sample decomposition.

Spectrometric analysis of a sample for the determination of the precious metals demands that the elements be in solution. The precious metals can be either solubilised directly by a variety of acid mixtures, the most successful of which has been aqua regia as detailed in Section 2.4, or taken into solution after prior attack by some form of oxidising reagent, the most frequently used of which has been fire assay as detailed in Section 2.2. Both aqua regia digestion and fire assay preconcentration have their limitations; both methods have been reported to suffer from losses of some of the precious metals from particular sample types. The present work was devised as a result of the limitations in the most widely used technique, nickel sulphide fire assay, and the need for an understanding of the actions of aqua regia.

Having described the previously documented decomposition procedures above, the three most commonly used methods for decomposition will be further summarised. Lead fire assay is more commonly used than nickel sulphide fire assay in the analysis of geochemical exploration samples largely due to the difference in cost and the superior collection of Au offered by the lead collection technique. Nickel sulphide fire assay is the preferred decomposition procedure when it is important to ensure full solubilisation of as many of the PGE as possible. For example, Bergeron (1990) described lead fire assay as one of the most appropriate methods for the analysis of exploration samples, but added that nickel sulphide fire assay had to be employed to provide determination of all the PGE as well as Au in subsequent analyses.

In comparing aqua regia digestion, nickel sulphide and lead fire assay, Bowditch (1973) concluded that whilst each had its own advantages and disadvantages, all three methods were capable of giving identical results for Pt, Rh and Au. The oxidative properties of aqua regia have been reported, although the action of the acid still defies thorough explanation. In comparison, fire assay is largely an empirical process assisted to a degree by some fundamental principles (Beamish, 1966, p. 166). Its mechanism remains largely unexplored and its theoretical foundations have not been fully characterised (Gil'bert and Shabanova, 1990). Both the fire assay procedures require fine balancing of the flux components to match the reduction-oxidation potential of the sample (Bumstead, 1984) and experimental conditions to accommodate a variety of sample types. Such precautions are less imperative for aqua regia digestion, although it is necessary to be aware that some samples (e.g. those containing carbonates) can effervesce violently on contact with strong mineral acids. Coombes and Chow (1979) reported that although less knowledge of sample composition was required for wet chemical extraction and the procedure provided the better precision, it showed no advantage in accuracy over fire assay, which was sometimes necessary to gain data of highest accuracy.

Despite the efficient collection of nickel sulphide fire assay, the subsequent button requires a complicated acid dissolution procedure. That the acid dissolution procedure could be applied to the sample directly would greatly increase the speed and simplicity of sample analysis. Methods using direct acid dissolution prior to separation are often more simple, rapid and economic and contamination problems are more easily controlled. Niskavaara and Kontas (1990) reported that fire assay requires more special facilities and equipment and more highly experienced staff than does aqua regia digestion. Malhotra et al. (1983) decided that fire assay was too arduous and slow to be recommended for application to a large number of samples in a geochemical exploration programme.

In a comparison of the techniques for the determination of Au from a variety of laboratories, Bumstead (1984) concluded that the fire assay technique appeared to be more accurate than the aqua regia technique in that variation between analyses of the same samples from different laboratories was smaller and theoretically the extraction should be more complete. However, Bumstead (1984) did point out if the mean of all fire assay values was regarded as the "true" value, then no one laboratory was consistently "accurate".

Hall and Bonham-Carter (1988), in comparing wet chemical digestion followed by GFAAS and INAA for the determination of Au, found that INAA data was about 30% greater than that obtained by GFAAS. On further investigation, Hall et al. (1989b) considered that this difference was due not to a positive bias in the INAA data,[2] rather to incomplete dissolution of the Au owing to incomplete wetting of the samples by the acids. It is of interest to note that, whereas recoveries of 58-70% of Au from soils were reported by Hall et al. (1989b) for aqua regia attack, recoveries of 81-86% of Au were obtained by lead fire assay, although these data were within the limits set by the associated standard deviations. Hall and Bonham-Carter (1988) concluded that despite the development of nickel sulphide fire assay, lead fire assay was probably still the most reliable means for sample preparation for analysis of most geological materials for the determination of Au, Pt and Pd, provided that appropriate modifications were carried out to suit the sample type. Moreover these authors advocated fire assay in preference to aqua regia digestion when the mineralogy of the

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[2] Despite the fact that INAA is limited to a great extent by sample size, which may itself introduce additional bias.

sample is unknown and the presence of chromite is suspected.

Although it is obvious that fire assay attains the most complete decomposition and separation of the precious metals, aqua regia digestion was examined as an alternative to fire assay particularly for the decomposition of geochemical exploration samples. In this application, acid digestion is the most viable, simple, economic and rapid alternative top fire assay. As a result of the work completed, interesting information has been elucidated concerning the mineralogical factors controlling the extent of attack by aqua regia (Chapter 7).

2.6.2 Secondary preconcentration.

Beamish (1966, p. 364) reported that the difficulties associated with all the dissolution methods were often magnified by the presence of associated base metals. Of those mentioned above, coprecipitation with Te, ion exchange and solvent extraction have received the most attention as methods employed for the separation of precious metals from concomitant base metals. Just as with the decomposition methods, each has its own limitations and is successful in the applications to which it has been applied.

Coprecipitation with Te has been reported as providing quantitative collection of Au, Pd, Pt, Rh and Ru, only 60-70% collection of Ir and poor collection of Os. Although being principally used for the mutual separation of the PGE, ion exchange preconcentration has been developed as a group separation procedure for all the precious metals except Rh, the chemistry of which does not lend itself to convenient manipulation. It has also been reported that Au, Pd, Ir, Os and Ru are susceptible to losses during the ion exchange separation stages of some extraction procedures. Solvent extraction has been the most successful group extractant of the precious metals, quantitative or near-quantitative recoveries of all the elements having been reported. All these three techniques are highly dependant upon the pH of the analyte solutions, which needs to be carefully controlled.

The simplicity and speed of solvent extraction techniques provided the reasoning for its adoption as the secondary solution preconcentration phase used in this work in preference to ion exchange, and coprecipitation techniques. The selection of solvent extraction was also based on the fact that GFAAS was to be used as the analytical technique (Chapter 3), and it is possible to analyse organic extracts directly by this technique (Chapter 5); ion exchange has most often been used in conjunction with INAA analysis of the solid resin. The reported quantitative extraction of all the precious metals with diphenylthiourea and triphenyl phosphine (Mojski, 1980; Seeverens et al., 1983) resulted in these two extracting ligands being examined in further detail (Chapter 5).

Chapter 3.
Analytical methods for the determination of the precious metals.

3.1 Introduction.

Techniques for the quantitative determination of Au were developed in pre-historical times in view of early recognition of the value of the metal. Techniques for the determination of the PGE were developed in the 17th and 18th Centuries, relating to the exploration in Spanish colonies in South America. Bearing in mind its current economic value, it is ironic to note that Pt was initially regarded as a contaminant of Au.

Kalinin and Vinit'skaya (1980) identified a number of requirements that should be met by analytical techniques suitable for the determination of Au and the PGE. The technique should have:
a) independence of chemical composition,
b) quantitative isolation of PGE, individually or as a group,
c) adaptability to both small and large samples,
d) acceptable analytical characteristics (including precision and accuracy),
e) minimal analysis time, and
f) minimal labour comsumption.

To be suitable for the analysis of samples as part of a geochemical exploration programme, an analytical technique should be able to recognise low concentration anomalies. Thus it is necessary that the technique should have a low detection limit, well the below background elemental concentrations, together with good analytical precision at these low concentrations (Xie and Wang, 1991).

3.1.1 Classical methods of analysis.

The first forms of analysis were developed from the Pb fire assay technique described in Chapter 2, in which the mass of Au isolated at the end of the assay procedure is measured and compared to the mass of sample initially taken for analysis[1]. Early developments of the fire assay procedure included wet chemical methods such as titrimetry and gravimetry, where a precipitate of a species of the metal was formed, weighed and its mass compared to that of the original sample (Werbicki, 1982). Modification of the latter of these methods led to electro-gravimetry (where the metal was plated out of solution onto a cathode of known mass, which is itself subsequently re-weighed). Werbicki (1982) reported that this "weigh-plate-weigh" technique was the standard method in the analysis of Rh concentrates. Deposition of the metal onto a dropping mercury electrode rather than a cathode has been used in the technique of polarography (Palaniappan, 1989; Medyantseva et al., 1989).

3.1.2 Instrumental methods of analysis.

Gravimetric, volumetric and related techniques are applicable to samples with relatively high concentrations of precious metals. However, when present at the low concentrations commonly found in geological samples, colorimetric and other instrumental techniques such as spectrophotometry and atomic absorption spectrometry (AAS) are preferred. Development of such instrumental methods of analysis has led to a variety of analytical schemes for the determination of the precious metals in a wide variety of sample matrices, for example, Fal'kova (1981) reported that many methods had been developed for Au (1672), Pt (501), Pd (459), Rh (262), Ir (90) and Ru (36).

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[1] This same procedure is still in use in the assay offices of Great Britain to certify the purity of Au. Indeed it is fondly remarked that the use of the hallmark on an object following assay was the first form of consumer protection ever to be used.

A number of reagents have been reported for the colorimetric analysis of the precious metals (e.g. Payne, 1960), although this technique has only mediocre sensitivity for easily reduced elements such as Au (Sandell, 1959). Pavlenko et al. (1980) used a spectrographic method for the simultaneous determination of the PGE but noted that this method did not provide sufficiently low detection limits for the analyte elements on a predominant background of co-existing elements (e.g. Cu, Fe, Ni and Co). Photometric methods of analysis have received much attention in Russian and Chinese laboratories (e.g. Pilipenko et al., 1990; Liu et al., 1990). Russian laboratories have also published widely on the use of potentiometry (e.g. Ezerskaya et al., 1989) and voltammetry (e.g. Ezerskaya, 1991). Adeloju et al. (1990) adapted the voltammetric determination of Pt to field-based instrumentation.

Table 3.1. Abbreviations of instrumental analytical methods used in this thesis.

Abbreviation	Analytical technique
AAS	atomic absorption spectrometry
INAA	instrumental neutron activation analysis
RNAA	radiochemical neutron activation analysis
ICP-AES	inductively coupled plasma-atomic emission spectrometry
DCP-AES	direct current plasma-atomic emission spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
XRF	x-ray fluorescence spectrometry

In recent years, an extensive range of methods for the determination of the precious metals in geological materials have been published, including: fluorometry (Pilipenko and Shevchenko, 1989; Kachin et al., 1991), high energy alpha-particle activation (Volfinger, 1989), second derivative spectrophotometry (Kus and Marczenko, 1989), laser photoionisation spectroscopy (Bekov et al., 1989) and plasma atomic fluorescence spectrometry (Caughlin, 1989). Table 3.1 lists the abreviations of commonly used instrumental methods that are referred to in this thesis. Hall and Bonham-Carter (1988) reported that, whereas flame AAS had played a major role and to a large degree had supplanted the previously popular methods of gravimetry, spectrophotometry and arc emission spectrography, INAA and ICP- and DCP-AES were now firmly entrenched as high-production oriented techniques. GFAAS has superior sensitivity to INAA and ICP-AES though its throughput rate is not as high and the technique is being challenged by ICP-MS – of approximately equal sensitivity and but possessing the advantages of speed, virtually simultaneous analysis and generally fewer matrix interference effects.

The application, for the determination of Au and the PGE, of GFAAS, ICP-AES and ICP-MS in the analysis of solutions and INAA and XRF in the analysis of solid samples will be summarised in the following sections.

3.2 Atomic absorption spectrometry.

The possibility of using atomic absorption spectra in analytical methodology was first realised by Walsh (1955) and independently by Alkemade and Milatz (1955). Since the early 1960s there has been rapid development of instrumentation and application of the technique.

3.2.1 Principles of AAS.

The principle of AAS is that light from an intense atomic emission source (e.g. a hollow cathode lamp) is directed through the atom cell (an atmosphere containing the analyte elements in the atomic state). Absorption of corresponding emission lines by these atoms then occurs. The reduction in intensity of light transmitted through the atom cloud due to atomic absorption at a selected atomic emission wavelength is measured. This absorbance can be related to the solution concentration of the analyte by application of Beer's Law[2] (Equ. 3.1).

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[2] At higher concentrations several types of interactions occur between each absorbing species, causing deviation away from the linearity of Beer's Law (ie. non-ideal behaviour). However, it is necessary

$$A = a\,b\,c \qquad \text{(Equ. 3.1)}$$

Absorbance= absorptivity (cm^2 mol^{-1}) x path length of atom cell (cm) x concentration of analyte species (mol cm^{-3}).

The first instruments generated an atom cloud by aspirating a solution into a flame (most commonly air/acetylene (2500°C) or nitrous oxide/acetylene (2900°C)). By this means, a wide range of elements (particularly the metals) could be determined with almost complete freedom from spectral interferences previously encountered in arc/spark source emission spectroscopy. Ionisation interferences could be controlled by the addition of an excess of an easily ionised element (e.g. Cs) to the sample solution. Some chemical effects could be alleviated and atomisation of refractory elements could be facilitated by the addition of a releasing agent (e.g. La). However, other limitations to analysis by flame AAS (e.g. relatively large volume of sample required for analysis and insufficiently low detection limits) prompted other methods of generating an atom cloud.

3.2.2 Electrothermal atomisation AAS.

One successful alternative atom generation device stemmed from commercial development of a graphite tube furnace first proposed by L'vov (1961). In this design a small aliquot (10-50 µl) of analyte solution is pipetted into a graphite furnace. The furnace is then heated by electrical resistance to dry the sample solution, ash the residue and atomise the analyte species into the furnace, through which radiation from a hollow cathode lamp (or sometimes an electrodeless discharge lamp) is directed. Absorption is then measured using an optical monochromator (the operation of GFAAS is discussed in more detail in Chapter 6).

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to operate in a region of ideal behaviour towards Beer's Law, such that absorbance is directly proportional to concentration. This characteristic, therefore, limits the concentration of analyte that can be determined by AAS.

3.2.2.1 Background correction.

GFAAS is capable of achieving much lower detection limits than flame AAS (by approximately 3 orders of magnitude for many elements) such that the detection limits are generally in the ng/ml rather than µg/ml range (i.e. ppb rather than ppm). This performance is attained at the cost of poorer precision, longer analysis times, greater background interferences and much greater sensitivity to matrix effects. The inclusion of ashing steps in the thermal heating programme for a sample results in the removal of much of the matrix that could enhance background caused by molecular absorption during atomisation. However, a significant residual molecular absorption background almost always contributes to the AAS signal and requires correction. Several techniques are available for this purpose (e.g. deuterium arc, Zeeman effect or Smith-Hieftje). The selection of the type of background correction is dependent on instrument design, although it has been claimed that background correction based on the Zeeman effect[3] can compensate for absorption of matrix interference lines and structured molecular background (Littlejohn et al., 1991) and is the most effective, offering correction of large background with much less degradation of signal-to-noise ratio (Slavin, 1987). Despite the effectiveness of this background correction technique, there is a degree of reduction in sensitivity that also affects other background correction techniques.[4]

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[3] A strong a.c. magnetic field applied to the atom cloud causes splitting of the spectral line into π and σ components. The π component(s) remain at the wavelength of the absorption line and the σ components are shifted to higher and lower wavelengths, and should ideally absorb practically no radiation from the atomic emission resonance line. Also, the π and σ components are polarised into mutually perpendicular planes (the π component(s) parallel to and the σ components perpendicular to the magnetic field) and it is simple to remove the π component with a polarising filter. Therefore, when the magnetic field is applied, the σ components of the analyte signal are largely removed by the splitting of the line and the π component(s) by polarisation filtering, such that practically the entire analyte signal is removed and only the background remains. The software then differentiates between atomic absorption signal plus background (magnet off) and background only (magnet on). The background corrected signal can then be displayed.
ie. (background + analyte signal) - background only = background corrected analyte signal.

[4] Ideally, the Zeeman splitting of the σ components away from the π components will result in lines that are well resolved away from the selected wavelength. In practice, however, the splitting is by no means absolute, such that, even after polarisation to remove the π component(s), a finite portion

Unlike flame AAS, GFAAS produces a transient absorption signal; the analyte atom cloud has only a short residence time in the furnace before it is swept out of the furnace by the combined effects of thermal expansion of the gas within the furnace and the Ar purge gas. These characteristics necessitate rapid electronics to record the transient analytical signal. Lack of appropriate electronic technology inhibited the early development of GFAAS.

3.2.2.2 Isothermal atomisation.

Apart from the correction of molecular absorption and the use of rapid electronics, one other development stands worthy of note: that of isothermal atomisation. In the first applications of GFAAS, the analyte was atomised from the wall of the carbon tube furnace into an inert atmosphere that was significantly cooler than the walls. Because the furnace was heated electrically with two electrodes, one at each end, the centre of the tube reached atomisation temperature more rapidly than the ends. This difference in heating rate due to electrical resistance was exacerbated by the fact that the temperature of the contact electrodes must be cooled by water flow to prevent damage. A considerable thermal gradient is thus present down the length of the graphite tube, consequently there is a risk of analyte condensing at the cooler ends of the tube, causing memory effects. Atomisation into an atmosphere, the temperature of which is changing rapidly, may also cause other vapour-phase interferences.

The first of the above problems has been overcome by the insertion of a pyrolytic

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of the analyte signal remains within the bandpass of the monochromator which can not be removed entirely from the background. This effect is further exacerbated at higher analyte concentrations when the changes to individual atoms induce secondary effects in their neighbouring atoms. These effects serve to broaden further the σ component lines. These broader lines are, by their nature, less well resolved away from the selected resonance wavelength, with the consequence that a greater proportion of the σ components will contribute to the background absorbance. The subsequent background corrected analyte signal will thus be lower than might be predicted.

graphite platform (called a L'vov platform) into the graphite furnace. The platform will have undergone practically no electrical heating during the atomisation cycle, instead, the heating is caused by thermal radiation (with a small contribution by conduction) from the electrically heated furnace walls. The consequential delay in heating the platform means that the analyte is atomised into an atmosphere that has more closely attained thermal equilibrium. Atomisation of analyte into an isothermal atmosphere has also been attempted by repetitive insertion of a probe into the furnace at each heating stage, especially atomisation (e.g. Manning et al., 1979).

The second of the problems has been approached by Whitley and Littlejohn. (1987, poster at J.M.Ottaway memorial meeting, Edinburgh) who noted that a sculptured tube produced more isothermal conditions or even reversed the thermal gradient (Ajayi et al., 1989). However the scheme that has received most attention (and subsequent commercial realisation) is the transverse heated tube of Frech et al. (1986) in which the atmosphere reaches a state of true temporal and spatial isothermality.

Further developments of AAS technology are the subject of ongoing research. The adaption of AAS to multielement analysis, with an increase in its linear dynamic concentration range, would make the technique competitive with ICP-AES and ICP-MS. At present, multielement status is being achieved at the cost of instrument sensitivity (e.g. Berglund et al., 1991), rendering AAS no more attractive than the ICP techniques. Probably the most significant attribute of AAS is its potential capability for absolute (standardless) analysis first alluded to by Walsh (1955) and recently reviewed by L'vov (1990).

3.2.3 GFAAS for determination of the precious metals.

AAS methods were applied to the determination of the precious metals almost immediately following the first developments of the technique. Indeed, GFAAS has been applied to the analysis of geological samples since its inception. In the analysis of geological samples, chemical separation of the analyte elements from the matrix is almost always found to be necessary, although Bettinelli (1983) described a method whereby siliceous materials were analysed for the determination for 11 elements (albeit non-PGE) without prior chemical separation. Preconcentration methods are essential for the accurate determination of Au and the PGE in geological samples (Chapter 2). The first application of GFAAS to the determination of Au was reported by Aggett and West (1971), and since then there have been many publications on the use of the technique for Au and the PGE (e.g. L'vov, 1979; Haines and Robért, 1982; Kasper et al., 1989; Wood et al., 1990; Boisvert et al., 1991; Terashima, 1991; and a comprehensive review by Sen Gupta 1989).

3.2.3.1 Analysis of aqua regia solutions.

One important application of AAS in the analysis of rocks is in the determination of Au extracted by an aqua regia leach. Although early attempts were made to aspirate aqua regia extracts of Au directly into the flame, the resultant Au determinations lacked precision and blank values were unacceptably high (Beamish and Van Loon, 1972, p.75). GFAAS, with its advanced background correction techniques, offers several advantages in the analysis of aqua regia solutions, particularly the higher elemental sensitivity and lower detection limits. Potts (1987, p.492) noted that it was desirable to remove nitrate ions from extracted solutions since NO_3^- interfered with AAS determination of many elements, particularly Au, Ru and Os. Sighinolfi et al. (1984) reported worse limits of detection for the precious metals in aqua regia compared to aqueous solution and postulated that this effect could be caused by a matrix suppression effect related to a high acid concentration. Encouragingly, Niskavaara and Kontas (1990) found that strongly acidic media did not affect, substantially, the lifetimes of the graphite tubes.

The effects of high acid concentration can be removed by dilution, but this action may reduce precious metal concentrations below the detection limits of the technique. The undesirable effects of high acid concentrations can also be overcome, for example by evaporating sample solutions to dryness to remove the acids and taking up the residue in a less acidified aqueous solution. Alternatively, a solvent extraction may be used to achieve the same effect, analysis of the organic extracts themselves can then be performed. Solvent extraction also results in the removal of some of the co-extracted matrix elements (Chapter 5) with the benefit of reducing the effects of matrix element interferences in subsequent analyses. The direct analysis of organic solutions by GFAAS should be no more difficult than analysis of aqueous solutions, although careful optimisation of drying and ashing steps in the thermal programme is required to avoid loss of analyte (de Castro et al., 1988). Care must be taken to avoid evaporation concentration in the analysis of organic solutions. For example Brooks and Bee-Saik Lee (1988) reported a 50% loss of methyl isobutyl ketone (MIBK) over an eight hour analysis run, resulting in an apparent doubling of the analyte concentration.

3.2.4 Summary.

Although flame AAS offers an accurate and convenient technique for the analysis of the PGE and Au (Bowditch, 1973), use of electrothermal atomisation (ETA) gives much improved detection limits, at the expense of a greater susceptibility to matrix effects. These matrix effects can be removed by sample preconcentration procedures (e.g. solvent extraction) and the application of background correction procedures.

3.3 Inductively coupled plasma-atomic emission spectrometry.

ICP-AES is acclaimed as one of the most versatile and robust analytical tools for quantitative multielement analysis, capable of determining 80% of all elements. It is a powerful technique in the analysis of geological materials when the appropriate decomposition procedures are applied, although it is generally accepted that variations in acid concentration and salt content must be adequately compensated if acceptable accuracy is to be achieved (Brenner et al., 1987).

Wemyss and Scott (1978) recommended the use of ICP-AES as an alternative to AAS in the determination of Au and the PGE in high and low grade ores and related plant materials in samples containing low concentrations of Cu, Ni and Fe. At higher concentrations, these elements cause significant spectrum overlap interferences. Kirkbright and Tinsley (1979) reported determination of all the precious metals by ICP-AES with no inter-element chemical interference effects, although several spectral interferences were observed with the spectrometer used. Watson and Moore (1984) utilised ICP-AES with introduction to the plasma of a slurry made up of ion exchange resin in water.

ICP-AES has not, however, found extensive application for the determination of the precious metals due to the superior detection limits of GFAAS and ICP-MS. A recent paper has documented the application of d.c. argon plasma emission spectrometry (DCP-AES) to the determination of Au in geological samples (Smolander and Kauppinen, 1991).

3.4 Inductively coupled plasma-mass spectrometry.

A more recently developed and arguably superior technique for the analysis of solutions for PGE and Au is ICP-MS. This technique combines the multielement and and rapid throughput capabilities of ICP-AES with the superior detection limits offerred by GFAAS, so necessary in the analysis of geological samples. The use of ICP-MS for precious metal determination has been assessed by Dolan et al. (1990) and Longerich et al. (1990) and has been the subject of a review by Jarvis and Jarvis (1992). The application of ICP-MS in the analysis of the PGE has prompted considerable interest (e.g. Date et al., 1987; Denoyer et al., 1989; Jackson et al., 1990).

Gregoire (1988) reported that sample introduction by electrothermal vaporisation rather than the conventional nebulisation increased the sensitivity of the technique and reduced interferences. Developments of laser ablation methods of sample introduction may ultimately remove the need for sample preparation, although this form of sample introduction is limited by sample homogeneity if it is to be applied to the direct analysis of powdered rocks. However, owing to its ability as a microprobe technique, laser ablation has been used in the analysis of individual grains within a sample (Chenery, pers. comm.).

The development of ICP-MS for the determination of the PGE (in particular due to the superior ionisation characteristics of the ICP when compared to thermal ionisation from a filament) has opened the way for further application of Os-Re systematics in the studying the age and origin of geological samples (e.g. Dickin et al., 1988) and understanding geological processes and mantle genesis (Burnham, PhD thesis, in prep). ICP-MS has also been used for the analysis of organic solutions (Evans and Ebdon, 1990; Hill et al., 1992). Totland et al. (1993) reported the use of ICP-MS in the determination of the precious metals from solid samples introduced into the plasma as a suspended aqua regia-based slurry.

The application of ICP-MS in this thesis was to analyse directly 20% aqua regia extracts from geological samples without a supplementary sample separation preconcentration. Use was made of ICP-MS in the optimisation and characterisation of the aqua regia leach procedure (Chapter 4; Gowing and Potts, 1991) and in the homogeneity evaluation of CHR-Pt+ and CHR-Bkg (Chapter 8; Potts et al., 1992). The choice of this particular technique for these applications was dominated by the multielement capability compared to GFAAS (especially for the second application which was undertaken under tight deadlines) and the capability of direct analysis of 20% aqua regia solutions by ICP-MS to facilitate analytical turn-round times.

3.5 Instrumental neutron activation analysis.

In contrast to the above solution analysis techniques techniques, INAA uses solid samples, often eliminating the need for sample preparation (e.g. Potts et al., 1985). When rocks are irradiated with a thermal neutron flux, some of the elements in the matrix (e.g. ^{51}Cr, ^{60}Co) become activated. Although the gamma-ray emissions from these radionucleides do not interfere with those of the precious metals, the activity contributes to the background spectrum, substantially degrading detection limits in the determination of the PGE and Au in geological samples (Parry, 1982).

The sensitivity of INAA is sufficient for the direct determination of Au and Ir and many pathfinder elements (e.g. As, Sb, Fe) in powdered geological samples but preconcentration is required for the determination of the other PGE. Therefore, in many schemes that use INAA for the determination of the precious metals, geological samples are first subjected to a chemical separation procedure to preconcentrate the noble metals. Such techniques include NiS-fire assay, followed by analysis of the residue after dissolution of the NiS button (Hoffman et al., 1978; Shazali et al., 1987; Asif and Parry, 1989), coprecipitation followed by analysis of the precipitate (Elson and Chatt, 1983; Stockman, 1983) or ion exchange followed by analysis of the resin (Nadkarni and Morrison, 1974). The activated isotope of ^{104}Rh has a half life of <5 minutes, which limits the applicability of INAA for the determination of Rh. Indeed, to determine Rh, the sample must be counted for a short time after a relatively short irradiation time (5 minutes compared to 16 hours for the other precious metals).

As an example of the capabilities of an INAA scheme of analysis, Hoffman et al., (1978) reported detection limits for the NiS fire assay/INAA procedure for Au and Ir

(0.1 ppb), Rh (1 ppb), Os (2 ppb), Ru (3 ppb), Pd and Pt (5 ppb). Despite its potential advantages as a non-destructive multielement technique with low limits of detection, INAA is a not a rapid technique, lengths of time of the order of hours are required for irradiation and days for cooling-off of highly active major elements and counting. INAA also has the disadvantage of having to handle radioactive materials.

The application of INAA to this thesis has been in the complementary analysis of residues after aqua regia leach in the optimisation of the leach procedure, in conjunction with XRF, (Chapter 4; Gowing and Potts, 1991). Unleached and leached samples were analysed for Au and Ir and pathfinder elements (As, Sb, Co, Fe) to gain an indication of the proportion of the precious metals extracted under different conditions.

3.5.1 Radiochemical neutron activation analysis.

RNAA is a complementary technique to INAA. In the most widely used form of this technique, samples are first irradiated in a reactor. After dissolution, the addition of carriers and subsequent chemical separation, isolated fractions of analytes are counted using gamma-spectrometers in the virtual absence of a background caused by matrix activity. This variant of neutron activation has not been used to contribute data to this thesis.

RNAA has been used for the determination of the precious metals and associated chalcophile elements at low-ppb levels (Brügmann et al., 1990). RNAA methods involving organic solvent extractions have also been developed for Ir, Ru and Au (Jackson et al., 1991).

3.6 X-ray fluorescence spectrometry.

XRF is one of the most commonly used methods of determination of major and trace elements in geological samples to a high precision. However, it has not found much application in the determination of the precious metals in such samples. XRF is a rapid, non-destructive method and can readily provide both qualitative and quantitative analyses. However, the detection limits of XRF are too high for accurate determination of the precious metals in most geological materials, but, like INAA, the technique has recently found use in the analysis of products of sample preconcentration, for example matte leach residues (Austen, 1977), chelating sorbents (Myasoedova et al., 1988), solvent extracts (Kasrai et al., 1988; Dmitriev et al., 1991), nickel mattes (Kolmogorov et al., 1989) and activated charcoal (Peräniemi et al., 1992). Khvostova et al. (1991) reported the use of synchrotron radiation XRF to determine Pd, Rh and Ru in geological materials.

The application of XRF to this thesis has been in the complementary analysis of residues after aqua regia leach in the optimisation of the leach procedure, in conjunction with INAA, (Chapter 4; Gowing and Potts, 1991) and in the qualitative analysis of insoluble interlayer precipitates encountered during solvent extraction (Chapter 5).

3.7 Summary.

The most important attribute of an analytical technique is that it should have low limits of detection, such that the technique is able to detect with accuracy and precision the low levels of Au and the PGE commonly found in geological samples. A comparison of the detection limits of commonly used solution analysis techniques (flame AAS, GFAAS, ICP AES and ICP-MS) is presented in Table 3.2. It can be seen from this table that ICP-MS offers the best detection limits for all the precious metals.

Table 3.2 Solution detection limits (µg/l unless otherwise stated) for commonly used solution analysis techniques.

Element	Flame AAS	GFAAS (pg)	GFAAS (soln equivalent)	ICP-AES	ICP-MS
Au	20	25	1.25	10	0.065
Pd	20	30	1.5	2	0.17
Pt	100	500	25	30	0.11
Rh	10	50	2.5	1.5	0.031
Ru	100	-	6.5*	2	0.22
Ir	600	1000	50	34	0.073
Os	100	-	290*	14	0.18

Flame AAS data from was obtained from Van Loon and Barefoot (1991, p.12). GFAAS data was obtained from Van Loon and Barefoot (1991, p.16), solution concentrations (soln. equivalent) were calculated using a 20 µl aliquot. ICP-AES data was obtained from Kirkbright and Tinsley (1979). ICP-MS data were obtained from Totland et al. (1993).

* Estimates for Ru and Os data by GFAAS is based on the relative characteristic masses for all the elements taken from the Perkin-Elmer recommended conditions.

Good detection limits of GFAAS have to be offset against the fact that only a single element can be determined at any one time. Its improved detection limits and multielement capability makes ICP-MS the most favoured technique if, as is so often the case, time and cost (taking into account sample throughput, manpower, automation, depreciation etc.) is of a premium. Analysis of organic solutions is possible on both instruments (although no attempt was made to analyse organic extracts by ICP-MS in this thesis). If available, ICP-MS will be the preferred technique once the interferences have become more fully characterised and methods of sample introduction have been refined.

This thesis is concerned with the application of GFAAS, using an in-house instrument (Perkin-Elmer Zeeman 3030 with HGA600 graphite furnace and an AS60 autosampler). Analyte-PGE and Analyte-matrix element interferences have been characterised and the analysis of aqueous, acidic and organic solutions have been studied (Chapters 5 and 6). ICP-MS has been used in the short term as an analytical tool in the characterisation of the aqua regia leach (Chapter 4) and in the application of the aqua regia leach to the homogeneity evaluation of candidate reference samples (Chapter 8). Complementary analysis of residues by INAA and XRF has proved most successful in the characterisation of matrix and selected trace elements during the aqua regia leach (Chapter 4).

Chapter 4.
Aqua regia dissolution.

4.1 Introduction.

The reactivity and oxidative potential of aqua regia relevant to its uses, benefits and limitations in sample dissolution have been reviewed in Section 2.4. This chapter details the development of a standard dissolution procedure, including observations made during the evaluation of optimum conditions for selective sample leaching. The results obtained from a number of analytical techniques used during the development are also described. A description of the standard dissolution procedure used for subsequent work is presented.

4.2 Analytical methods employed during optimisation.

To make use of the analytical facilities available and to characterise fully optimum conditions for the aqua regia leach procedure, analyses were made of both the final 20% acid solution and the residue after the acid attack. Analyses of the residue were made by INAA and energy dispersive-XRF (ED-XRF) and of the solutions by ICP-MS. Here follows a brief description of the capability and experimental procedure required by these techniques.

4.2.1 Instrumental neutron activation analysis.

INAA provides a simple, non-destructive method of rock analysis, the major hazard being the necessity of handling radioactive material. A sample is irradiated with neutrons in the core tube of a nuclear reactor. The neutrons interact with the nuclei of various atoms which become activated by a neutron capture reaction. These activated nuclei are radioactive and decay with a specific half life by various routes that normally involve the emission of beta-particles and gamma-rays.

The energy of the emitted gamma-rays is dependent upon the differences in energy levels of the excited nucleus. Because the nucleus of each isotope has a unique pattern of energy levels, the energy of emitted gamma-rays is specific to that isotope. The gamma-ray emission spectrum can then be measured and calibrated against standards that have been irradiated and counted in an identical manner. INAA is virtually free from matrix element interference effects as most matrix elements do not become activated to form radioactive isotopes. Some spectral overlap interferences occur but these are in general well characterised and the technique is, to a large degree, free of other matrix effects because only a small fraction of the available neutron flux is attenuated within the sample.

The degree of activation of each isotope is dependent upon the nature of its nucleus; some isotopes gain a higher activity than others when irradiated under the same conditions. Although INAA can be used successfully for the analysis of these high activity isotopes, the trace elements of interest in this work generally have lower activities and the presence of the high activity isotopes would cause an enhanced gamma spectrum background caused by the detection characteristics of the gamma ray spectrometer. Where possible, therefore, it is advantageous to allow the high activity isotopes to decay before the analyte isotopes are counted.

4.2.1.1 Experimental.

Sample preparation.

300 mg of dried and disaggregated aqua regia leach residue was weighed into a low density polythene vial, which was then capped and heat sealed so that no loss of irradiated sample powder could subsequentially occur. After labelling with a ballpoint pen, the vial was immersed in acetone to test the seal of the vial (if the vial was not

air-tight it was discarded and another prepared). After drying, the vial was placed with 10 others in a low density polythene irradiation canister, which was then sealed. A calibration standard (OUPGE3) was placed in the centre position in the canister.

Irradiation and handling.

The irradiation canister was then dispatched to the Imperial College Reactor Centre, Silwood Park, Ascot and subjected to a neutron flux of approximately 5×10^{12} n cm^{-2} s^{-1} for 7 hours. After removal from the reactor, the canister was stored in a lead pot for 7 days to allow high activity isotopes such as ^{24}Na and ^{56}Mn to decay and render the sample safe to handle under "supervised radiation area" conditions.

The lid of the canister was removed behind a lead wall and each vial was tested for signs of degradation of the polythene material (by immersion in acetone). Providing no faults were observed, the vials were placed in an appropriately labeled box to await counting. The irradiation canister, bench cover and disposable gloves were sealed in a polythene bag with warning tape. Once the activity of this waste had been determined to be <400 kBq, the bag was disposed of in 0.1 m^3 of non-radioactive general laboratory waste, in accordance with the site licence. The activities of both the lead pot and the irradiation canister were monitored before unpacking and the activities of the waste, bench top and all tools used in the unpacking were monitored for residual contamination after unpacking.

Counting and analysis.

The sample vials were placed in alternate positions of a perspex auto-sampling wheel arranged such that each sample in turn could be counted in front of a high resolution coaxial and planar solid state germanium gamma-ray detector. The in-house standard was placed in the first position and each analysis was calibrated against a standard irradiated with the batch. Once calibrated, the software corrected for variations in decay caused by differences in the half-lives of the nucleides so that all activities were representative of the same nominal time. Each sample was counted for a live time of 7000 s. The following isotopes were monitored at the ascribed gamma energies: ^{192}Ir (468.0 and 604.4 keV), ^{198}Au (411.8 keV), ^{76}As (559.1 and 657.1 keV), ^{122}Sb (564.0 keV), ^{124}Sb (1691 keV), ^{59}Fe (1099 and 1291 keV), ^{60}Co (1332 and 1173 keV) and ^{65}Zn (1115 keV).

The technique was used only to observe trends in the aqua regia dissolution procedure and, although the accuracy of the technique has been shown to be very good (Potts et al., 1985), any systematic errors in the procedure would not affect the interpretation of the results. The precision of the technique can be represented by an estimate of the relative standard deviation for each isotope calculated from counting statistics. For concentrations sufficiently above the limit of detection, these relative standard deviations are typically: Ir (1-6%), Au (1-4%), As (1-4%), Sb (2-6%), Fe (1%), Co (1%), and Zn (10%). During the course of the experiment, 8 unattacked samples of CHR-C were analysed, data from these samples are presented in Table 4.1, these data indicate a full procedural precision ranging of 9-19%. Any isotope that was calculated to have a relative error >30% was excluded from further interpretation.

Table 4.1. Element concentrations for eight individual analyses of different 300 mg aliquots of CHR-C. Simple statistics have been calculated for each isotope monitored. The 8 aliquots of CHR-C are labeled Ca-Ch.

isotope	^{192}Ir	^{192}Ir	^{198}Au	^{76}As	^{76}As	^{122}Sb	^{124}Sb	^{59}Fe	^{59}Fe	^{60}Co	^{60}Co	^{65}Zn
(keV)	468.0	308.3	411.8	559.1	657.1	564.0	1691	1099	1291	1332	1173	1115
Ca	21	15	4.8	611	608	31	22	14	17	214	220	–
Cb	14	9	4.0	476	441	25	20	11	14	170	170	–
Cc	17	12	4.8	588	535	29	31	15	14	227	233	307
Cd	15	11	4.0	485	475	23	22	13	12	188	197	222
Ce	20	14	4.7	564	790	32	34	14	15	200	224	281
Cf	16	12	4.2	493	915	27	28	12	13	177	199	243
Cg	18	13	4.5	495	487	27	30	13	13	189	207	245
Ch	18	13	5.0	420	–	27	28	13	12	182	204	204
mean	17	12	4.5	516	607	28	27	13	14	193	207	250
std dev	2	2	0.4	65	180	3	5	1	2	19	20	38
CV	13%	14%	9%	13%	30%	11%	19%	9%	12%	10%	9%	15%

All concentrations µg/g, except Fe (wt% oxide).
- relative error >30%, so concentration not reported.

The neutron flux variation along the length of the canister was accounted for by placing identical samples of unattacked CHR-C in the second and tenth positions of the eleven place canister. The flux correction required for each sample was subsequently determined by linear interpolation of the concentrations of each isotope in the two samples of CHR-C. Although this procedure did not account for any non-linearity in the flux density along the length of the irradiation canister, associated errors were not expected to exceed the uncertainties in the calibration procedure.

4.2.2 X-ray fluorescence spectrometry.

Like INAA, ED-XRF provides a non-destructive method of rock analysis. The powdered sample is prepared as a pellet which is then subjected to x-ray radiation. This radiation excites atoms within the sample and causing ionisation of inner shell orbital electrons. Resulting transitions that occur as the atom returns to its electronic ground state causes the emission of x-rays (by fluorescence). One of the most common x-ray emissions results from the ionisation of a K-shell electron. The associated L- to K-shell electronic transition results in the emission of a Kα fluorescence x-ray. Because the atoms of each element have a unique electron structure (the Pauli exclusion principle), the energy of this fluorescence emission is unique to each element. For quantitative analysis, the intensity of selected fluorescence x-rays is compared with that from previously analysed standards.

The use of ED-XRF as described in this chapter was in a qualitative/semi-quantitative capacity. The energy dispersive system is ideally suited to this application as one Si(Li) detector (a Li drifted Si crystal) simultaneously measures the entire emitted x-ray spectrum (0-20 keV). Since samples were prepared in the same manner (as powder pellets) and were excited under identical conditions, the relative concentration differences (based on x-ray intensities) could be determined.

Depending on excitation conditions, the $K\alpha$ transition normally offers maximum sensitivity. Consequently, the $K\alpha$ lines for each element were measured as follows: Cr $K\alpha$ (5.41 keV), Mn $K\alpha$ (5.89 keV), Fe $K\alpha$ (6.40 keV), Ni $K\alpha$ (7.47 keV), Cu $K\alpha$ (8.04 keV), Zn $K\alpha$ (8.63 keV), and As $K\alpha$ (10.53 keV).

4.2.2.1 Experimental.

Sample preparation.

A sub-sample[1] of 7-8 g of dried and disaggregated aqua regia residue was mixed to a uniform consistency with an agate pestle and mortar with 6 drops of a binding agent (a saturated aqueous solution of polyvinyl alcohol and pyrrholodine). The moist powder was then transferred to a hardened steel pellet mould and compressed at 12 ton in^{-2}. The pellet was then carefully removed from the mould and placed onto a clean board. When a number of pellets had been made, the batch of moist pellets was dried overnight in an oven at 110 °C to remove excess moisture and to provide a tougher,

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[1] The exact mass of sample used to prepare a powder pellet is not important; the critical dimension is the thickness of the pellet. The pellet should be infinitely thick with respect to penetration by the fluoresced secondary x-rays of all the elements determined. A pellet thickness of about 4 mm is generally considered to be adequate for determining the x-ray lines required here.

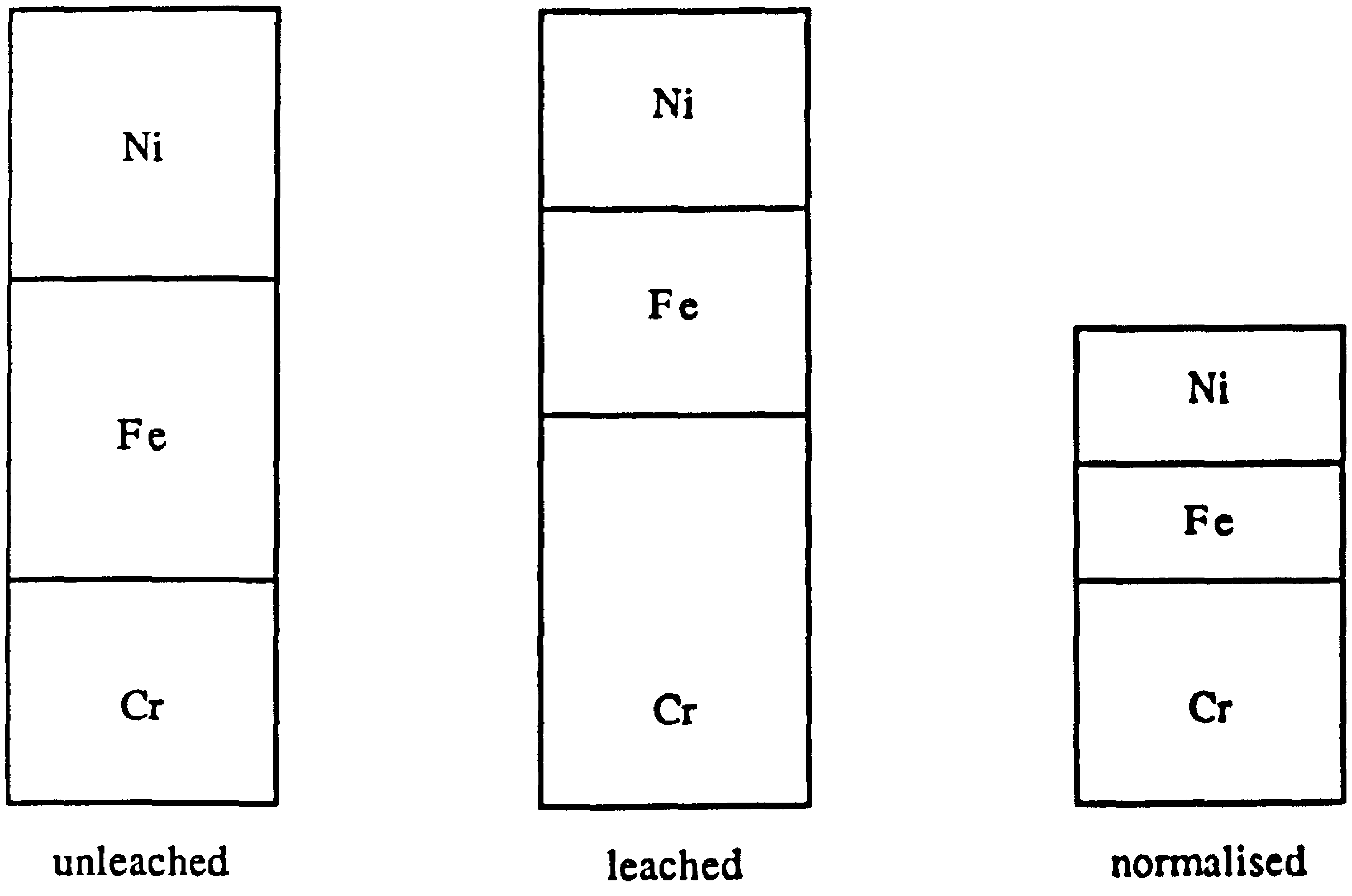
more easily handled specimen. When cool the pellet was stored in a sealed polythene bag awaiting analysis.

Analysis.

Analysis of the sample was carried out using a Link Analytical (MECA 10-44) ED-XRF spectrometer incorporating a low power (49 W) Ag target x-ray tube. A silver foil filter was used (placed between the primary x-ray source and the sample) to reduce dead time and improve peak-to-background ratios. The samples were excited by primary x-rays generated at 45 kV, 0.3 mA for 800 s (live time). The secondary x-rays were collimated and detected using a Si(Li) detector. The x-ray spectrum was stored on floppy disc and subsequent peak fitting was carried out using the deconvolution programme supplied by Link Analytical.

The proportion of each element leached by aqua regia was calculated from the ratio of measured intensity data between the leached sample and an unleached sample. As an analyte is leached from the sample, its residual concentration in that sample decreases. If all analytes were leached at the same rate, then the residue would have the same relative concentrations of all these analytes and these experiments would have no practical use. But, because chromite is insoluble in aqua regia, data can be normalised against Cr to gain an idea of the extent of the removal of each of the analytes from each residue sample. This normalisation also offered a degree of compensation for drift and any matrix effects. The effect of normalisation is depicted in the simplified cartoon in Figure 4.1.

Figure 4.1. Simplified diagram showing the effects of the normalisation procedure described in the text. Removal of Ni and Fe serves to enrich the residue in Cr relative to the initial sample. Normalisation of the concentrations of the leached sample to that of Cr permits more accurate evaluation of the proportion of other elements leached from the sample. The height of each rectangle represents the relative proportion of each element.



4.2.3 Inductively coupled plasma - mass spectrometry.

Inductively coupled plasma-mass spectrometry (ICP-MS) is a state-of-the-art, extremely sensitive technique for the determination of most elements in aqueous solution down to ppb or sub-ppb levels. This technique combines the multielement capability of ICP-AES with the superior detection limits of GFAAS (all these techniques have been discussed in Chapter 3). In comparison with GFAAS, ICP-MS can be used to analyse directly the highly acidic solutions with high total dissolved solids content generated in this work with markedly lower interference and will determine simultaneously all 7 analytes (Au and the PGE) enabling a faster turn around of samples.

In conventional ICP-MS, a liquid sample is pumped at a constant rate into a nebuliser and spray chamber. A flow of Ar gas carries the fine mist thus generated (about 1-2% by mass of the original sample) into the centre of an Ar plasma generated at the end of a 'torch'. The torch consists of 3 concentric tubes. The sample aerosol is transported up the central channel (injector tube) by the carrier flow of Ar. A low flow of Ar gas (the auxiliary flow) is supplied up the middle concentric channel, to lift the plasma off the end of the torch, ensuring that the plasma does not come into contact with and damage the torch. A significantly greater flow of Ar (the coolant gas) is supplied up the outer of the three channels. The plasma itself is formed by excitation of the Ar gas (largely the coolant gas) by the radio-frequency energy coupled into the plasma from water-cooled work coils which surround the end of the torch. The core of the argon plasma reaches temperatures in excess of 8000 °C.

As the sample enters the plasma, it undergoes almost immediate desolvation, atomisation and ionisation. The positive ions thus generated are then sampled through a small orifice and pass into a series of 3 evacuated chambers. A series of ion lenses focuses the ions into a quadrupole mass analyser. The quadrupole can be adjusted such that ions of a specific mass/charge ratio pass through the exit slits and are detected by an electron multiplier detector.

The instrument was calibrated immediately before each batch of samples by analysing a solution containing relevant analyte elements at known concentrations. The precision of ICP-MS measurements is not normally as good as, say, ICP-AES and particularly in view of the high acid strength and dissolved solid content of solutions here analysed, it was necessary to perform frequent drift correction measurements by running a monitor solution (a sensitivity standard) at regular intervals.

4.2.3.1 Experimental.

This technique was used to analyse directly the 20% aqua regia solutions generated during the course of this work; the sample preparation procedures are described later in this Chapter.

Of the precious metals, only Rh and Au are mono-isotopic, all the other analytes having more than one naturally-occurring isotope. Isobaric interferences at any of the mass/charge ratios monitored can occur in 3 ways. Many of the isotopes have the same relative atomic mass (RAM) as isotopes of other elements (e.g. ^{104}Ru and ^{104}Pd, ^{198}Pt and ^{198}Hg). Analyte isotopes will have the same mass/charge ratio as oxide species of other elements with isotopes 16 a.m.u. lighter than the analyte (e.g. $^{104}Pd^+$ and $^{88}Sr^{16}O^+$, $^{198}Pt^+$ and $^{182}W^{16}O^+$). Isobaric interferences can also occur in the presence of doubly charged ions of isotopes of twice the RAM (which would have the same mass/charge ratio). This problem is of no concern in this application as there are no elements with twice the RAM of the higher mass range (Os-Au) and the second ionisation energies of elements that could cause isobaric interferences at the lower mass range (Ru-Pd) are too high to be generated in an Ar plasma where the maximum available excitation energy of 15.76 eV is buffered by the first ionisation energy of Ar.

Care was taken in selecting the isotopes for study to avoid isobaric interferences. Fortunately, such interferences on the Rh and Au isotopes were not expected to be severe. Isotopes of the other elements were selected as those with the greatest natural abundance providing they were subject to no, or minimal[2], elemental isobaric interferences. Oxide interferences at the selected mass/charge ratios were not expected to be significant. The isotopes measured and their relative natural abundances were: ^{101}Ru (17.1%), ^{103}Rh (100%), ^{105}Pd (22.2%), ^{115}In (95.7%, used as an internal standard (Sections 4.5 and 7.4)), ^{185}Re (37.5%, used as an internal standard (Sections 4.5 and 7.4)), ^{189}Os (16.1%), ^{193}Ir (37.4%), ^{195}Pt (33.8%) and ^{197}Au (100%).

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[2] There is a minor isotope of ^{115}Sn (0.35% abundance) under ^{115}In, which was used as an internal standard in the quantificaton of the technique (Sections 4.5 and 7.4). The concentration of Sn in samples analysed in this thesis should be low enough as to appear insignificant for internal standardisation purposes.

Analysis.

Solutions were run on a VG Elemental Plasmaquad inductively coupled plasma-mass spectrometer either at the NERC ICP-MS facility, then based at the University of Surrey, or at the British Geological Survey, then based in London.[3] The instrument was run using the normal running conditions as detailed by Gray and Williams (1987) with a few minor alterations. The running conditions (system parameters) are detailed together with the operating conditions in Table 4.2. The instrument was set up using a standard containing nine elements spanning the entire mass range. The ion lens settings were optimised to maximise the signal of ^{115}In (an isotope in the middle of the mass range) and to minimise doubly charged ion and oxide interferences as monitored by $^{140}Ce^{2+}$ and $^{140}Ce^{16}O^{+}$ (Ce has one of the lowest second ionisation energies).

Table 4.2. Normal system parameters and operating conditions for multi-element determination by ICP-MS.

System parameters	
Plasma power	1300 W
Reflected power	<10 W
Coolant Ar flow	14 l/min
Auxiliary Ar flow	0.5 l/min
Carrier Ar flow	0.73 l/min
Pumped sample uptake rate	0.5 ml/min
Spray chamber temperature	10 °C
Sampling aperture diameter	1.0 mm
Skimmer diameter	0.7 mm
Load coil-to-aperture spacing	10 mm

PlasmaQuad operating conditions	
No. of channels	2048
No. of scan sweeps	200
Dwell time (per channel)	160 µs
Channel points per peak	5
DAC steps between points	5
No. of peak jump sweeps	20
Collector type	pulse
Skipped mass regions (a.m.u.):	11.4-21.6 39.4-41.6 117.0-183.0
Measured mass regions (a.m.u.):	94.9-117.0 183.0-206.5

A standard solution was prepared containing each of the precious metals at a concentration of 100 ng/ml in 20% aqua regia (Aristar-grade acids). This solution was analysed after the calibration blank (20% aqua regia), at the beginning of each batch of analyses, then after every third or fifth sample to act as a drift monitor. Dissolution

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[3] The Natural Environment Research Council Inducively Coupled Plasma-Mass Spectrometry Unit was transferred subsequently to Royal Holloway University of London. The British Geological Survey analytical laboratories have now relocated to Keyworth, Nottingham.

blanks were analysed prior to any samples to minimise potential memory effects.

Analysis of a drift monitor throughout the analytical run allows a crude drift correction to be applied. This correction was made by interpolation of count data from adjacent drift monitors. In the course of this work it was realised that additional interference effects were occuring owing to the suppression of signals in solutions containing particularly high contents of dissolved solids. In the studies of the characterisation of the technique (Section 4.5) and the effects of roasting as a sample pretreatment step (Section 7.4), an additional correction was applied by adding to all solutions Re and In (both 100 ng/ml in the analysed solution) as internal standards in an attempt to minimise any mass dependant effects. Data for Rh, Ru and Pd were normalised against In data and Os, Ir, Pt and Au against Re. Data used in the optimisation work, however, were not corrected with the aid of these internal standards.

4.3 Optimisation of the dissolution procedure.

A standard dissolution procedure will involve a specified volume of aqua regia (of specified composition) being used to attack a specified mass of sample. Variables that require optimisation include contact time, reaction temperature and degree of agitation. Taking into account the values of these variables reported in previous publications, the starting points for the variables in these investigations were as follows: 10 g of sample attacked by 20 ml of a conventional 3:1 mixture of HCl and HNO_3, continuously stirring for two hours at room temperature (without applying an external source of heat). The variables listed above were then altered in a systematic manner to determine the optimum conditions for maximum extraction of the precious metals.

All the experiments described below used some or all of three chromitite samples from the Unst ophiolite, Shetland (Section 1.1.3) and the one certified reference material (platinum ore, SARM 7 (Steele et al., 1975). The Shetland samples were: CHR-A, a chromitite from Harold's Grave containing enhanced PGE abundances, particularly Os, Ru and Ir; CHR-B a "barren" chromitite; CHR-C, an exceptionally mineralised chromitite from Cliff containing enhanced abundances of all the precious metals (particularly Pt and Pd). The chromitites are representative of samples that are particularly difficult to analyse by conventional fire assay techniques (Chapter 2). SARM 7, was included in these studies as it is a gabbroic rock, and as such is representative of silicate materials.

The basic procedure used involved the following steps:

1. Weigh out sample powder into a beaker and dry the sample and reweigh dried sample.
2. Add the acid to the beaker.
3. Stir the sample with a teflon rod to wet the powder.

After completing the extraction of Au and the PGE under appropriate conditions :

4. Filter the residue and collect the filtrate (containing the precious metals in solution) by pouring the entire contents onto a wetted filter paper in a Büchner funnel and using vacuum filtration.
5. Rinse all the residue and liquid from the beaker. Pass washings from the beaker over the residue in the filter funnel and combine with the filtrate.
6. Dry the residue, by continuing forced air flow through it, and retain for subsequent analysis.
7. Rinse the filtrate into a volumetric flask and dilute to volume.
8. Transfer solution to polythene bottle for storage prior to analysis.

The standard procedure finally adopted will be described in full in Section 4.4.

If, during the filtration, it was observed that some of the fine residue passed the filter paper, the solution was refiltered through a second filter paper with clean apparatus and the original Büchner flask was rinsed with the mininum volume of deionised water. If the total volume exceded 100 ml, part of the solution was poured into an evaporating basin and placed in the entrance of the fume cupboard at room temperature (to avoid analyte losses that may occur when heating the solution) until the volume had reduced to <100 ml. The solution was then transferred back to the volumetric flask and the evaporating basin was rinsed with the minimum volume of deionised water.

Optimisation of and variations to these steps are detailed in the following sections, each of the variables are considered in turn.

4.3.1 Mass of sample.

As mentioned in Section 1.2.1, the most important criteria for the selection of the appropriate mass of a sample is to ensure that the aliquot of the sample taken for analysis is representive of the whole sample. However, to minimise the size of this sample is beneficial in terms of both economy and ease of sample handling. Selecting an appropriate mass for analysis is not simple and requires information on particle size distribution of the PGE minerals and Au, information which is often not available.

It is possible to predict the size of sample required to give analyses with acceptible precision knowing the average particle mass and the approximate grade of the sample. For an element that is present only as discrete particles, the precision is proportional to the number of particles present in the sample aliquot taken for analysis. A particular concentration of Au, say, in a sample can be represented either by a few large particles of Au or many small particles, i.e. for a given whole rock grade, the number of particles of Au in a sample of specific size decreases as the particle mass increases. Similarly, for a given grade, the size of sample required to contain a specific number of particles increases as the particle mass increases. Clifton et al. (1969) identified that 20 particles of Au in a sample afforded an "acceptable precision", i.e. that it was 95% probable that the actual concentration of Au in the sample was no more than approximately 50% larger or smaller than the concentration found by analysis.

Analytical errors apart, the number of Au particles in the sample is the only factor controlling the precision of analysis if it is assumed that the particles are of uniform mass, distributed randomly throughout the sample, make up <0.1% of the entire sample and more than 1000 particles are present in the sample (Clifton et al., 1969).

Figure 4.2. Size of sample required to contain an expected 20 particles of Au as a function of Au particle size and sample grade, assuming all Au particles to be of uniform size and randomly distributed in the deposit. The fields plotted within the grid represent grain size/grade distribution in samples from Shetland, Cyprus and South Africa. The grid is adapted from Clifton et al. (1969). Data for the Shetland fields are from: Prichard et al. (1985); Cyprus: Prichard and Lord (1990); South Africa: Steele et al. (1975). Although its concentration range is known, there is no information about the mineral grain sizes in CHR-B. To identify possible required sample sizes, two fields (1 & 2) have been identified within a range defined by reasonable estimates of grain sizes for this material.

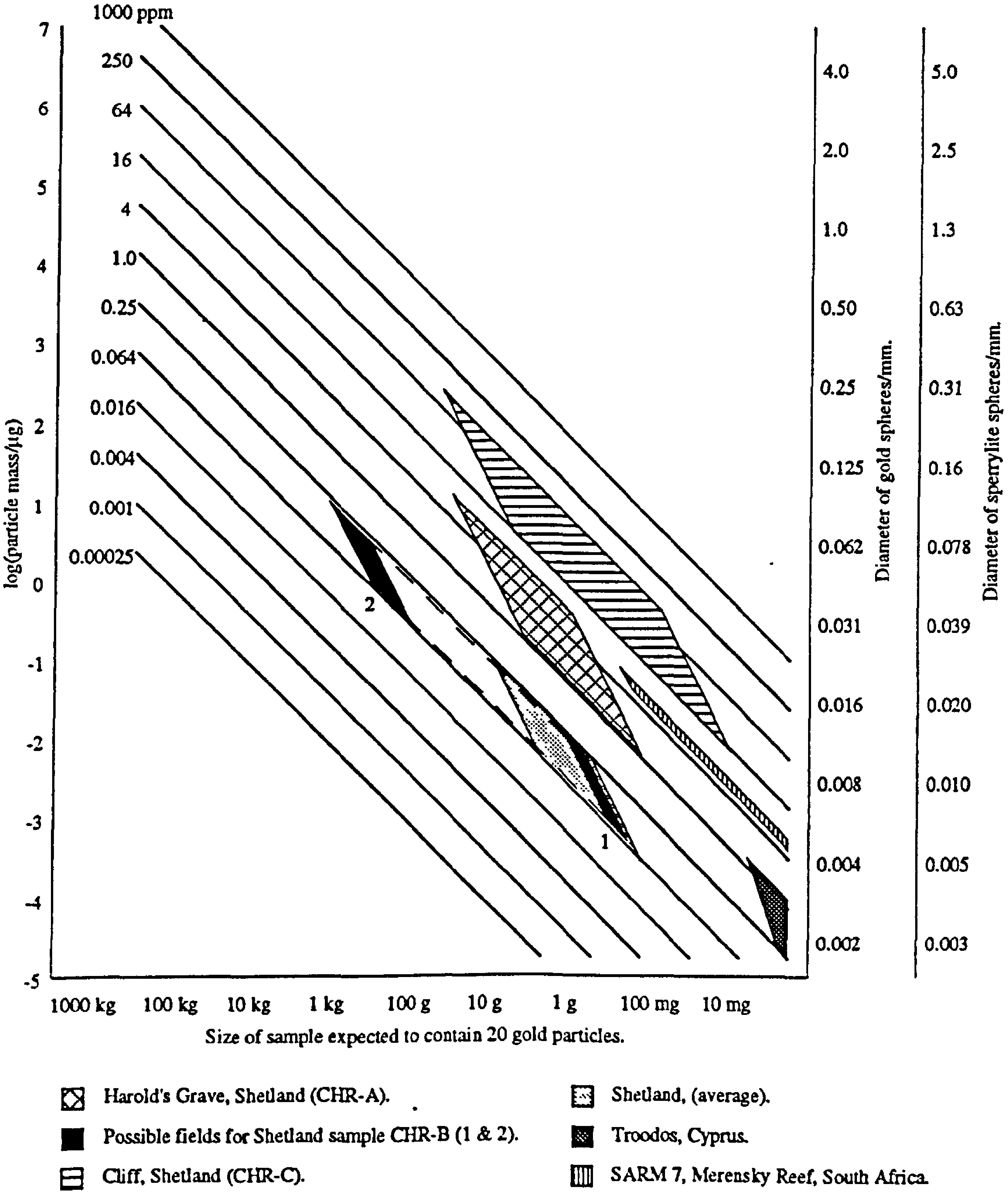

Figure 4.2 is adapted from Clifton et al. (1969) and shows the size of sample required to contain 20 particles of Au at various combinations of particle size and grade. This figure can be used to determine the size of sample required to provide the desired particle-to-sample ratio. Although this figure was constructed for Au, which has a specific gravity (s.g.) in the range 15-19.3 in natural samples, it can be applied without modification for particles of native platinum (s.g.14-19), iridosmine (s.g. 19.3-21.1) and native osmium (s.g. 22). However, precious metal arsenides and sulphides have specific gravities about half that of Au (e.g. sperrylite, $PtAs_2$, s.g. 10.5), consequently the size of a sample expected to contain 20 particles of sperrylite, say, would be half the size of a sample expected to contain 20 Au particles. A scale for spheres of sperrylite has thus been added to the right hand side of Figure 4.2.

Individual platinum-group minerals (PGM) have been observed in samples from localities on Unst, Shetland (Prichard et al., 1985), Troodos, Cyprus (Prichard and Lord, 1990) and the Merensky Reef, South Africa (Steele et al., 1975). Fields representing these observed grain sizes in relation to the overall grade of the sample are plotted on Figure 4.2. These fields are defined above and below by the grain sizes of the reported minerals and on the left and right by the associated whole rock concentration (grade) of PGE and Au in the samples. Because it was observed that the samples with the larger grains were those that gave the higher precious metal concentrations and that few large grains were observed in samples with low precious metal concentrations, the right and left hand ends of the fields were truncated to give the plotted fields.

The fields representing the sources of CHR-A and CHR-C are shown as Harold's Grave and Cliff, respectively. Although no PGM have been observed in CHR-B, the potential range of fields for this sample have also been plotted on Figure 4.2. If the known content of precious metals occurs as 5-10 μm grains then the field will plot at the lower end of this area (area 1). If, however, the precious metals occur as a few, larger 30-100 μm grains then the field will plot in the upper end of the area (area 2), dictating the necessity of a sample size of the order of 1 kg to ensure representative samples. Moreover, a smaller sample would not be representative of the whole and would result in degraded analytical precision due to sample inhomogeneity effects (this point will be further considered in Chapter 8).

Although the fields are plotted in the correct bulk concentration grid, their upper and lower boundaries (grain size) are constrained by experimental observations. The grains were identified in thin section, which only represents a very small sample mass (unlikely to be representative of the whole sample) and the grains measured are likely to be the larger ones and those with higher reflectance. This method may have led to a bias such that smaller minerals and those with lower reflectance could have been overlooked. If overlooked, the presence of smaller minerals would serve to decrease the lower boundary of a field, and the presence of large, low reflectance grains would serve to increase the upper boundary.

Steele et al. (1975) found that 10 g was an acceptable mass for the characterisation of SARM 7 and that samples of <0.1 g resulted in Au inhomogeneity effects. These observations concur with conclusions that can be drawn from the position of the SARM 7 field on Figure 4.2.

From Figure 4.2, it can be seen that a sample mass of less than about 10 g would not contain a sufficient number of particles to ensure adequate analytical precision. A sample greater than 10 g would ensure homogeneous distribution of the precious metals, but would lead to complications in the analytical procedure and greater likelihood of contamination from the larger quantities of analytical reagents that then have to be used. A sample mass of 10 g would seem, therefore, to be acceptable for the type of samples studied here. Consequently, all analyses in this work were performed with 10 g samples.

To allow for unpredictable sample inhomogeneity effects (e.g. Figure 4.2, CHR-B area

2), it would be advisable to perform all analyses in duplicate, thus giving some warning when sample inhomogeneity effects were significant. Such a procedure is particularly important in the analysis of some exploration samples, where it has been reported that sub-samples of 1-50 kg were required to overcome inhomogeneity effects (Haffty et al., 1977). It is also likely that, if inhomogeneity effects are not too severe, 10 g samples will still allow identification of those localities with high precious metal abundances so that more reliable data on larger and more representative sample aliquots can be obtained.

4.3.2 Volume of aqua regia used for attack.

The volume of acid used to effect the leach is important. Too little acid may result in inadequate wetting of the sample powder and incomplete dissolution of the analyte elements. Too much acid may give rise to interference effects in subsequent determinations made by AAS and ICP-MS. Furthermore, dilution of such samples to reduce the acid strength to a level whereupon the solutions can be presented to the spectrometer for interference-free analysis may reduce analyte concentration to a level close to or below the detection limit of the technique.

The dissolution capabilities of three volumes of aqua regia were tested using 10 g samples of CHR-A, CHR-B and CHR-C. These volumes were 10 ml, 20 ml and 50 ml of freshly prepared aqua regia.

4.3.2.1 Observations and results.

To avoid problems and hazards in handling the acids with conventional glass pipettes, automatic hand pipettes were used initially to dispense the acids. However, it was found that the fumes caused premature release of the acids from the pipettes as well as attacking their barrels, causing corrosion and subsequent leakage. Consequently, aqua regia was prepared by pouring HCl into a measuring cylinder containing HNO_3, thus overcoming the problems of using pipettes. In subsequent analyses, the acids were added to the samples from teflon coated dispensers to increase the precision with which the composition of the aqua regia was prepared. These dispensers combined the precision of hand pipettes with the ease of handling of the measuring cylinder method.

Table 4.3. Proportion of concomitant elements (Mn, Fe, Ni, Cu, Zn and As) remaining in residue from 20 g sample after aqua regia attack. Analyses were made by EDXRF.

sample	volume of aqua regia	Mn	Fe	Ni	Cu	Zn	As
CHR-A	unattacked	100%	100%	100%	-	100%	-
	10 ml	95%	93%	69%	-	95%	-
	20 ml	90%	93%	66%	-	94%	-
	50 ml	90%	95%	72%	-	97%	-
CHR-B	unattacked	100%	100%	100%	100%	100%	-
	10 ml	90%	86%	45%	21%	98%	-
	20 ml	85%	84%	44%	33%	98%	-
	50 ml	81%	83%	41%	22%	96%	-
CHR-C	unattacked	100%	100%	100%	100%	100%	100%
	10 ml	83%	80%	21%	11%	89%	15%
	20 ml	87%	82%	21%	11%	94%	12%
	50 ml	86%	82%	20%	10%	98%	10%

The concentration of Cu in CHR-A and As in CHR-A and CHR-B were below detection limit.

The results from analysis of the residues are shown in Table 4.3, from which it can be seen that the 20 ml leach did not increase significantly the proportion of Ni, Fe, Cu, Zn and As and Mn extracted from CHR-C in comparison with 10 ml. Nor did the 50 ml leach increase significantly the proportion of the elements extracted compared with the 20 ml leach. Difficulty was encountered in ensuring complete wetting of the 10 g sample with just 10 ml aqua regia, a problem that was overcome in the 20 ml and the 50 ml leaches.

Based on the assumption that the extraction of these concomitant elements could be considered representative of the behaviour of the PGE, 20 ml aqua regia was selected as the optimum volume for extraction from 10 g sample.

4.3.3 Composition of aqua regia.

Throughout this section, where the ratio of HCl to HNO_3 is specified, the first number refers to the parts of HCl and the second to parts of HNO_3 (e.g. 3:1 aqua regia is composed of 3 parts HCl plus 1 part HNO_3). Although the equilibrium encountered in conventional aqua regia (Section 2.4.1.1) relies on the acids being in exactly the 3:1 ratio, other authors have used HCl-rich and HNO_3-rich mixtures of the acids covering a wide range of proportions, from 6:1 to 1:3 (Section 2.4.1.1). Excess HCl ensures the presence of additional chloride ions to effect precious metal dissolution and to stabilise the precious metal species in solution. Excess HNO_3 enhances oxidative properties of the mixture and permits the more thorough attack on some primary sulphide host minerals.

The following acid mixtures were investigated: conventional 3:1 aqua regia, reversed (i.e. 1:3) aqua regia and an intermediate composition of 1:1 aqua regia, all tests were carried out using CHR-C. Each aliquot of aqua regia was prepared to a volume of 20 ml, i.e. 15 ml + 5 ml, 10 ml + 10 ml and 5 ml + 15ml, respectively. Aristar-grade[4] acids were used for the leaches of natural geological samples, once the method had been fully optimised to minimise the levels of reagent blanks. The less pure Analar-grade acids were used during the development of the method and for washing the glassware.

4.3.3.1 Observations and results.

Freshly prepared 3:1 aqua regia rapidly turned pale yellow, passing through a more orange colour before becoming a more intense translucent orange/red over a period of a few hours. After three days the solution had reverted back to a pale yellow/green colour. 1:3 aqua regia turned pale yellow more rapidly than 1:1 aqua regia, which turned yellow more rapidly than 3:1 aqua regia. These observations suggested that the colours are due to oxides of nitrogen in the solution, the darkening then lightening of the

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[4] ARISTAR and AnalaR are the marketing names for ultra pure and pure acids, respectively, supplied by BDH (Merck) Ltd.

colour being due to gradual formation and subsequent decomposition of these oxides. Fresh aqua regia has the characteristic odour of Cl_2.

Table 4.4. Concentration (conc.) and proportion (prop.) of analyte (identified with their ascribed energies) remaining in CHR-C residue after aqua regia attack compared with an unattacked sample. The composition of aqua regia is as indicated ($HCl:HNO_3$). Analyses were made by INAA.

aqua regia	Ir 468.0		Au 411.8		As 559.1		Sb 564.0		Fe 1099		Co 1332		Zn 1115	
composition	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.
1:3	18.9	109%	0.32	7%	66.7	13%	5.08	18%	12.4	94%	150	77%	266	106%
1:1	19.6	112%	0.37	8%	64.6	13%	4.46	16%	12.1	92%	148	76%	264	106%
3:1	18.4	105%	0.33	7%	63.1	12%	3.75	14%	13.0	98%	158	82%	325	130%

aqua regia	Ir 308.3		Sb 1691		Fe 1291		Co 1173	
composition	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.
1:3	13.4	109%	4.88	18%	13.2	97%	158	76%
1:1	14.0	115%	4.35	16%	13.1	96%	155	75%
3:1	12.9	106%	4.77	18%	13.9	102%	166	80%

The Zn datum, 130% remaining in residue, is not significant as the Zn concentration is very close to the detection limit.

Results of the extraction efficiencies of the combinations examined are presented in Table 4.4, from which it can be seen that changing the composition of aqua regia had no effect on the extent of leaching of Ir, Au, As, Sb, Fe and Co, as judged by the concentration of these elements remaining in the residue, determined by INAA. It would appear that the conventional 3:1 aqua regia was not as efficient at promoting the dissolution of Zn as the other 2 acid combinations, however, the concentrations determined by this method were close to the detection limit.

The HNO_3-rich mixtures of aqua regia favour the extraction of Ni and, arguably, Fe (Section 2.4.1.4) and these elements cause interference problems in subsequent spectrometric analysis. Based on the assumption that the extraction of these concomitant elements could be considered representative of the behaviour of the PGE, it is thus most favourable to use conventional 3:1 aqua regia.

4.3.4 Time of attack.

Previous publications have reported that the aqua regia attack should be allowed to proceed overnight, i.e. sometimes for as long as 16 hours. Part of the aim of this work was to create a rapid technique, so that reduction of attack time would offer a significant benefit. Too short an attack time would result in incomplete extraction of the precious metals and too long an attack time would increase the probability of a loss of volatile reaction products (e.g. OsO_4) and may unnecessarily increase the the proportion of concomitant interfering matrix elements taken into solution.

Identical samples were prepared and left in contact with aqua regia for periods ranging from 15 minutes to 4 hours. After the specified period, the leach solution was filtered from the residue as described above and both filtrate and residue were retained for analysis. All four test samples listed above (Section 4.3) were used.

4.3.4.1 Results.

The results of the analyses of both the filtrate and residues are presented in Tables 4.5-4.7. Data for the PGE show that most of the elements are extracted in the first 15 minutes from both SARM 7 and CHR-C and increasing the extraction time beyond 40 minutes does not significantly enhance their recovery. An apparent decrease in recovery of Ru and Os beyond 40 minutes may be caused by volatilisation losses of their respective oxides or an increased interference in the ICP-MS signal due to an increase in dissolution of matrix elements.

Of the elements taken into solution, the greatest proportion was extracted in the first 15-20 minutes, with little further extraction within 1 hour and insignificant further extraction after 4 hours. Some data from EDXRF appear to contradict these observations, namely the extraction of Ni from CHR-A, where one full hour was required for quantitative extraction, and the extraction of Cu from CHR-B and CHR-C and Ni from CHR-B, where significant extraction occurred after 1 hour.

Table 4.5. Proportion of Pd, Rh, Pt, Os and Ru extracted from CHR-C and SARM 7 by aqua regia extraction at room temperature for the specified times. Data have been arbitrarily normalised to the maximum measured value. Data were obtained by ICP-MS.

sample	time/min.	Pd	Rh	Pt	Os	Ru
CHR-C	0	0%	0%	0%	0%	0%
	15	100%	100%	100%	100%	100%
	40	99%	94%	97%	86%	70%
	60	95%	97%	92%	76%	67%
	120	93%	82%	90%	54%	63%
SARM 7	0	0%	0%	0%	-	-
	15	100%	100%	79%	-	-
	40	93%	100%	81%	-	-
	60	89%	98%	97%	-	-
	120	87%	89%	100%	-	-

Table 4.6. Proportion of Mn, Fe, Ni, Cu, Zn and As remaining in residue after aqua regia attack. Data have been normalised to Cr. Data are from semiquantitative analyses by ED-XRF.

	time/mins	Mn	Fe	Ni	Cu	Zn	As
CHR-A	0	100%	100%	100%	-	100%	-
	20	92%	96%	77%	-	98%	-
	40	95%	95%	71%	-	97%	-
	60	90%	93%	66%	-	94%	-
	120	86%	93%	66%	-	92%	-
	240	93%	92%	66%	-	96%	-
CHR-B	0	100%	100%	100%	100%	100%	-
	20	84%	83%	50%	33%	93%	-
	40	83%	86%	48%	36%	101%	-
	60	85%	84%	44%	33%	98%	-
	120	91%	83%	39%	22%	99%	-
	240	87%	82%	36%	14%	100%	-
CHR-C	0	100%	100%	100%	100%	100%	100%
	15	90%	85%	25%	18%	103%	15%
	30	83%	83%	23%	14%	96%	13%
	60	87%	82%	21%	11%	94%	12%
	120	86%	84%	21%	9%	94%	12%
	240	90%	82%	18%	7%	100%	11%

The concentration of Cu in CHR-A and As in CHR-A and CHR-B were below detection limit.

Table 4.7. Proportion of Fe, Co, Zn, Ir, Au, Sb and As remaining in CHR-C residue after aqua regia attack. Data have been normalised to Cr. Data are from semiquantitative analyses by INAA.

Time/mins.	Fe	Co	Zn	Ir	Au	Sb	As
0	100%	100%	100%	100%	100%	100%	100%
15	84%	68%	94%	84%	11%	13%	13%
40	85%	69%	110%	95%	7%	13%	7%
60	96%	76%	90%	99%	7%	15%	11%
120	85%	69%	110%	89%	6%	13%	11%

Although most of the extraction occurred during the first 15 minutes, a longer time was required for certain elements from specific matrices (e.g. Pt from SARM 7). One hour was thus identified as the optimum extraction time for 10 g samples with 20 ml aqua regia.

4.3.5 Temperature of reaction.

Some published schemes of analysis using aqua regia involve leaching at room temperature,[5] but others advocate heating the reaction vessel on a hotplate for the duration of the attack. The assumed benefit in heating the reaction mixture is the substantial increased reaction rate. However, the potential loss of volatile reaction products, and more importantly the reactive components of aqua regia, NOCl and Cl_2 (Section 2.4.1.1), is often overlooked. Furthermore, as well as increasing dissolution of the precious metals, heating will promote dissolution of potentially interfering matrix elements, which could cause severe matrix suppressions in the analysis of resultant filtrate solutions.

The effect of temperature on this acid attack was studied by comparing two sample extractions using both CHR-C and SARM 7. One extraction mixture was heated on a hotplate at about 60°C for the duration of the attack, while the other was conducted at room temperature, no stirring was applied to either sample after the initial mixing with a teflon rod. The comparison temperature was set at 60°C as this was significantly greater than room temperature, while being sufficiently far below the boiling point of the aqueous mixture to minimise the loss of solution by evaporation from the sample vessel.

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[5] The aqua regia dissolutions would, in fact, proceed at a temperature defined by the reaction conditions, there being no external source of heat. Experimental observations suggested that the action of aqua regia on some sulphide materials was exothermic.

4.3.5.1 Results.

The results of the analyses of both the filtrate and residues are presented in Tables 4.8 and 4.9. Analysis of solutions indicated that heating had a detrimental effect on the extraction of the Pd, Pt and Rh from SARM 7 and CHR-C and Ru and Os from CHR-C. The reasons for this apparent low recovery could include enhanced extraction of interfering matrix elements and/or decreased extraction efficiency of the aqua regia caused by volatilisation and/or decomposition of Cl_2 and NOCl. Ru and Os may also be lost, but not entirely so, by enhanced volatilisation. It would therefore be necessary to conduct the extractions at room temperature.

Table 4.8. Proportion of Pd, Rh, Pt, Os and Ru extracted from CHR-C and SARM 7 by aqua regia extraction for 2 hours at the specified temperature. Data have been arbitrarily normalised to the maximum measured value determined from the experiments on time of attack (Table 4.5). Data were obtained by ICP-MS.

sample	Temp.	Pd	Rh	Pt	Os	Ru
CHR-C	20°C	93%	82%	90%	54%	63%
	60°C	54%	52%	59%	40%	30%
SARM 7	20°C	87%	89%	100%	-	-
	60°C	42%	58%	58%	-	-

Table 4.9. Proportion of Fe, Co, Zn, Ir, Au, Sb, As and Cr remaining in CHR-C residue after aqua regia attack for 2 hours at the specified temperature. Results of 2 separate analyses by INAA are shown. Data tabulated>100% indicate that the concentration of the particular analyte in the residue was apparently greater than that in the unattacked sample.

	Temp	Fe	Co	Zn	Ir	Au	Sb	As	Cr
Analysis 1	20°C	102%	86%	118%	112%	11%	26%	-	142%
	60°C	98%	82%	100%	108%	10%	28%	-	134%
Analysis 2	20°C	100%	81%	130%	105%	7%	16%	13%	118%
	60°C	111%	95%	122%	127%	7%	83%	13%	79%

Not only did there appear to be no benefit in heating the extraction mixtures, but the observations indicated that analytical deficiencies could be minimised by performing aqua regia extractions at room temperature. Data for Au and As from Table 4.9 corroborate this conclusion, but data for the other analytes are inconclusive.

4.3.6 Agitation of sample mixture.

Most published methods of aqua regia attack rely on a long time of attack to effect maximum dissolution of the precious metals. As well as heating a reaction mixture, the reaction rate may also be increased by stirring or shaking. Shaking glass containers of concentrated aqua regia is hazardous and can lead to loss of analyte (and analyst!). However, stirring the mixture offers an ideal way of potentially increasing the effectiveness of dissolution with the advantage of thorough wetting of the sample powder for the duration of the attack. Continuous stirring can be achieved by use of a teflon-coated magnetic follower placed into the reaction vessel, itself positioned on a magnetic stirring table.

The benefits of stirring were ascertained by comparing the results from a leach sample after stirring with the results obtained from a leach sample that was placed on the stirring table without a magnetic follower. Both samples were mixed with a teflon rod immediately after the addition of the acids to ensure complete wetting of the powder. The 3 chromitite test materials (CHR-A, CHR-B and CHR-C) were used in this experiment.

4.3.6.1 Results.

Table 4.10. Concentration (and proportion of CHR-C) of Fe, Co, Zn, Ir, Au, As and Sb in specified residues after an aqua regia leach for 2 hours at room temperature with the specified agitation. Analyses were made by INAA.

		Fe 1099		Fe 1291		Co 1332		Co 1173		Zn 1115	
		conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.
CHR-A	stir	19.0	-	20.4	-	240	-	257	-	628	-
	stand	18.6	-	19.7	-	236	-	251	-	641	-
CHR-B	stir	13.3	-	14.3	-	158	-	173	-	272	-
	stand	12.5	-	13.3	-	151	-	161	-	256	-
CHR-C	stir	13.0	98%	13.9	102%	158	82%	166	80%	325	130%
	stand	12.4	94%	13.2	96%	147	76%	157	76%	261	104%

		Ir 468.0		Ir 308.3		Au 411.8		As 559.1		Sb 564.0		Sb 1691	
		conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.	conc.	prop.
CHR-C	stir	18.3	105%	12.9	106%	0.33	7%	63.1	12%	3.75	14%	4.77	18%
	stand	20.0	114%	14.2	116%	0.40	9%	56.8	11%	3.17	11%	2.62	10%

The proportion remaining was not calculated for CHR-A and CHR-B because the unattacked powdered had not been analysed. Direct comparison of the 2 variants of the method is possible by examination of the concentration data.

The results from this experiment are shown in Table 4.10, from which it can be seen that stirring the leach mixture arguably increased the extraction of Sb, but did not increase significantly the extraction of the other concomitant elements over the 2 hour period. From this observation, it can be inferred that the determinative step is to ensure that the sample powder is fully wetted by the aqua regia. Continuous stirring during the extraction procedure appeared to offer neither further benefit nor disadvantage in the recovery of the analyte elements. However, stirring will permit a degree of control over the effervescence that may occur when strong oxidising acids come into contact with reactive materials (e.g. sulphide-rich samples). Stirring should also ensure complete wetting of a sample that may not have been efficiently wetted by the initial mixing. Moreover, automated stirring can remove any inconsistencies between samples caused by variable manual stirring. For these reasons it was decided to include stirring in the analytical procedure.

4.4 The standard procedure.

The standard dissolution procedure developed in the above work is described in full below, when water is specified in the experimental procedure, it is inferred that deionised distilled water was used, except where indicated. All the following operations, except step 1, were undertaken within a fume cupboard.

1. Sample powder (10.0 ± 0.1 g) was added to a preweighed150 ml borosilicate beaker, the beaker was put into a drying oven for 30 minutes and reweighed while warm to determine dry weight of sample. The beaker was then covered with a watchglass to prevent contamination, awaiting the addition of acid.
2. Concentrated Aristar-grade HNO_3 (5 ml) was dispensed into a 25 ml measuring cylinder from a teflon dispenser with ruby ball valves. Concentrated aristar-grade HCl (15 ml) was then added to the measuring cylinder from a second teflon dispenser. This mixture of aqua regia (20 ml) was then immediately added to the sample powder in its beaker.
3. The mixture was then stirred with a teflon rod until completely wetted, at which point a magnetic stirring follower was added to the beaker. The beaker was then covered with the watchglass to prevent spillage and contamination and placed on the designated position on a 15 place magnetic stirring table, and set to stir at 250 rpm.
4. A vacuum filtration system was assembled, comprising of a Büchner flask and Büchner funnel with a 5.5 cm diameter Whatman 40 filter paper, wetted with a minimal amount of water.
5. After one hour, the beaker was removed from the stirring table and its contents, including the magnetic follower, were poured onto the filter paper. The watchglass and residue were then rinsed into the Büchner funnel with the minimal volume of water.

6. When the level of liquid had subsided, the beaker was more thoroughly rinsed into the funnel with the minimal volume of water, such that all the residue was washed from the beaker. If the volume of liquid in the Büchner flask was less than about 100 ml, the residue on the filter paper was again rinsed with a further small portion of water. The apparatus was then left standing for a few minutes to drain excess solution from the residue and to dry the residue.
7. After the vacuum line had been disconnected, the filter paper and residue were lifted off the bottom of the Büchner funnel with a teflon rod and transferred to a polythene bag, which was labeled and sealed awaiting subsequent analysis (Sections 4.2.1 and 4.2.2).
8. The filtrate was then decanted into a graduated 100 ml flask. The Büchner flask was then twice rinsed into the graduated flask with water. The solution in the volumetric flask was then made up to volume using the required amount of water.
9. The graduated flask was inverted three times to ensure homogenous dilution of the solution. Then, either the graduated flask was placed at the back of the fume cupboard awaiting solvent extraction (Chapter 5) or the solution was transferred to a 120 ml polythene sample bottle for storage and transport to the analytical facility (ICP-MS or GFAAS).

Following this procedure, duplicate extractions of 12 samples can be achieved within 7 hours. A procedural blank was undertaken with each batch of 12 samples by performing the entire extraction procedure but without the addition of sample powder.

The glassware used in the dissolution procedure was stored overnight in a 2% solution of Decon 90 laboratory cleaning solution and was thoroughly rinsed with water, then 50% Analar-grade HNO_3 and then rinsed clean with water and dried in a drying oven before use. Although there were sufficient beakers for each batch of samples, there were not enough sets of vacuum filtration apparatus or watch glasses. Consequently, between daytime uses, these items were washed with 50% HNO_3 three times then rinsed with water six times and left to drain. The beakers, watch glasses and the Büchner funnels were first brushed clean of any solid matter under flowing tap water then rinsed three times with water before their relevent washing procedures.

The limitation to increasing the number of samples processed in each 7 hour period by a single operator is the provision of additional glassware and stirring facilities. An advantage of this procedure is, therefore, the large number of samples that could be analysed by scaling up the operation described above.

4.5 Quantification of the dissolution technique.

The aqua regia dissolution method thus far described was principally developed using one sample material (CHR-C), although other samples were used to corroborate the conclusions for some parameters (CHR-A, CHR-B, and SARM 7). This section describes the application of the method to a number of reference materials and other samples for which independent analytical data were available. These samples covered a wide range of geological matrix types and had a range of precious metal concentrations at readily detectable levels. It was necessary to use non-certified materials for some of these quantification studies as there were so few reference materials with well-characterised precious metal concentrations and there were no reference materials in which these elements are characterised in a chromite-rich matrix (the lack of such materials will be approached in Chapter 8).

The reference materials used were: PTA-1 (platiniferous black sand), PTC-1 (sulphide concentrate, PTM-1 (Ni-Cu matte), SARM 7 (platinum ore, previously called PTO-1), GXR-1 (jasperoid soil), GXR-4 (copper mill head) and SU-1a (Ni-Cu-Co ore). The other samples included 14 chromitites, 3 pyroxenites and 2 wehrlites. Two of the chromitites (2/77 and 14/75) were in-house reference materials used by the laboratory that prepared SARM 7 (kindly supplied by Rob Robért of MINTEK, South Africa). Six of the chromitites (Brag 2 - 78) were from an ophiolite complex near Bragança, Portugal (kindly supplied by John Bridges, OU). Three of the chromitites (CHR292, RLM007 and RLM098), the pyroxenites (CMR163, MR63 and MR65) and the wehrlites (MR16 and RLM008) were from the Unst Ophiolite Complex, Shetland (kindly supplied by Hazel Prichard and Richard Lord, OU). The remaining 3 chromitites (OU-BX, OU-CX and OU-HGX) were also from the Unst Ophiolite Complex, Shetland and represented in-house reference materials prepared at the OU as part of an interlaboratory study.

The reported values of the precious metal concentrations in these other samples, against which the values derived from the aqua regia dissolution were compared, were obtained by the following methods. The reported values for the 3 in house reference materials (OU) were the best estimate data derived from 5 commercial laboratory analysis (Potts, pers. comm.). Analysis of the South African samples were made by Pb- or NiS-fire assay with an ICP-MS or AAS finish, data being supplied by Robért. Analysis of the remaining samples were made by NiS-fire assay followed by ICP-MS by a commercial laboratory (Sheen Analytical, Perth, Australia) as part of an ongoing geochemical project.

The procedure used for the analysis of these samples was the aqua regia dissolution method described in Section 4.4 followed by ICP-MS (Section 4.2.3).

4.5.1 Results.

The results of these analyses are shown in Tables 4.11 and 4.12. These results will be discussed by analyte below:

Platinum. The aqua regia extraction offered quantitative or near-quantitative extraction for a few samples, but typical recoveries were 20-40 %. Noticeably low recoveries were recorded for PTC-1, PTM-1 and SU-1a and these data will be discussed later.

Table 4.11. Comparison of extraction efficiency of the aqua regia leach (this work) with samples independently analysed by nickel sulphide fire assay/ICP-MS. Concentrations of Pt, Pd, Rh, Ru, Os, Ir and Au are reported for as many as possible of the 14 chromitites, 3 pyroxenites and 2 wehrlites.

	Pt		Pd		Rh		Ru		Os		Ir		Au	
	this work	fire assay	this work	fire assay	this work	fire assay	this work	fire assay	this work	fire assay	this work	fire assay	this work	fire assay
chromitites														
14/75	200	2800	730	1300	216	470	85	960	–	–	30	380	30	70
2/77	110	3110	490	1670	191	610	76	1200	–	–	16	<	13	50
Brag2	30	83	36	66	6	20	29	110	<	42	9	57	–	–
Brag28	200	510	300	340	79	120	460	390	9	88	18	250	–	–
Brag52	17	52	50	83	3	13	<	69	<	34	5	50	–	–
Brag57	1390	4050	3600	3150	159	605	250	1150	<	675	29	1550	–	–
Brag71	<	16	<	11	1	9	<	45	<	24	<	25	–	–
Brag78	8	51	<	18	4	46	<	310	<	160	2	180	–	–
CMR292	130	500	450	520	6	55	35	190	6	50	3	97	2	6
OU-BX	230	300	–	–	–	–	–	–	–	–	–	–	2	30
OU-CX	7290	40000	51000	53000	662	3700	–	–	–	–	70	12000	2960	2700
OU-HGX	210	280	226	220	–	–	–	–	–	–	18	3000	–	–
RLM007	1140	870	2200	2100	87	110	290	190	45	98	17	120	155	130
RLM098	7	9	8	10	1	5.5	74	44	<	12	<	14	<	2
pyroxenites														
CMR163	120	110	<	4	<	6	<	26	<	4	<	4.5	16	8
MR63	29	44	40	62	<	3	<	4	<	4	<	2.5	<	6
MR65	65	100	180	220	3	9.5	12	13	<	6	<	5.5	34	28
wehrlites														
MR16	<	48	22	18	<	4	<	19	<	2	<	5	–	–
RLM008	22	22	37	48	<	2.5	<	5.5	<	4	<	4	<	2

All data listed in ppb (whole rock).
– not analysed by NiS-FA.
< below detection limit.

Palladium. Quantitative extraction was achieved for 5 of the samples tested, with 50-90 % recoveries from most of the other samples. The most noticeable exception to this trend was the extremely low recovery of Pd from PTM-1. The concentrations of Pd in GXR-1 and GXR-4 appeared to be far in excess of the reported values, however there is some uncertainty as to the reliability of the compiled recommended values for these samples.

Rhodium. Rh was extracted from these samples in variable proportions. Although 80 % recovery was noted from RLM007, the recovery was typically <30 % for the other samples, including the sulphide-rich reference materials.

Ruthenium. The extraction of Ru followed the same pattern as that described for Rh, with the exception that quantitative extraction was achieved for 4 of the samples. This observation underlies the variable recovery of this element by aqua regia.

Table 4.12. Comparison of aqua regia dissolution data (this work) with expected compositions (given value) of selected reference samples. Concentrations of Pt, Pd, Rh, Ru, Os, Ir and Au are reported for as many as possible of the 7 reference materials.

	Pt		Pd		Rh		Ru		Os		Ir		Au	
	this work	given value	this work	given value	this work	given value	this work	given value	this work	given value	this work	given value	this work	given value
platinum ore SARM 7 (PTO-1) [a]	1400	3740	1180	1530	174	240	115	430	9	63	19	74	302	310
platiniferous black sand PTA-1 [b]	3320	3050	16	-!	5	-	<	-	<	-	15	-	363	-
sulphide concentrate PTC-1 [c]	210	3000	6010	12700	71	620	171	650*	49	240*	<	170*	136	650
Ni-Cu matte PTM-1 [d]	45	5800	5	8100	132	900	294	590*	31	140*	44	470*	<	1800
Ni-Cu-Co ore SU-1a [e]	59	410	265	370	16	80*	29	56*	<	11*	<	25*	105	160*
jasperoid soil GXR-1 [f]	<	<10	181	<0.1	12	-	<	-	<	-	<	-	2830	3300
copper mill head GXR-4 [f]	<	<10	55	0.2	2	-	<	-	<	-	<	-	618	470

All data listed in ppb (whole rock).

– no reported data.

< below detection limit.

! Sen Gupta and Gregoire (1989) reported a Pd concentration of 20 ppb in PTA-1.

'Given value' data are as follows (data marked * are additional non-certified values):

[a] SARM 7: *South African Bureau of Standards certified values from Steele et al. (1975), previously* called PTO-1.

[b] PTA-1: Canadian Certified Reference Material Project recommended values from McAdam et al. (1971).

[c] PTC-1: Canadian Certified Reference Material Project recommended values from McAdam et al. (1973a).

[d] PTM-1: Canadian Certified Reference Material Project recommended values from McAdam et al. (1973b).

[e] SU-1a: Canadian Certified Reference Material Project recommended values from Steger and Bowman (1980).

[f] GXR-1 and GXR-4: compiled values from Gladney and Roelandts (1990).

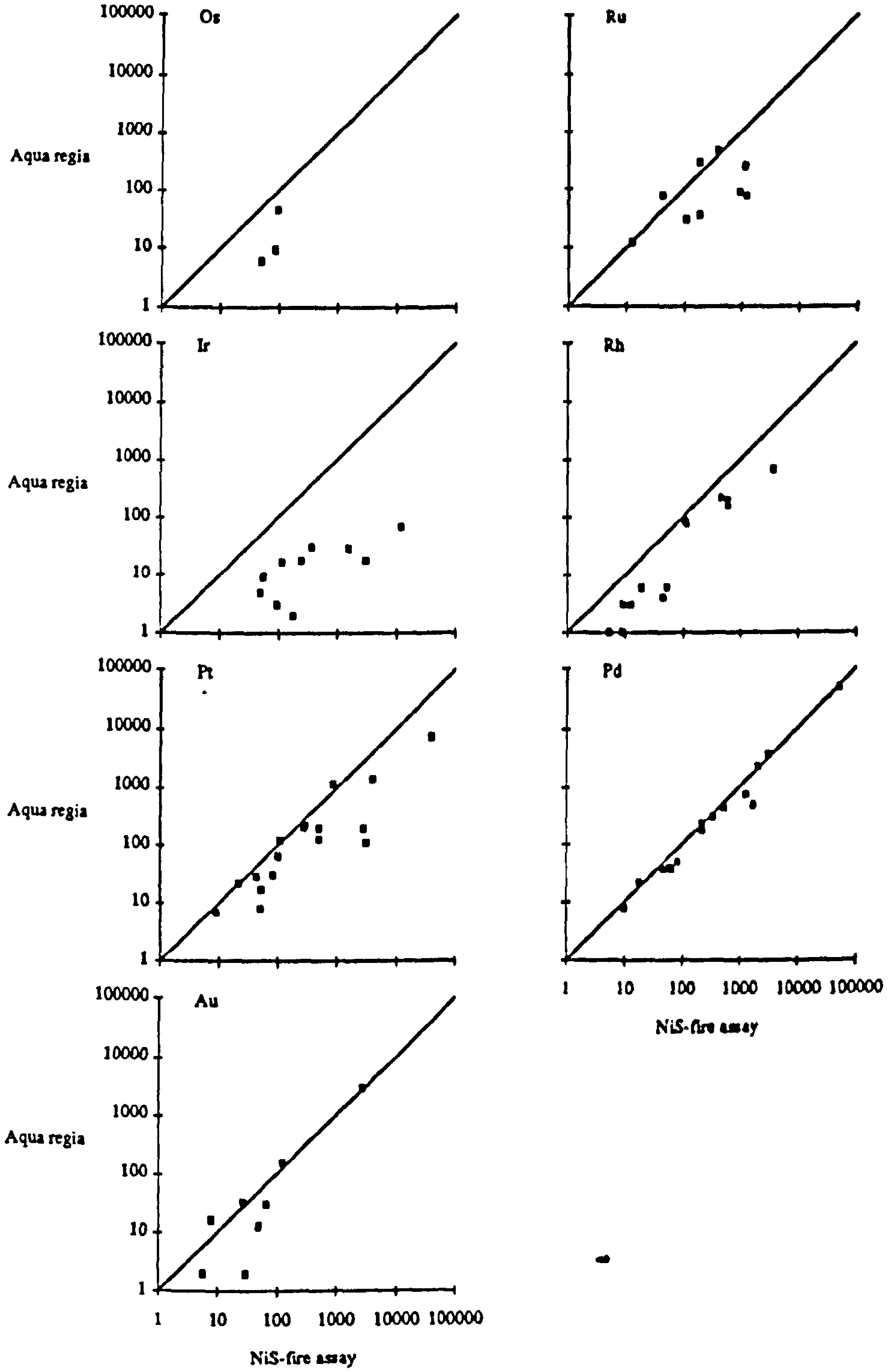
Osmium. Like Ru, the recovery of Os is variable and usually low. Further identification of a pattern of recovery was hampered by the lack of reported data for this analyte, as it was often lost during sample digestion.

Iridium. Extraction of Ir from these samples was typically <15 % except from SARM 7. The very low recoveries reflect the difficulty with which this analyte was taken into solution. However, it was encouraging to have detected at least a portion of Ir, bearing in mind the very low/nil recovery from CHR-C encountered in the optimisation work (Section 4.3).

Gold. Quantitative or near-quantitative extraction extraction of Au was usually observed from these samples, although some low recoveries were noted for some chromitites and the sulphide-rich reference materials, paticularly PTM-1.

4.5.1.1 Comparison aqua regia extraction with NiS-fire assay.

Figure 4.3. Concentrations of the PGE extracted by aqua regia/ICP-MS (this work) compared to analyses with NiS-fire assay preparation (data obtained from a commercial laboratory). The diagonal line drawn onto each plot is a line of equivalence (i.e. 1:1 ratio) and is not a regression line.



The data from Table 4.11 have been plotted in Figure 4.3. Each chart represents the concentration of an analyte obtained in this work by the aqua regia dissolution method plotted against the concentration obtained with NiS fire assay, using results obtained from a commercial laboratory.

It can be seen from the charts plotted in Figure 4.3, on each of which is marked a 1:1 line of equivalence, that there is a general trend showing a degree of correlation between the results obtained by the 2 methods for Ru, Rh, Pt and Pd and Au, at the higher concentrations. The recoveries of Ir by aqua regia were so low that it was difficult to identify a trend in the data for this analyte. There is not enough data for Os to show a clear trend, other than to indicate that, like Ir, Os determination with an aqua regia leach leads to low results compared with NiS-fire assay. The distribution of many of the data points below the line of equivalence indicates low recoveries for some of the analytes. However, the general trend for all the analytes determined by aqua regia extraction is indicated graphically and the general agreement between the 2 methods is quite encouraging.

4.5.2 Discussion of the results.

The low recoveries for the sulphide-rich samples indicate that the aqua regia dissolution is, as it stands, not suitable for such materials. There are a number of explanations for these low recoveries. These samples may contain precious metal sulphides that are insoluble in aqua regia. The sulphides, themselves, on the other hand, may be oxidised by the aqua regia leading to a loss in the potency of the acid. The relatively high base metal content of the solutions may have led to excessive interferences when determinations were made by ICP-MS that could not be corrected by the simple drift correction procedures here used.

The analytical uncertainty in the values reported for the reference materials is indicated for by the error limits published on certificates of analysis for these samples. When interpreting the data in Table 4.11, it is appropriate to consider that equivalent uncertainties may have affected the results from external laboratories with which the comparison of data has been made.

Excluding analytical discrepancies, which are in any case largely unquantifiable, factors relating to sample composition that may affect significantly the efficiency of precious metal extraction include differences in matrices, which have already been alluded to as a reason for the low recoveries from sulphide-rich samples. The different associations of precious metals with their matrices should also be considered as explanations for the observed low recoveries. Two factors may act independently or combine together to offer further explanation of the low recoveries. Individual precious metals may be present in solid solution within base metal sulphides (e.g. Pd is in solid solution with Ni in pentlandite $(Ni, Fe)_{9-x}Pd_xS_8$ (Brynard et al., 1976; Crocket et al., 1976)) or even present in minerals that are themselves totally occluded within insoluble matrix grains (e.g. Prichard et al. (1989) observed grains of laurite within grains of chromite, which is itself not attacked by aqua regia).

The second factor brings into question the solubility of individual precious metals in aqua regia. Gold is usually present as native metal or as alloys of Ag and/or Cu, all of which are known to be soluble in aqua regia. This fact correlates with the high Au recoveries observed above. Three of the more common PGE minerals, sperrylite ($PtAs_2$), laurite (RuS_2) and osmiridium (IrOs) are known to be insoluble in aqua regia (Schoeller and Powell, 1955, p.325). The presence of these minerals may, therefore, help to explain the low recoveries of Pt, Ru, Os and Ir in some of the samples studied. The presence of these with other minerals that are soluble in aqua regia may explain the variable extraction extraction efficiency of the PGE, particularly Pt, noted in the previous Section. The influence of PGE mineralogy upon efficient sample dissolution will be considered further in Chapter 7.

4.6 Conclusions.

Development of a dissolution method based on aqua regia showed that optimum extraction conditions could be achieved using 10 g samples with 20 ml conventional 3:1 aqua regia for 1 hour duration, stirring at room temperature. Application of this method to a variety of samples revealed high and for ophiolitic rocks, near-quantitative recoveries of Au and Pd, variable, but typically 20-40 % recovery of Pt, Rh Ru and Os and <15 % recovery of Ir. The variability of recovery from all samples can be explained by differences in both the matrix composition and the PGE mineralogy of the samples.

The capabilities of ICP-MS in detecting ppb-levels of these trace elements in aggressive solutions (high acid and total dissolved solids) have been well evaluated in this development programme. Indeed, without such a multielement technique with its superior sensitivity, the optimisation and characterisation of this method would have been far more difficult. However, some problems were encountered in the running of solutions with such high levels of dissolved solids, for example sampling and skimmer cone orifices at the entrance to the evacuated chambers of the mass spectrometer tended to become blocked in the course of an analytical run, resulting in serious degradation of analytical signal. The consequential dynamic changes in instrument performance can be compensated by drift correction. Although the use of internal standards may have compensated for such fluctuations, changes in nebulisation efficiency, sample introduction rate or plasma characteristics between samples are less easy to define and together may have contributed to the variable recovery observed for the different elements.

A reduction in the total dissolved solid content of analyte solutions within the global aim of developing a practical analytical technique will be discussed further in Chapter 5.

Chapter 5.
Solvent extraction of aqua regia leaches.

5.1 Introduction.

An aqua regia leach, as described in Chapter 4, involves a partial digestion and, as such, offers the advantage of a potential decrease in the interference effects caused by high total dissolved salt (TDS) content and the presence of matrix elements. However, these advantages are not fully realised as significant proportions of matrix elements are co-extracted with the precious metals by aqua regia, resulting in an unfavourably large presence of matrix elements and a high TDS content. These concentrated leaches, in strongly acidic solution, were analysed by ICP-MS in the short term, but routine use of this technique was unlikely to be satisfactory due to analytical problems (Chapter 4). Preliminary analyses of these leaches by GFAAS indicated that the absorbance signals were significantly disrupted by the presence of the high TDS[1]. (Chapter 6). To maintain a simple and rapid procedure, detailed assessment was made of a solvent extraction procedure to overcome these problems.

This chapter starts with a summary of the principles of solvent extraction and choice of extractants. Subsequent sections describe the analytical methods employed, the optimisation of the solvent extraction procedure (both the physical and chemical parameters) and application of the procedure to artificial and actual samples. The summary includes a drawing together of the conclusions from the full aqua regia leach/solvent extraction sample preparation procedure.

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[1] These samples caused excessive background absorption and deterioration of analytical signal. Moreover, the presence of white clouds and acidic fumes in the graphite tube furnace were detrimental to the operation of the instrument. These interferences and analytical problems are discussed further in Chapter 6.

5.1.1 The principles of solvent extraction for the precious metals.

Analytes can be separated from interfering elements by a simple procedure involving shaking their aqueous solution with a suitable immiscible organic solvent. To be effective, the analytes must be present in a chemical form that is readily and favourably partitioned into the organic phase. As mentioned in Section 2.6.2, solvent extraction has been one of the most successful group separation procedures for the precious metals, with quantitative or near-quantitative recoveries of all the elements being reported. The speed and simplicity of solvent extraction are further reasons for adopting this method as a preconcentration procedure. One of the greatest additional advantages of solvent extraction is the potential for direct analysis of the organic extracts by AAS. Not only does this action serve to eliminate any potential interferences caused by the presence of acids, but organic solvents have been known to enhance atomic absorption signals compared to those resulting from aqueous solutions (Van Loon, 1977; Samchuk et al., 1988).

Reports of previous applications of solvent extraction for the concentration and separation of the precious metals have been documented in Section 2.3.4. The solvent extraction procedure described in this chapter involves three stages: (i) labilisation of the precious metals, (ii) selective complexation of the precious metals in aqueous solution and (iii) extraction of precious metal complexes into an organic solvent.

5.1.1.1 Labilisation.

As ions in aqueous solution, Au, Pd and Pt are classified as soft Lewis acids and Rh, Ru, Ir and Os as intermediate Lewis acids (Pearson, 1966). Soft Lewis acids preferentially associate with soft Lewis bases (e.g. molecules containing electron donor atoms such as P or S). The concomitant interfering elements, from which extraction is being sought, are hard (e.g. Fe^{3+}, Mg^{2+}) or intermediate (e.g. Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})

Lewis acids. The hard Lewis acids will preferentially associate with hard Lewis bases (e.g. Cl^-, NO_3^-). Use of Pearson's principle of preferential association leads to the following predictions: i) selective complexation of Au, Pd and Pt with soft Lewis base ligands would be possible; ii) complexation of intermediate Lewis acids (e.g. Rh, Ru, Ir and Os) may form extractable complexes with an appropriate soft Lewis base (although other transition elements (e.g. Fe, Ni, Cu, Zn) may be co-extracted, decreasing the selectivity of the complexing agents for the precious metals).

5.1.1.2 Selective complexation.

N,N'-Diphenyl thiourea (DPTU) ($(PhN)_2CS$) and triphenyl phosphine (TPP) (PPh_3) have been found to be suitable complexing agents in promoting the extraction of precious metals by formation of uncharged coordination compounds (Mojski, 1980; Seeverens et al., 1983). However, low extraction rates for PGE complexes with these reagents have been attributed to the kinetic inertia of PGE complexes in aqueous solutions. The PGE form relatively labile complexes with $SnCl_3^-$ and $SnBr_3^-$ ligands (Vorob'eva et al., 1974). The addition of $SnCl_2$ or $SnBr_2$ to the solution may, therefore, increase the reaction kinetics, thus increasing the rate of extraction. $SnBr_2$ is unsuitable as it is too active a reductant, reducing Au and Pd to the metal (Vorob'eva et al., 1974). $SnCl_2$ has been widely used as a labilising agent for the formation of PGE complexes (e.g. Zolotov et al., 1978; Mojski, 1980). $SnCl_2$ acts as a catalyst; the formation of a neutral soft ligand complex (MCl_nL_m) is facilitated by substitution of the ligand (L) for the more labile $SnCl_3^-$ in preference to Cl^- (Al-Bazi and Chow, 1984).[2]

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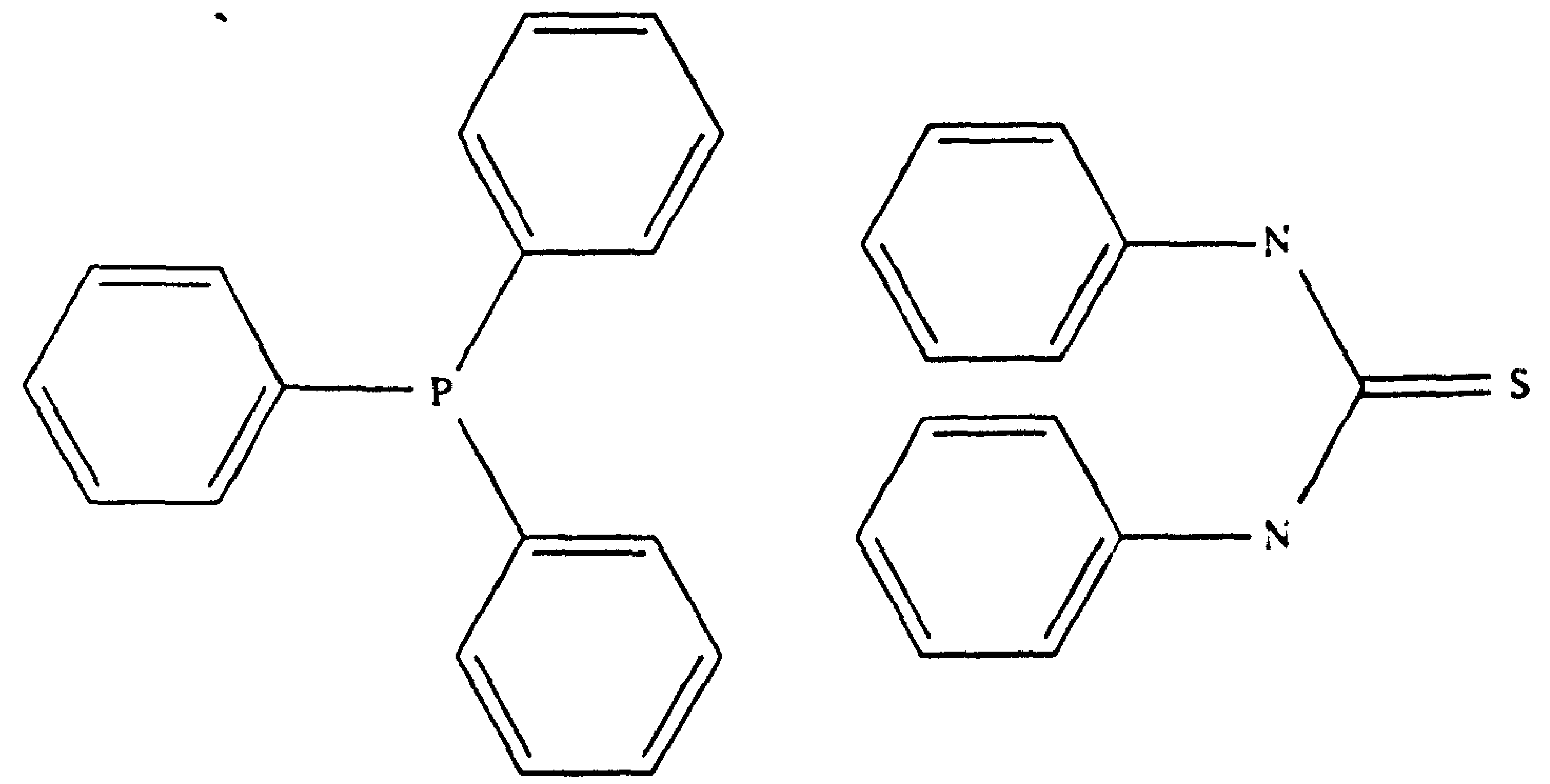
[2] If the bonding ligand atom has vacant valency d electron orbitals in addition to its free electron pair (eg. S, P), it can, in principle, be both a donor and acceptor of electrons (Zolotov et al., 1978). Back donation of electrons from the metal may thus stabilise the complex.

Figure 5.1. The structures of the complexing agents (ligands) a) N,N'-diphenyl thiourea (thiocarbanilide) (DPTU) and b) triphenyl phosphine (TPP).



Mojski (1980) showed that although there was quantitative extraction of Pt, Pd and Rh when TPP was added directly to the organic extractant, the extraction efficiency or Ir, Ru and Os was not quantitative but was highly dependent upon pH of the analyte solutions. The extraction of Ir and Ru was greatly improved (and became less dependent upon pH) when the complexing agent was added to the aqueous solution, permitting formation of the extractable complex prior to the addition of the extracting solvent. Both TPP and DPTU are insoluble in water. So, to achieve the formation of a neutral complex, a solvent had to be found that would dissolve TPP and DPTU such that the resulting solution was miscible with water. Vorob'eva et al. (1974) tested five solvents as carriers of DPTU into the aqueous phase. Reported were the following extraction efficiencies of Ir with 0.05 M DPTU in: acetone (97-99%), dimethyl formamide (92-93%), dioxane (86-88%), ethanol (79-84%) and dimethyl sulphoxide (57-62%). Acetone has the additional advantage of being the cheapest and most readily available of these solvents. Acetone was subsequently selected as the solvent for the complexing agents.

Selective extraction and separation.

Vorob'eva et al. (1974) reported selective extraction of Pt, Pd, Rh, Ir and Au (Ru and Os were not determined) from solutions containing 0.2-60 mg/ml Ni, Co, Fe, Mn and Zn and <60 µg/ml Cu. Zolotov et al. (1978) reported further that only copper, as Cu(I), was extracted with the PGE. Mojski (1980) reported quantitative extraction of Pd, Pt, Ru, Rh and Ir with 0.1 M TPP in acetone from 1-4 M HCl solution and good separation from Fe and some non-ferrous metals from 1-3 M HCl solutions. However, the addition of $SnCl_2$ caused a deterioration in the degree of extraction of Os such that only 25% extraction could by achieved in the final method.[3] Seeverens et al. (1983) reported extraction efficiencies with $SnCl_2$ labilisation and 0.01 M TPP and DPTU in acetone from 1-4 M HCl solution of Pt, Pd (90-100%), Ir (30-40%), Rh (80-100%: DPTU; 30%: TPP). Contrary to earlier papers, these authors also reported extraction of Au (80-100%) without $SnCl_2$ labilisation and a marked decrease in the extraction, with both TPP and DPTU, when $SnCl_2$ was used. These observations suggested that $SnCl_2$ may, like $SnBr_2$, reduce Au(III) to Au(0), especially at higher acid concentrations.

Aqua regia vs chloride solutions.

All previous work on the solvent extraction of the precious metals has been concerned with solutions of the elements in dilutions of HCl. Work was undertaken to test the effect of using solutions of the precious metals in aqua regia. The prospects of success were good due to a high concentration of chloride ions in the aqua regia solution. However, the potential beneficial effects and/or associated problems that might arise due to the presence of the nitrate ion, or any other product of aqua regia (e.g. nitrosyl chloride which has been used as an ionising solvent to prepare complexes such as

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[3] In this thesis, however, the low recovery of Os did not cause undue concern as it is not possible to determine Os by GFAAS.

$NOAlCl_4$, $NOFeCl_4$, $NOSbCl_6$ and $(NO)_2SnCl_6$ (Greenwood and Earnshaw, 1984, p. 507), are unknown. For example, the presence of hard Lewis bases, such as the nitrosyl group (NO^+) or the nitrate ion (NO_3^-), may stabilise the aqueous complexes of hard Lewis acids, such as Fe^{3+} and Mg^{2+} (e.g. $NOCl + FeCl_3 = [NO^+][FeCl_4^-]$, (Durrant and Durrant, 1970, p. 689), and intermediate Lewis acids, such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, thus improving the selectivity of the procedure.

5.1.1.3 Extraction.

The final stage of the extraction of the complex into a solvent was accomplished using either chloroform (Vorob'eva et al., 1974) or 1,2-dichloroethane (DCE) (Mojski, 1980; Seeverens et al., 1983). Initially DCE was used in this study to optimise the technique (Section 5.3). A comparison was then made between the extraction capabilities of the two solvents (DCE and chloroform) with either TPP or DPTU (Section 5.4).

5.2 Analytical methods employed.

After solvent extraction, two immiscible solutions are available for analysis. The organic solution will be referred to as the extract and the aqueous as the raffinate. GFAAS was used to analyse both solutions generated during the optimisation of the solvent extraction procedure. Initially, only the raffinate was analysed because the organic solvents tended to dissolve the autosampler cups used on the spectrometer. Once this problem was overcome (by use of autosampler cups manufactured from PTFE), aliquots of both the extract and the raffinate were analysed to determine the degree of extraction; ideally the extract should contain all the analyte and the raffinate none. The starting solution was always analysed so that an approximation of the degree of extraction could be calculated.

Analytical programmes and modifications made to permit analysis of organic solutions are fully described in Chapter 6. The analytical method used, where more than one was available, is detailed in this paragraph. The atomisation of Au can be achieved either from the wall of the carbon furnace or from a platform inserted into the tube. When platform atomisation was used a more thorough atomisation was achieved by the addition of an excess of Ni to act as a matrix modifier. The transient absorption signal produced in the analysis can be evaluated in two ways, by measuring either the maximum height of this analyte peak or the integrated area under the peak. Generally the latter form of data analysis was used but peak height was used in the interpretation of Rh data and Au data generated from wall atomisation. Wall atomisation was used in the analysis of the solutions for Au described in Section 5.3 and platform atomisation with peak integration was used for solutions of Sections 5.4 and 5.5.

ED-XRF was used to identify (non-quantitatively) the presence of precious metals in any precipitate that did not pass from suspension in the raffinate into the organic solution. In a couple of these rare instances, the precipitate was collected, filtered using a Hirsch funnel away from the residual organic and aqueous solutions and subsequently dried. The filter paper was then attached, precipitate-down, to a hollow cylindrical adapter using a sheet of mylar-film and an O-ring. Since the instrument was used in a non-quantitative manner, no attempt at calibration was made, rather the spectrum from each precipitate was compared to the one derived from a control filter paper (one that had been used to filter 25 ml deionised water). A silver filter was used in the primary x-ray beam to maximise the peak to background ratio of the elements of interest. ED-XRF is briefly described in Chapter 4.

5.3 Optimisation of a solvent extraction method.

A standard solvent extraction procedure involves labilisation (by heating a sample solution of specified acidity with a solution of a labilising agent of known concentration), complexation (by heating this solution with a complexing agent of known concentration) and extraction (by thoroughly and intimately mixing this solution with a specified volume of organic solvent). Values of the above parameters used in initial experiments were as follows:[4] 25 ml of a 10% aqua regia solution containing 0.1 M $SnCl_2$ (0.474 g/25 ml) was heated to boiling for 10-15 minutes. After cooling, 3 ml of 0.01 M TPP in acetone was added to this solution and the mixture was heated to boiling for a further 5-8 minutes. After cooling, this mixture was shaken vigorously with 25 ml DCE for 10 minutes.

To optimise the solvent extraction procedure, the following variables were examined: acidity of solution, concentration of $SnCl_2$, reaction time for complex formation and duration of shaking. By using equal volumes of aqueous and organic solvents optimal mixing was achieved with no dilution problems. Previous workers have advised heating the reaction mixture to boiling in both instances and that 10 minutes is sufficient for the first heating step (e.g. Seeverens et al., 1983). A 0.01 M solution of TPP was successfully used by Seeverens et al. (1983). TPP was selected in preference to DPTU on the basis of some preliminary studies (further comparison of the two complexing agents will be made in Section 5.4). Bearing in mind the results of Vorob'eva et al. (1974) (Section 5.1.1.2) acetone was used as the carrier of the complexing agent (TPP) into aqueous solution. DCE was used as the extractant following the lead of Mojski (1980) and Seeverens et al. (1983) (further comparison of extracting solvents will be made in Section 5.4). When one parameter was altered, the others remained at the initial values defined above.

The basic procedure involved the following steps:

1. Weigh out $SnCl_2$ into a beaker and add 25 ml sample solution (made up in aqua regia).
2. Cover the beaker with watchglass and place on hotplate for 10 minutes.
3. Dissolve the required mass of TPP in acetone.

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[4] Preliminary studies indicated that complexing with TPP offered higher PGE recovery than complexing with DPTU.

4. Pipette 3 ml of this acetone solution to the sample in the beaker.
5. Cover the beaker and return to hotplate.
6. Transfer the contents of the beaker to a separating funnel (100 ml).
7. Rinse out the beaker with 25 ml DCE into the separating funnel.
8. Shake the separating funnel containing the immiscible liquids.
9. Allow the two liquid phases to separate and decant both organic extract and aqueous raffinate.[5]
10. Analyse solutions by GFAAS.

Usually, the $SnCl_2$ would dissolve in the acidified solution before the beaker could be placed onto the hotplate, however a quick swirl of the beaker was sometimes necessary to ensure full dissolution before heating. A white or pale yellow (the colour depending upon the solution composition) emulsion formed upon addition of the complexing agent. This emulsion became thinner upon heating. The precipitate contained in this emulsion passed from aqueous to organic solution during shaking, resulting in a finely misty extract and a clear raffinate.

The standard procedure developed is detailed in Section 5.4.1. Optimisation of and variations to these steps are detailed in the following sections, each of the optimised variables is considered in turn.

5.3.1 Test solutions.

Two solutions were prepared from Spectrosol AAS standard solutions (1000 μg/ml) for use in the optimisation of the solvent extraction procedure. The first contained just Pt and Au acidified with aqua regia to test the effectiveness of extraction of these two

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[5] Only the first 15-20 ml of the extract and the last 15-20 ml of the raffinate were collected for analysis to avoid contamination of aliquots of either layer by the other or by interlayer deposits. The remainder of the extract and the raffinate were discarded unless any precipitate caught at the solvent interface was required for further analysis.

elements. The second contained Fe, Ni and Cu at ratios likely to be found in leaches of natural geological samples,[6] in addition to Pt and Au, to identify changes in extraction efficiency caused by the presence of high concentrations of matrix elements and to test the selectivity of the procedure. In the following sections, the first solution will be referred to as the matrix-free solution and the second as the matrix-matched solution.

Table 5.1. Concentration of solutions prepared for use in the optimisation of the method

Element	Volume of stock solution (diluted to 50 ml)	solution concentration (μg/ml)	Approximate concentration in CHR-C leach (μg/ml)
Au	1 ml of a 200 μl/50 ml dilution	0.08	0.8
Pt	20 μl	0.4	4.5
Cu	600 μl	12	150
Ni	5 ml	100	800
Fe	25 ml*	500	5500

* when large volumes of the second solution were being prepared, the Fe component was prepared by dissolving 203.8 g of Fe foil (99.5%) in a minimum volume of HCl and diluting to 10 ml. 5 ml of this more concentrated solution (20 g/ml) was then added to a 200 ml volumetric flask and the other aliquots were increased pro rata.

The concentration of Pt and Au was selected to enable determination of both elements without further dilution. The solutions were prepared by pipetting the volume of stock solution detailed in Table 5.1 into a 50 ml volumetric flask acidified with 7.5 ml Analar HCl and 2.5 ml Analar HNO_3 (to represent 20% "aqua regia") and diluting to volume with deionised water.

5.3.2 Acidity of analyte solutions.

A number of solution characteristics must be evaluated before successful solvent extraction can be achieved. Complex lability and subsequent reaction kinetics have been mentioned above, but extraction efficiency is also dependent upon solution acidity. Indeed, Seeverens et al. (1983), complexing with 0.01 M TPP and extracting into DCE, reported 75% recovery of Au from 1 M HCl but only 10% recovery from 8 M HCl. They

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[6] Approximate concentrations were determined from a semi-quantitative analysis by ICP-MS of a leach from 10 g of CHR-C with 20 ml aqua regia, as described in Chapter 4.

also reported 30% recovery of Rh from 4 M HCl but 80% recovery from 8 M HCl. Mojski (1980), however, reported quantitative recovery of Rh from 1 to 6 M HCl using a higher concentration of TPP (0.1 M).

Test solutions were prepared containing Pt and Au as described in Section 5.3.1 but having aqua regia concentrations of 0%, 2%, 4%, 10%, 20% and 40%. These solutions will be referred to respectively as AR0, AR2, AR4, AR10, AR20 and AR40. In a second experiment, test solutions were prepared containing Pt, Au, Cu, Ni and Fe as described in Section 5.3.1 (using the Fe foil standard) but having aqua regia concentrations of 2%, 10% and 20% (results from the first experiment permitted the use of fewer samples covering a smaller aqua regia concentration range). These solutions will be referred to respectively as AR2m, AR10m and AR20m.

5.3.2.1 Results and observations.

Results from the atomic absorption analyses of the extracts and raffinates are tabulated in Table 5.2. Both the analyte elements (Au and Pt) are sensitive to the concentration of aqua regia in solution (indicated by the variation in intensity of the absorbance signals of the initial solutions (INIT) with different aqua regia concentrations). The absorbances of the extracts and raffinates were, therefore, normalised to the absorbance of the respective initial starting solution to allow comparison between the samples of the degree of extraction. Further comparison of the data (e.g. calculation of a distribution coefficient without calibration) is not possible due to differences in the thermal atomisation programmes used in the analysis of the aqueous and organic solutions.

Table 5.2. Absorbance readings of test solutions of different acidity, their raffinates and extracts (Pt and Au only).

Element	matrix-free solution					matrix-matched solution				
aqua regia conc.	blank subtracted absorbance			absorbance normalised to INIT		blank subtracted absorbance			absorbance normalised to INIT	
	INIT	AQ	ORG	AQ	ORG	INIT	AQ	ORG	AQ	ORG
Pt										
0%	113	6	0	5.3	0	-	-	-	-	-
2%	126	20	0	16	0	129	16	51	12	40
4%	164	5	58	3	35	-	-	-	-	-
10%	183	9	143	5	78	180	0	160	0	89
20%	220	53	164	24	75	180	43	144	24	80
40%	255	72	141	28	55	-	-	-	-	-
Au										
0%	902	0	0	0	0	-	-	-	-	-
2%	792	21	14	3	2	394	46	291	12	74
4%	765	30	123	4	16	-	-	-	-	-
10%	1612	69	121	4	8	247	0	196	0	79
20%	1269	0	261	0	21	2114	0	551	0	26
40%	1156	0	758	0	66	-	-	-	-	-

A value of zero indicates that the absorbance was indistinguishable from blank analyses.
The absorbances have been normalised to the absorbance of the initial solution (INIT) to account for the different effects of the acids on the atomisation and/or absorption and allow comparison of the degree of extraction between samples of different acidity. These values, expressed as percentages represent the proportion of the analyte extracted.

Extraction of Pt was most efficient from AR10. A substantial extraction is observed from AR20, but both this sample and AR40 have rather large raffinate absorbances caused by analyte that had remained in the aqueous layer. The pattern of Pt extraction from the matrix-matched solutions copies and enforces that observed from the matrix-free solutions.

Extraction of Au appeared to be favoured by high acid concentration and at concentrations of aqua regia less than 40%, there did appear to be a loss of Au, perhaps in the solvent extraction procedure or, more likely, during thermal pretreatment in the graphite furnace prior to atomisation.[7] Data from the extracts show a reasonable extraction independent of acidity, the low relative absorbance probably being attributable to the very high absorbance of the initial solution.

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[7] The atomisation temperature used in the determination of Au was 1600 °C, subsequent work suggested that the atomisation temperature should be higher than this, closer to 2000°C (Section 6.2.1.2). It is suggested that the increased concentration of chloride ions somehow increased the volatility of Au such that a strong AA signal was observed for solutions with the higher acid concentrations and solutions with lower concentrations of aqua regia suffered premature loss of analyte.

It can be seen that the optimum aqua regia concentration for the extraction of Pt is 10% and for Au is 40%. However, extracts generated by the procedure described in Chapter 4 result in 20% aqua regia solutions. It can be inferred that there will be a reasonable level of extraction of the precious metals from these 20% aqua regia solutions because, within analytical limitations, the extraction of Pt and Au from the 20% aqua regia solutions do not differ widely from the optimum concentrations identified above: the extraction of Pt from AR20 was 96% of that from AR10 and the extraction of Au from AR20 was 32% of that from AR40.

After separation, all the matrix-free solution samples except the non-acidified (AR0) and least acidified (AR2) showed a clear raffinate and a slightly misty extract, indicating that there was good separation of the phases and good extraction of the precious metal complexes into DCE. A white interlayer deposit formed at the solvent interface of AR2 (perhaps indicating that a species of precious metal complex had formed but the precipitate had not passed into the DCE). The raffinate of AR0 appeared cloudy, containing a fine emulsion (persisting from a phase that would not fully dissolve after the first heating step) and the extract was clear, indicating that no significant extraction of precious metal complexes had occurred. Sample AR20m changed to a dark translucent yellow colour after the first heating step and this solution develops a coagulating white precipitate as expected at the second heating step. The colour was simply an artefact of the high concentration of matrix elements and did not appear to affect the extraction of the precious metals. These observations corroborate the conclusions inferred from the results in Table 5.2.

5.3.2.2 Interlayer precipitate at solvent interface.

In a separate experiment, four solutions were prepared, two containing Pt (8 μg/ml) and two containing Au (0.8 μg/ml) . One of each of these solutions was prepared in

20% aqua regia and the other in 2% aqua regia. These samples will be referred to as PT20, PT2, AU20 and AU2, respectively. The solvent extraction procedure described above was applied to all four of the solutions in duplicate.

After addition of a TPP solution in acetone, a white precipitate formed in all the beakers except PT2, the precipitates from which were pale orange. The raffinates and extracts of AU2 were colourless compared to those of AU20, which were slightly misty white and pale yellow, respectively. Raffinates and extracts of PT20 resembled those of AU20, but those of PT2 were pale orange with traces of a fine precipitate. The mixtures were left overnight to settle. All the raffinates were then observed to be colourless except those of PT2 which contained a pale orange suspension that was slowly settling. The extracts of PT20 and AU20 were both pale yellow as expected. The extracts and raffinates were analysed by GFAAS to identify the degrees of extraction of the analyte from each solution. The results of these analyses and of the XRF analyses described below are tabulated in Table 5.3.

Table 5.3. Absorbance readings of raffinates and extracts of test solutions of different acidity and XRF peaks from interlayer precipitates and/or raffinate suspensions to identify the loss/non-extraction of analyte element.

Sample	AQ	ORG	peaks identified from XRF spectra
Blank	-	-	Zn Cl
AU2	18	4450	Zn Cl Sn
AU20	11	10800	-
PT2	417	0	Zn Cl Sn Pt
PT20	329	2140	-

The solid deposits from the raffinates of PT2 and AU2 were filtered off and analysed by ED-XRF as described in Section 5.2. The peaks identified from x-ray spectra are shown in Table 5.3. The spectra of blank filter paper and mylar-film showed strong peaks for Cl and Zn (both of which are known to be present in the mylar-film). The spectra of deposits from AU2 showed strong peaks for Sn, in addition to Zn and Cl, indicating that the deposit is an insoluble Sn species. The spectra of deposits from PT2 showed strong peaks for both Pt and Sn, in addition to Zn and Cl, indicating that the precipitate contained both these elements in relatively high concentrations. These results concurred with analyses of the raffinates which showed quantitative recovery of the analyte elements from AU2 but not from PT2.

These results indicated that some of the Pt was still bound up with the $SnCl_2$ in the precipitate and was not extracted into the DCE as expected. Therefore, the orange precipitate formed upon the addition of TPP may not have been the conventional $PtCl_n(SnCl_3)_m$ complex, as proposed by Mojski (1980), but may exhibit a different form of Pt/$SnCl_2$ association, which does not contain the labile $SnCl_3^-$ ligand that enables formation of the extractable Pt/TPP species.

It is concluded from these observations that the presence of any insoluble material in either the raffinate or the extract may directly result in a loss of the analyte element from solution, such that the total concentration of analyte determined in the raffinate and extract is, in fact, less than the concentration of analyte determined in the initial solution. This conclusion helps to explain the low recoveries of Pt and Au observed for solutions AR0 and AR2 (Section 5.3.2.1).

5.3.3 Concentration of tin (II) chloride labilising agent.

The presence of a labilising agent has been found to be beneficial for efficient extraction of the precious metals. The role of $SnCl_2$ in labilising the precious metal complexes has been documented previously, but the optimum concentration of $SnCl_2$ required is unknown. It is necessary to add a small excess of labilising agent to sample solutions, but too much $SnCl_2$ may cause problems in the extraction stages. Test solutions were prepared as described in Section 5.3.1, and were made up with $SnCl_2$ concentrations of 0.025 M (matrix-free solution only), 0.05M, 0.1 M and 0.2M.

5.3.3.1 Results.

Absorbances of the solutions, their raffinates and extracts are shown in Table 5.4. The extraction of Pt and Au from the matrix-matched solution was attempted twice. Both sets of results are reported but low results were obtained for Au in the first experiment. The reason for these low results was because a too low atomisation temperature was selected (1600 °C as advised in the instrument manufacturer's handbook). The second set of results were obtained with atomisation at a higher temperature (2300 °C).

Table 5.4. Absorbance readings of test solutions of different labilising agent concentrations, their raffinates and extracts (Blank subtracted absorbance readings of Pt and Au only).

Element	matrix-free solution			matrix-matched solution				
concentration of $SnCl_2$	AQ	ORG	proportion extracted	AQ	ORG	AQ	ORG	proportion extracted *
Pt								
INIT	173			185		180		
0.025M	0	124	72%	-	-	-	-	-
0.05M	0	138	80%	5	189	3	194	105%
0.1M	0	155	90%	2	176	0	160	92%
0.2M	3	142	82%	12	171	2	165	92%
Au								
INIT	966			12**		247		
0.025M	1	265	27%	-	-	-	-	-
0.05M	18	304	31%	0	355	0	465	188%
0.1M	49	202	21%	0	215	0	196	79%
0.2M	85	169	17%	0	85	4	251	102%

A value of zero indicates that the absorbance was indistinguishable from blank analyses.
* the proportions presented for Pt was calculated as the mean from both analyses, but the proportions presented for Au were calculated only from the second analysis. ** see text.
As all these solutions were in 10% aqua regia, it was not necessary to normalise data against the initial solution absorbance (INIT) as was done in Table 5.2.

Analyses of the raffinates and extracts show good Pt extraction and, from the extract, arguably favouring a $SnCl_2$ concentration of 0.1 M in the matrix-free solution and 0.05 M in the matrix-matched solution. Analyses of the raffinate show good Au extraction from the matrix-matched solution, extraction of Au from the matrix-free solution, however, seems to be inversely proportional to the concentration of $SnCl_2$. Analyses of the extracts from both solutions indicated that a higher concentration of $SnCl_2$ hindered the extraction of Au.

The optimum concentration of $SnCl_2$ for the extraction of Pt was between 0.05 M and

0.1 M and for Au was ≤0.05 M, leading to the conclusion that the optimum concentration of the labilising agent was 0.05 M. However, because quantitative extraction of the other PGE (except Pd) is more dependent upon the presence of higher concentrations $SnCl_2$ (Mojski, 1980), it would be prudent to follow the lead of Mojski (1980) and Seeverens et al. (1983) and use 0.1 M $SnCl_2$ in the standard procedure.

5.3.4 Reaction time for complex formation.

Complete reaction of precious metals with the complexing agent is the most critical step in promoting their quantitative extraction into an organic solvent. Consequently, it is important that the second heating stage should be sufficiently long to allow formation of the extractable complex. A matrix-free solution containing Pt and Au in 10% aqua regia was prepared as detailed in Section 5.3.1. The beakers were left simmering on the hotplate for 7, 14 and 24 minutes.

5.3.4.1 Results.

Absorbances of the solutions, their raffinates and extracts are shown in Table 5.5. The raffinates were not analysed for Au because no Au was detected in the initial solution, due to the lower atomisation temperature used.[8]

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[8] The Au-TPP species seems to have been released at a lower temperature. It was not realised at the time of the experiment that an increase in the atomisation temperature might result in a detectable absorbance signal.

Table 5.5. Absorbance readings of test solutions of different labilising agent concentrations, their raffinates and extracts (Blank subtracted absorbance readings of Pt and Au only).

Element	matrix-free solution		
duration of heating	AQ	ORG	proportion extracted
Pt			
INIT	140		
7 min	109	98	70%
14 min	142	66	47%
24 min	142	60	43%
Au			
INIT	-		
7 min	-	1044	-
14 min	-	1234	-
24 min	-	1098	-

A value of zero indicates that the absorbance was indistinguishable from blank analyses.
As all these solutions were in 10% aqua regia, it was not necessary to normalise data against the initial solution absorbance (INIT) as was done in Table 5.2.

Raffinate analyses for Pt appeared to show that the extraction was unsuccessful, perhaps due to incomplete formation of a sufficiently Pt complex species. However, the extract analyses showed that there was no benefit in heating beyond 7 minutes and to heat for longer than this time was detrimental to Pt recovery. A heating time of 5 minutes as suggested by Seeverens et al. (1983) should, therefore, be ideal for optimal complex formation.

5.3.5 Duration of shaking immiscible liquids.

It was important to keep the time spent shaking the immiscible liquids to a minimum, whilst ensuring that quantitative extraction of precious metals into organic solution occurred. Additionally, extended shaking may increase the chance of transfer of some of the concomitant matrix elements, from which the precious metals were to be separated. Test solutions were prepared as detailed in Section 5.3.1. Different aliquots of the matrix-free solutions were shaken for periods of 150 shakes,[9] 1, 5 or 10 minutes and the matrix-matched solution for periods of 2, 5 or 10 minutes.

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[9] It was intended to use just 100 shakes as the minimum trial, but after this short time, the raffinate was decidedly cloudy (indicating that the extraction was not yet complete), so a further 50 shakes were administered.

5.3.5.1 Results.

Absorbances of the solutions, their raffinates and extracts are shown in Table 5.6. The extraction of Pt and Au from the matrix-matched solution was attempted twice, the first time very low results were obtained for Au (see footnote 7), both sets of results are reported for Pt.

Table 5.6. Absorbance readings of test solutions, their raffinates and extracts after different amounts of shaking (Blank subtracted absorbance readings of Pt and Au only).

Element	matrix-free solution			matrix-matched solution				
Shaking duration	AQ	ORG	proportion extracted	AQ	ORG	AQ	ORG	proportion extracted *
Pt								
INIT	347			185		180		
150 shakes	2	119	34%	-	-	-	-	-
1 min	0	123	35%	-	-	-	-	-
2 min	-	-	-	0	170	4	181	96%
5 min	2	115	33%	2	176	0	160	92%
10 min	1	155	45%	0	173	5	185	98%
Au								
INIT	966			12		247		
150 shakes	49	204	21%	-	-	-	-	-
1 min	36	189	20%	-	-	-	-	-
2 min	-	-	-	0	238	0	244	99%
5 min	31	234	24%	0	215	0	196	79%
10 min	50	202	21%	0	183	0	292	118%

A value of zero indicates that the absorbance was indistinguishable from blank analyses.

* the proportions presented for Pt were calculated as the mean from both analyses, but the proportions presented for Au were calculated only from the second analysis.

As all these solutions were in 10% aqua regia, it was not necessary to normalise data against the initial solution absorbance (INIT) as was done in Table 5.2.

Data for the extraction of Pt show that there was near-quantitative extraction after just 1 minute. There was no discernible increase in extraction from the matrix-matched solution with extended shaking, and only slight, if any, increase in extraction from the matrix-free solution. Although extraction from the matrix-free solution was not as efficient for Au, there was again little change in the extent of extraction after the first minute.

The optimum extraction time was 1 minute, but to allow for the potentially slower transfer rate of the other PGE complexes into organic solution, it is suggested that the shaking should be extended to 2 minutes.

5.3.6 Conclusions.

The optimal extraction method would involve labilising a solution (20% "aqua regia") with $SnCl_2$ at a concentration of 0.1 M, selective complexation with a complexing agent enhanced by heating for 5 minutes and extraction into an organic solvent, by shaking the immiscible liquids vigorously for 2 minutes.

During use of this procedure it will be noticed that $SnCl_2$ dissolves entirely in the acidified solutions generated by the aqua regia leach method (Chapter 4). Addition of a solution of the complexing agent in acetone to the labilised sample solution usually results in the formation of a fine white suspension that settles to the bottom of the beaker during heating. This precipitate is the PGE/complexing agent complex, the formation of which was described in Section 5.1.1.2. The precipitate is insoluble in aqueous media but soluble in certain organic solvents. It should, therefore, be noticed that the precipitate will pass out of the aqueous layer into the organic layer during the shaking of the separating funnel, and subsequently dissolve in that solvent. The path of the PGE through this reaction scheme is summarised in the following sequence.

PGE in aqueous solution
[add $SnCl_2$
labilised $PGE(Cl)(SnCl_3)$ complex in aqueous solution
[add TPP/DPTU in acetone
organic PGE(Cl)(TPP/DPTU) complex, precipitate in aqueous phase
[shake with organic solvent
organic PGE(Cl)(TPP/DPTU) complex in the organic solvent

5.4 Choice of complexing agent and extracting solvent.

In the way that the physical parameters of the procedure require optimisation (detailed in Section 5.3) so do the chemical parameters. Preliminary studies indicated that complexing with TPP, rather than DPTU, and extracting into DCE offered the more efficient PGE recovery. Even if this combination did not provide quantitative extraction, the use of one method throughout Section 5.3 enabled comparison of the effects of altering the specified variables.

The following experiments were carried out to identify which combination of complexing agent and organic solvent offered the most complete extraction of each of the precious metals and to get a feel for the use of aqueous standards in the analysis of organic solutions.[10] The extraction efficiencies of TPP and DPTU were compared by extraction into DCE and chloroform. Thus for each element, there were four extractions, all 4 of which were performed in duplicate. This scheme is summarised in Table 5.7.

5.4.1 Experimental.

During these tests, all solutions contained just one of the precious metal elements in 20% aqua regia. Aldrich atomic absorption standard solutions were used as the stock solution for Ir (800 μg/ml), Ru (560 μg/ml), Rh (80 μg/ml), Pd (80 μg/ml) and Spectrosol atomic absorption standard solutions were used for Au (240 μg/ml) and Pt (1600 μg/ml). The solutions containing Pt and Ru were respectively diluted x $\frac{3}{10}$ (480 μg/ml Pt) and x4 (140 μg/ml Ru) to allow analysis in the linear calibration range of the spectrometer (see Chapter 6). The height of the absorption peak was measured to represent the magnitude of the analytical signal in the determination of Rh and the integrated peak area was measured in the determination of the other elements (peak height measurement in the determination of Ru was suggested in the manufacturer's handbook, but the measurement of peak area was found to give more reproducible results for these solutions).

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[10] A different atomisation mechanism could be expected due to the difference between the aqueous and organic complex species present in the furnace after thermal pretreatment. Thus a different thermal atomisation programme might be required in the analysis of organic solutions.

A standard procedure was followed, based upon the criteria discussed in the previous section. Acids were dispensed from teflon dispensers incorporating ruby-ball valves, the standard solutions from hand pipettes. Acetone and chloroform were dispensed from a measuring cylinder and DCE from a tilt pipette.

1. The 20% aqua regia solutions were prepared with 12.5 ml HNO_3 and 37.5 ml HCl and dilution to 250 ml using deionised water in a graduated flask containing one analyte from: Pt (400 µl), Pd (20 µl), Au (60 µl), Ru (140 µl), Rh (20 µl) or Ir (200 µl).
2. Weigh out 0.474 g $SnCl_2$ into eight beakers.
3. Add 25 ml of the solution prepared in step 1.
4. Cover the beakers and place on hotplate for 10 minutes (solution temperature: 85-95°C).
5. Remove beakers and allow to cool.
6. Weigh out 0.3428 g DPTU and 0.3926 g TPP into two clean beakers.[11]
7. Add 15 ml acetone to beaker containing TPP and, immediately after all the powder has dissolved, add 3 ml aliquots of this solution to each of four of the beakers from step 5. (Beakers 1, 2, 5 & 6).
8. Repeat step 7, using DPTU instead of TPP. (Beakers 3, 4, 7 & 8).
9. Return all eight beakers to the hotplate for a further 5 minutes (solution temperature: 89-95°C).
10. Remove beakers and allow to cool.
11. Transfer the contents of each beaker to a separating funnel and twice rinse out the beaker with a total of 25 ml organic solvent. DCE was added to four of the separating funnels (1, 2, 3 & 4) and chloroform to the remaining four (5, 6, 7 & 8).
12. Vigorously shake each duplicate pair of separating funnels for 2 minutes.

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[11] Although Seeverens et al. (1983) advised the use of 0.01 M solutions, Mojski (1980) used 0.1 M TPP in acetone. Because it was necessary to have excess complexing agent, the more concentrated solutions (0.1 M) were prepared and used for these experiments, as described earlier in this chapter.

13. Allow to separate and decant extracts and raffinates into numbered test tubes.
14. Analyse solutions by GFAAS.

Table 5.7. Complexing agent and solvent used in each of the beakers in these experiments.

	Complexing agent	Solvent
Beaker 1	TPP	DCE
Beaker 2	TPP	DCE
Beaker 3	DPTU	DCE
Beaker 4	DPTU	DCE
Beaker 5	TPP	chloroform
Beaker 6	TPP	chloroform
Beaker 7	DPTU	chloroform
Beaker 8	DPTU	chloroform

All the raffinates were run immediately after the initial solutions, followed by the DCE extracts then the chloroform extracts. Analysis of the solutions was performed in duplicate. Disagreement between these duplicates prompted reanalysis of both duplicate sample raffinates or extracts immediately after the first full analytical run of solutions in the particular solvent. The initial solution was analysed after every four raffinates to permit drift correction if necessary. Drift correction over the organic analyses was accomplished by reanalysing the first analysed extract after the other three and comparing the absorbance values. Memory effects were investigated by analysing blank aliquots of the relevant solvent before, during and after the analyte aliquots.

5.4.1.1 Evaporation concentration.

The increased volatility of the organic solvents, compared to aqueous media, gave rise to concern that samples at the end of an analytical run would suffer a degree of concentration due to evaporation of the solvent at room temperature. To test the effects of this, a PTFE sample cup containing 2 ml of chloroform was placed on a balance at room temperature (21 °C). It was found that there was about 15% decrease in mass due to evaporation in 30 minutes (the approximate time for one analytical run). Consequently, concentration of the analyte in solution through evaporation may have significant influence on the results and should be compensated by the implementation of a correction for drift in the analytical results. The boiling point of DCE (83 °C) is higher than that of chloroform (61 °C), so no test was done to quantify its volatility, but attention was paid to the possibility that significant concentration of analyte could also occur in these solutions by evaporation of solvent.

5.4.1.2 Matrix modification for Au analyses.

To aid the atomisation of Au in the AAS, Ni was added to the graphite furnace in aqueous solution (the use and need for a matrix modifier in the analysis of Au will be further discussed in Chapter 6). Whereas this is ideal for analysis of the raffinates, the addition of an aqueous matrix modifier to the organic extracts may be problematic. Although there would obviously be no mixing of the matrix modifier and analyte solutions, both Ni and Au species will be present in salt form on the furnace platform after drying. This association should be sufficient to facilitate the atomisation of Au. The main problem might be that the denser, lower boiling solvent would boil off (potentially vigorously) before the water adjacent to it, which could potentially cause dissipation of the aqueous solution down the furnace away from the dried analyte species. This problem was largely alleviated by slow drying of the sample to minimise perturbance on the platform and the fact that most of the solvent will have evaporated during the 30 seconds or so required to add the aqueous modifier solution.

5.4.2 Observations and results.

Generally, after shaking the separating funnels, both extract and raffinate of the TPP solutions were colourless and those of DPTU were colourless-to-very pale translucent yellow in colour, the colour of the extract being more intense than that of the raffinate.

The ground glass joints were coated in a silicon-based vacuum grease to ensure a seal and to allow easy turning of the taps. Whereas this grease was ideal for aqueous solutions, a problem was encountered with chloroform solutions. Either chloroform tended to dissolve the grease, or it was sufficiently non-viscous (0.58 relative to water at 20°C) that it was able to seep out of the funnel past the joint and down the exit tube. However, it was judged that these losses were minimal and should not effect the interpretation of the results.

Table 5.8 shows the absorbances of the initial solutions, the eight raffinates (four in duplicate) and the eight extracts. Since the same initial solution was used for each of the different extraction combinations, no normalisation to this initial value was strictly necessary, except for Ir, whose extracts and raffinates were run in different tubes. The tabulated normalised values allow a crude comparison of the degrees of extraction of each of the elements. Results for each of the elements will be considered in turn.

Platinum: The second DPTU/DCE experiment had a brown suspension in a clear solution and resulted in a deep orange coloured extract. These observations may have heralded a peculiar result. Analysis, however, showed no difference between duplicate extracts. All eight samples showed a good extraction, the only discrepancy being one high raffinate value from the first extract of DPTU into chloroform. The low value recorded from this sample cannot be explained by any observation noted during the experiment and probably indicated poor extraction from this particular sample.

In summary, complexation with both TPP and DPTU resulted in good extraction from 20% aqua regia solutions into both DCE and chloroform and DCE was arguably the better extractant. The magnitude of the absorbances were greater from DCE solution compared to chloroform solution, as were those with analyte derived from complexes DPTU compared to TPP. The optimum extraction combination for Pt was, therefore, complexation with DPTU followed by extraction into DCE.

Table 5.8. Blank subtracted absorbance readings of single element test solutions, their raffinates and extracts using different extraction combinations. Raffinate and extract absorbances are normalised to the absorbance of the initial solution to allow comparison of relative extraction efficiencies between the elements.

Element	blank subtracted absorbance					absorbances normalised to ORIG				extent of extraction (from AQ)
extraction combination	ORIG	AQ1	ORG1	AQ2	ORG2	AQ1	ORG1	AQ2	ORG2	
Pt	532									
TPP/DCE		3	391	0	426	0.6	73	0.0	80	100%
DPTU/DCE •		4	460	2	466	0.8	86	0.4	88	99%
TPP/Chlfm		6	350	3	389	1.1	66	0.6	73	99%
DPTU/Chlfm		24	413	3	426	4.5	78	0.6	80	97%
Pd	217									
TPP/DCE •		39	209	35	198	18	96	16	91	83%
DPTU/DCE		34	219	44	233	16	101	20	107	82%
TPP/Chlfm		49	210	44	201	23	97	20	93	79%
DPTU/Chlfm		55	220	53	215	25	101	24	99	75%
Au	1670									
TPP/DCE ai		4	603	3	726	0.2	36	0.2	43	100%
TPP/DCE aii		5	685	4	939	0.3	41	0.2	56	100%
	840									
TPP/DCE		0	153	0	186	0.0	18	0.0	22	100%
DPTU/DCE •		7	739	3	776	0.8	88	0.4	92	99%
TPP/Chlfm		16	45	2	258	1.9	5	0.2	31	99%
DPTU/Chlfm		8	93	4	404	1.0	11	0.5	48	99%
Ru	1040									
TPP/DCE		796	203	820	203	77	20	79	20	22%
DPTU/DCE •		476	453	464	460	46	44	45	44	55%
TPP/Chlfm		856	200	788	178	82	19	76	17	21%
DPTU/Chlfm		516	373	560	377	50	36	54	36	48%
Rh	618									
TPP/DCE		18	569	18	567	2.9	92	2.9	92	97%
DPTU/DCE •		2	637	5	636	0.3	103	0.8	103	99%
TPP/Chlfm		18	587	21	563	2.9	95	3.4	91	97%
DPTU/Chlfm		4	569	1	575	0.6	92	0.2	93	100%
Ir	165 (re: aqueous)/151 (re: DCE)/237 (re: chloroform)									
TPP/DCE •		16	138	22	147	10	91	13	97	88%
DPTU/DCE		95	79	73	98	58	52	44	65	49%
TPP/Chlfm		26	183	72	106	16	77	44	45	70%
DPTU/Chlfm		80	66	71	77	48	28	43	32	54%

A value of zero indicates that the absorbance was indistinguishable from blank analyses.
• signifies optimum extraction combination for each element.

Palladium: A white precipitate formed upon addition of acetonic DPTU to the first DCE extract sample, the other DPTU extracts developed a yellow precipitate that turned brown upon heating and settled in the beaker. This difference was not reflected in the analytical results, except there was the possibility of a slight loss of Pd from the first DPTU extract into DCE. All combinations produced about 80% extraction although there was slightly better extraction after complexation with TPP compared to DPTU and DCE compared to chloroform. These low extractions may be in part due to partial reduction of Pd by $SnCl_2$, as suggested by Vorob'eva et al. (1974). The extraction efficiency of Pd may be increased by missing out either the first or both heating stages of the procedure. The optimum extraction combination for Pd is complexation with TPP followed by extraction into DCE.

Gold: The solution of $SnCl_2$ that became the first TPP/chloroform extract was the only one not to boil during then first heating step. This observation may account for this sample's larger raffinate absorbance and lower extract absorbance than its duplicate, but there did appears to be severe loss of Au from this sample. That this loss of Au may have been due to reduction the metal seemed unlikely as it was more probable that the solutions that boiled would undergo reduction to a more significant extent. The first DPTU/chloroform extract was the only one not to form a white precipitate upon addition of the acetonic solution; a brown precipitate formed which turned yellow upon heating and an opaque orange material was observed at the solvent interface after shaking . This observation could explain the low extract absorbance tabulated for this sample, there being a loss of Au into the orange deposit.

The other six extractions worked well and there was good agreement between both duplicate DCE extracts. It is interesting to compare the results for TPP/DCE extractions with some earlier tests (also tabulated in Table 5.8; TPP/DCE ai and aii) which show the same pattern: good extraction but poor precision in DCE solution analyses. The relative values cannot be compared as the earlier analyses were made with twice the amount of matrix modifier.

The very different absorbance values for the extracts showed that more sensitive analyses (greater magnitude of absorbance reading) result when Au was in a DPTU complex species. There were no obvious optimum extraction conditions for Au, but sensitive and relatively precise analyses resulted when DPTU extraction into DCE was used.

Ruthenium: Observation of the reaction mixtures indicated that the solvent extraction of Ru should have been successful. It was, therefore, surprising to find high raffinate absorbance values. There was good agreement between all four duplicate extractions. DPTU offered significantly better extraction than TPP and the proportion of complexes extracted into DCE was slightly higher than into chloroform. The optimum extraction combination was, therefore, DPTU complexation followed by extraction into DCE.

Rhodium: The results for Rh were the most consistent of the elements examined. It was noticeable that none of the solutions actually boiled during either heating step. There was remarkable agreement within all four of the duplicate pairs. It can be seen that complexation with DPTU offered superior extraction compared to TPP and the use of DCE allowed more sensitive analysis than did chloroform. However, there was no discernible difference between the analyses of either solvent used for TPP complexes. In summary, the optimum extraction combination for Rh was DPTU complexation followed by extraction into DCE.

Iridium: Of the DPTU precipitates, only the second DCE extract had a white precipitate, the other three had brown precipitates that turned pale yellow upon heating. These latter three solutions and that of the second TPP/chloroform extraction were allowed to boil during the second heating step and in all five of the above samples there was a white deposit at the solvent interface after shaking. The presence of these deposits may account for the loss of some Ir. That the mixtures were allowed to boil may account for the unfavourable extraction observed for the respective four samples, particularly when it was considered that the duplicate extracts of the poorly extracted DPTU/DCE and TPP/chloroform, which did not boil, showed more efficient extractions.

TPP offered better extraction than DPTU and there was better extraction of both complexes into DCE compared to chloroform. The optimum extraction combination, although even this combination offered only 90% extraction, was complexation with TPP followed by extraction into DCE. The low extraction efficiency of Ir was not totally unexpected when it is considered that $SnCl_2$ complexes with Ir show the least labile character of all the PGE (Vorob'eva et al., 1974).

5.4.3 Conclusions.

If this solvent extraction procedure is to be used as part of an analytical scheme to determine just one element, then it would be most advisable to use the optimum extraction combination indicated above, i.e. DPTU complexation followed by extraction into DCE for Pt, Au, Ru or Rh and TPP/DCE for Pd or Ir. The common factor in these two methods is the use of DCE rather than chloroform. Although the choice is sometimes rather arbitrary, two other factors strengthen the argument for the use of DCE. The first is that DCE, being less volatile, is easier to use as a solvent in GFAAS analysis and the second is that DCE was not observed to have leaked past ground glass joints, as was observed for chloroform.

If the solvent extraction procedure is to be used as part of an analytical scheme in which all or a combination of the precious metals are to be determined it would be most advisable to use the DPTU/DCE extraction combination. This combination is preferred for four of the elements and produces about the same degree of extraction of Pd as observed with the TPP/DCE combination. For Ir, however, it is far less efficient, but does offer a significant degree of extraction.[12]

That the solutions should boil was detrimental to the extraction of Ir but possibly necessary for the extraction of Au. Despite the evidence that boiling promoted formation of the labile complexes (Mojski, 1980), boiling appeared not to be required for

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[12] The importance of Ir's poor recovery is rendered largely insignificant in this application when it is considered that Ir is so poorly extracted from geological samples by aqua regia (Section 4.5 or Section 7.2). Without modification, this sample preparation scheme is not suitable for the determination of Ir.

the extraction of Rh and did not affect the extraction of Pt, Pd or Ru. Consequently, unless the extraction of Ir is required, it would seem advisable to ensure that the solutions actually boil during the two heating steps of the procedure.

5.5 Application of the solvent extraction procedure to complex solutions.

Having identified the optimum extraction procedure on simple solutions, the DPTU/DCE procedure was then applied to more complex solutions. Three solutions were prepared containing Pt, Pd (0.4 µg/ml), Au (0.2 µg/ml), Rh, Ru and Ir (0.08 µg/ml) in 20% aqua regia. These analyte concentrations were chosen to be at levels that were representitative of geological matrices. Two of these solutions had added Cu, Ni, Fe and Mg. The concentrations of these matrix elements in one of the solutions was 10 µg/ml and the other 100 µg/ml, representing the range that may be recovered from aqua regia leaches of geological samples. These three samples will be referred to as PM0, PM1 and PM2 respectively. The precious metal solutions were prepared by dilution of Aldrich AAS standard solutions and the matrix elements from spectrosol standard solutions.

Seven leaches of geological materials were also prepared following the procedure described in Chapter 4. The seven samples had been well characterised for PGE and Au concentrations and represented a wide range of sulphide concentrations. The samples were: certified reference material (SARM 7), candidate reference material (CHR-Pt+), South African chromitite (14/75), and samples from Unst, Shetland (MR65, CMR292, RLM007, RLM008), the PGE concentrations of which had been determined by NiS fire assay/ICP-MS.[13] PTC-1 was also leached but the reaction of the powder with aqua regia was so violent that the mixture spilt out of the beaker and

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[13] Sample 14/75 was supplied by Rob Robért (Mintek, South Africa), MR65 and CMR 292 by Hazel Prichard (OU) and RLM007 and RLM008 by Richard Lord (OU).

an unknown quantity of the sample was lost, rendering the leach unusable. PTC-1 has a sulphide content of 24%, it is suggested that the observed effervescence was a result of the rapid formation and release of H_2S formed as a product of the action of aqua regia on the sulphides.

Procedural blanks.

The solvent extraction extraction procedure was also applied to a blank 20% aqua regia solution and to the same 20% aqua regia solutions that had been run as procedural blanks during the aqua regia leaches of the geological samples. The first of these solutions will be referred to as SE blank and the second as AR blank.

Analysis by GFAAS of the blank solutions, their raffinates and extracts showed no discernible peak above background for any element except Pd in the raffinates; there was no Pd detected in the corresponding extracts. Because analysis of the initial blank solution showed no Pd, some Pd contamination must have been picked up from the glassware or the graphite furnace. If the Pd was picked up in the beakers during the leach, then AR blank would contain Pd and SE blank would not, it can be seen from Table 5.9 that this was not the case, as both blanks were clean. If Pd was picked up during the solvent extraction, then the presence of Pd would be expected in the extracts, as the metal is easily extracted (Section 5.4.2). Pd could have been present in the four test tubes used to store the raffinates prior to analysis. The chance of these four test tubes being contaminated (presumably from the previous experiments, Section 5.4) and the four extract test tubes remaining clean was very remote. It is most likely, therefore, that the Pd was not picked up from the glass-ware but was, in fact, a memory effect due to the retention of Pd in the graphite furnace after each analysis. These analyses were made using a graphite furnace that had already been well used, its age and associated deterioration of the pyrocoating may have had unforseen implications leading to the occurrence of the observed memory effects.

Blank water samples run during the analysis of the initial solutions, PM0, PM1 and PM2, immediately before the analysis of the raffinates showed no sign of a Pd absorbance peak, whereas a blank water sample run after the raffinates showed a significant Pd absorbance peak above background. Drift correction standards analysed every six samples during the raffinate analysis run showed broad variability. The data set of the raffinate analyses was drift and blank corrected to arrive at the results tabulated in Tables 5.9 and 5.10. The upshot of this is that these Pd analyses from the raffinates are all subject to varying degrees of memory effects. The data is therefore, unsuitable for detailed analysis and can only be used to give a general indication of the extent of Pd extraction. The extracts were analysed the previous day and blank DCE aliquots analysed during the analytical run identified no memory effects.

5.5.1 Application to artificial solutions.

The SE blank and PM0 gave clear raffinates. The raffinates of PM1 and PM2 had a misty white colour and pale yellow extracts, except for the second duplicate of PM1 which was a pale yellow-brown. The fine white precipitates seemed to be caused by the presence of the matrix elements (precipitates were observed in single element solutions (Section 5.4) but, generally, no precipitates were observed in the raffinates). The difference in colours between the duplicate extracts of both PM1 and PM2 did not relate to any significant difference between duplicate analyses of the extracts. It was, however, noticeable that the second raffinate gave a larger absorbance peak than its duplicate for each of the matrix elements. Table 5.9 shows AAS absorbance values from analyses of PM0, PM1, PM2, their raffinates and extracts.

Table 5.9. Blank subtracted absorbance readings of multi-element test solutions, their raffinates and extracts using DPTU/DCE extraction. Raffinate absorbances are normalised to their respective initial solution absorbances. Extract absorbances are normalised to the absorbance of an analysis of PM0 run immediately before the extracts. Normalisation has been made to allow comparison of relative extraction efficiencies between the elements.

Element	blank subtracted absorbance					absorbances normalised to ORIG				extent of extraction (from AQ)
Sample	ORIG	AQ1	ORG1	AQ2	ORG2	AQ1	ORG1	AQ2	ORG2	
Pt	184 (re: organic)									
SE blank		1	1	0	0					
AR blank		2	0	0	0					
PM0	199	0	202	3	170	0	110	2	92	99%
PM1	188	21	181	17	180	11	98	9	98	90%
PM2	135	21	175	27	178	16	95	20	97	82%
Pd	239 (re: organic)									
SE blank		53	0	42	0					
AR blank		34	1	39	0					
PM0	155	45	458	56	269	29	192	36	113	67%
PM1	172	377	190	340	266	219	79	198	111	*
PM2	200	567	64	375	127	283	27	187	53	*
Au	890 (re: organic)									
SE blank		4	3	1	4					
AR blank		1	5	1	5					
PM0	819	0	900	57	675	0	140	7	105	97%
PM1	729	54	932	44	893	7	145	6	139	93%
PM2	282	29	947	12	911	10	148	4	142	93%
Ru	108 (re: organic)									
SE blank		0	2	0	1					
AR blank		0	0	0	0					
PM0	150	100	78	48	127	67	73	32	118	51%
PM1	131	76	100	74	107	58	93	56	99	43%
PM2	202	148	144	138	143	73	133	68	133	29%
Rh	509 (re: organic)									
SE blank		3	0	0	0					
AR blank		0	0	0	0					
PM0	680	20	718	46	670	3	141	7	132	95%
PM1	603	123	440	137	480	20	86	23	94	78%
PM2	776	240	462	201	481	31	91	26	94	72%
Cu										
PM1	251	208	-	277	-	83	-	110	-	3%
PM2	210	171	-	250	-	81	-	119	-	0%
Ni										
PM1	111	90	-	94	-	81	-	85	-	17%
PM2	69	70	-	89	-	101	-	129	-	*
Fe										
PM1	317	68	-	71	-	21	-	22	-	78%
PM2	114	32	-	77	-	28	-	68	-	52%
Mg										
PM1	81	100	-	74	-	123	-	91	-	*
PM2	8	0	-	32	-	0	-	400	-	*

A value of zero indicates that the absorbance was indistinguishable from blank analyses.
* indicates apparent enrichment of element in extract over initial solution! - see text.

The degree of extraction of all the precious metals from PM0 was very much the same as that observed for the single element solutions studied in Section 5.4. The only departure from this similarity was that Pd seemed to be more poorly extracted but, considering the blank and memory effect problems described above, the extraction may well have been more quantitative. Interpretation of the raffinate data indicated that, even considering of the differences in absorbances of the initial solutions due to matrix element interference in analysis, the presence of increasing amounts of matrix element· decreased the extraction efficiency of Pt (by 9-17%), Au (4%), Ru (8-22%) and Rh (17-23%). The data for Pd did not concur with this pattern and it would appear that, despite the blank problem, Pd extraction was severely hindered by the presence of matrix elements. Interpretation of the extract data led to the same conclusions as those arrived at from the raffinates except for Ru, for which there appeared to be better extraction with a higher concentration of matrix elements.

5.5.1.2 Co-extraction vs separation.

Samples PM1, PM2 and their raffinates were analysed for the determination of Cu, Ni, Fe and Mg to measure the degree of retention of these elements. Cu, Ni, Fe and results were based upon measurement of the height of the absorbance peak after atomisation from the furnace wall and Mg on the integrated area of the peak after platform atomisation. To determine these elements by GFAAS, PM1 had to be diluted x500 and PM2 by x5000. The determination of Mg required a further dilution x40. Bearing in mind the dilutions used in these analyses, the absorbances from both PM1 and PM2 should have been the same. It was, therefore, curious that the absorbances of PM2 were consistently lower than than those of PM1.

Determination of Mg in the deionised water used for the initial dilutions resulted in an absorbance of 220. Determination of Mg in a blank twice teflon distilled water sample, used for the final dilution, resulted in an absorbance of 142. Thus, the tabulated absorbances represent the additional Mg in solution detected above a large blank peak. The matrix element results gave only an indication of the tendency for their co-extraction, and,due to the high levels of Mg even in ultra-pure water, any information gleaned from the Mg data will have resulted in a particularly non-specific indication of the extent of Mg co-extraction.

Data from Table 5.9 indicated that Cu did not appear to be extracted to any significant extent, despite previous authors (e.g. Zolotov et al., 1978) suggesting that this is the one element that may be extracted. Ni appeared to have been extracted from PM1 but not from PM2. Bearing in mind the large differences between the absorbances of PM1 and PM2, this data may be subject to large errors and one might expect 10-20% extraction of Ni. There appeared to be significant extraction of Fe (up to 72% from PM2!) despite predictions to the contrary. Any conclusion regarding the extent of extraction of Mg from PM1 was overshadowed by the blank problem mentioned above and the Mg absorbance from PM2 was too close to the blank to allow any reasonable comparison of the raffinates with the initial solution.

5.5.2 Application to geological samples.

The extractions from the geological samples appeared to work well, each sample extraction forming a clear or pale yellow raffinate, except those of SARM 7, where the raffinate became a misty white and those of CHR-Pt+, which became a misty grey. The AR blank extracts turned from a misty white to colourless with time. The extracts of RLM008, MR65, CMR292, RLM007 and 14/75 were pale yellow in colour each developing a deeper shade of yellow with time, the extracts of RLM008 and MR65 were also very slightly misty. The extracts of SARM 7 and CHR-Pt+ were pale grey in colour, turning yellow (SARM 7) or a dirty brown colour (CHR-Pt+) with time. There was a dark green/brown interlayer deposit at the solvent interface of both the extracts of CHR-Pt+.

Table 5.10. Blank subtracted absorbance readings of sample leaches, their raffinates and extracts using DPTU/DCE extraction. Raffinate and extract absorbances are normalised to the absorbance of an analysis of PM0 run immediately before the full run of raffinates/extracts. Normalisation has been made to allow comparison of relative extraction efficiencies between the samples.

Element	blank subtracted absorbance					absorbances normalised to ORIG				average
Sample	ORIG	AQ1	ORG1	AQ2	ORG2	AQ1	ORG1	AQ2	ORG2	ORG/AQ
Pt	199 (re: aqueous); 184 (re: organic)									
AR blank		2	0	0	0					
RLM008		0	1	8	0	0	1	4	0	-
MR65		4	2	4	1	2	1	2	1	0.4
CMR292		6	5	6	5	3	3	3	3	0.9
RLM007		8	49	9	70	4	27	5	38	7.5
14/75		8	5	8	4	4	3	4	2	0.6
SARM7		4	40	5	53	2	22	3	29	11
CHR-Pt+		12	402	35	410	6	218	18	223	24
Pd	155 (re: aqueous); 239 (re: organic)									
AR blank		34	1	39	0					
RLM008		210	10	198	8	135	4	128	4	0.03
MR65		100	15	95	12	64	6	61	5	0.1
CMR292		61	95	57	72	40	40	37	30	0.9
RLM007		106	162	92	304	69	68	59	127	1.6
14/75		80	119	69	111	52	50	45	46	1.0
SARM7		109	141	111	80	70	59	72	34	0.7
CHR-Pt+		748	935	929	960	482	391	599	402	0.7
Au	819 (re: aqueous); 890 (re: organic)									
AR blank		1	5	1	5					
RLM008		28	54	70	13	3	8	9	2	1.4
MR65		11	21	5	28	1	3	1	4	4.8
CMR292		2	14	3	11	0	2	0	2	6.7
RLM007		37	61	42	114	5	9	5	18	2.8
14/75		5	33	2	31	1	5	0	5	14
SARM7		3	197	5	254	0	31	1	40	74
CHR-Pt+		32	2608	50	2816	4	407	6	439	88
Ru	150 (re: aqueous); 108 (re: organic)									
AR blank		0	0	0	0					
RLM008		117	13	186	13	78	12	124	12	0.1
MR65		101	8	112	6	68	7	75	6	0.1
CMR292		18	19	24	8	12	17	16	8	0.9
RLM007		265	94	241	102	176	87	160	95	0.5
14/75		18	35	18	33	12	32	12	30	2.7
SARM7		186	29	180	33	124	27	120	30	0.2
CHR-Pt+		453	1413	464	1469	302	1309	309	1360	4.4
Rh	680 (re: aqueous); 509 (re: organic)									
AR blank		0	0	0	0					
RLM008		6	0	57	0	1	0	8	0	0
MR65		14	0	24	0	2	0	4	0	0
CMR292		15	1	7	5	2	0	1	1	0.5
RLM007		5	78	3	87	1	15	0	17	30
14/75		19	180	12	186	3	35	2	37	17
SARM7		8	97	10	124	1	19	1	24	16
CHR-Pt+		44	638	61	663	6	125	9	130	17

A value of zero indicates that the absorbance was indistinguishable from blank analyses.

Table 5.10 shows AAS absorbance values from analysis of leaches of the seven samples detailed above, their raffinates and extracts. Simple comparison of extract and raffinate data showed high extraction of Pt, Au and Rh from geological samples. Ru extraction was more variable, sometimes being reasonable (14/75, CHR-Pt+) and sometimes poor (RLM008, CMR292, RLM007, SARM 7) and may be dependent upon the concentration of co-extracted matrix elements. Information regarding the extraction of Pd was obscured by high blank analyses and memory effects as described above. Generally the extraction of Pd, like Ru, was variable, reasonable in a few cases (RLM007, CHR-Pt+), poor in others (RLM008, MR65) and rendered indeterminable in the remainder due to the afore-mentioned memory effects. Also like Ru, Pd extraction may be affected by the extent of co-extraction of matrix elements.

5.6 Summary.

Previous workers (e.g. Vorob'eva et al., 1974; Mojski, 1980; Seeverens et al., 1983) have described the application of solvent extraction procedures, specifically for the isolation of the precious metals, using chloride solutions. A solvent extraction technique, based on the discoveries of these workers, has been optimised to separate analyte precious metal elements from potentially interfering matrix elements co-extracted during an aqua regia leach to facilitate determination of these analytes by GFAAS. The effects on the extraction 6 of the precious metals from 20% aqua regia solutions were examined. The experimental parameters were optimised and experiments were conducted using 2 of each of the recommended complexing agents and extracting solvents.

The final optimised technique was based on labilisation with $SnCl_2$, complexation with DPTU and extraction into DCE. Both raffinate and extract were analysed to characterise extraction efficiency. The procedure was evaluated using simple, single element solutions. It was then applied to leaches of geological samples and artificial matrix solutions to identify the effects that the presence other elements would have on the extraction efficiency and determination of each analyte.

Determination of Pd in geological samples was plagued by memory effects during

GFAAS analysis, but there was evidence that this element was extracted, although its extraction was hindered by the presence of matrix elements (Fe and possibly Mg). The extraction of Ru was also dependent upon the matrix element content of the starting solution and was at best only partially extracted by the DPTU/DCE procedure. The extraction of Pt was less dependent upon sample type. Good extraction was achieved whenever Pt was present in the leachate, although a greater concentration of matrix elements in the solution tended to lead to a slight retention of Pt in the raffinate. The extraction of Rh and particularly Au appeared to be quantitative and largely independent of the presence of matrix elements in the starting solution. Although analysis of raffinates and extracts of the artificial solution indicated a poorer extraction of Rh from solutions with high concentrations of matrix elements, this restriction in the degree of extraction was not evident in the analysis of leaches of actual samples.

5.6.1 Aqua regia dissolution and solvent extraction.

The solvent extraction procedure described in this chapter resulted in the extraction from 20% aqua regia of all the precious metals to variable degrees. Of all the elements Au was the most efficiently extracted, followed by Rh > Pt > Pd > Ru > Ir. Together with observations regarding the extent of extraction by aqua regia (Chapter 4), predictions can be made as to the suitability of the combined sample preparation procedure for the determination of precious metals in geological samples. The proportion of Pt, Pd, Rh, Ru and Au extracted by aqua regia during leaches of 7 selected samples have been calculated from results presented in Tables 4.11 and 4.12 and are presented in Table 5.11 together with the proportions of these elements extracted from the leachates by the solvent extraction procedure calculated from data presented in Table 5.10. Ir was not determined in the aqua regia leachates (because of the typically low extraction of Ir by aqua regia from geological materials) and Os was not determined because of analytical difficulties (Section 6.1.3.1).

Table 5.11. Proportions of Pt, Pd, Rh, Ru and Au extracted by aqua regia (AR) from selected samples, proportions of these elements extracted from these leachates by the solvent extraction procedure (SE) and the overall recovery of the procedure (combined). Independently analysed concentrations and certified concentrations of these materials are given in Tables 4.11 and 4.12.

	Pt			Pd			Rh		
	AR	SE	combined	AR	SE	combined	AR	SE	combined
RLM008	100%	50%	50%	77%	3%	2%	-	0%	-
MR65	65%	33%	21%	82%	8%	7%	32%	0%	0%
CMR292	26%	50%	13%	87%	47%	41%	11%	25%	3%
RLM007	131%	88%	115%	105%	59%	62%	79%	97%	77%
14/75	7%	38%	3%	56%	50%	28%	46%	93%	43%
SARM 7	37%	91%	34%	77%	39%	30%	73%	96%	70%
CHR-Pt+	18%	95%	17%	96%	42%	40%	18%	94%	17%

	Ru			Au		
	AR	SE	combined	AR	SE	combined
RLM008	-	11%	-	-	45%	-
MR65	92%	8%	7%	121%	78%	94%
CMR292	18%	46%	8%	33%	100%	33%
RLM007	153%	35%	54%	119%	71%	85%
14/75	9%	72%	6%	43%	92%	40%
SARM 7	27%	19%	5%	97%	99%	96%
CHR-Pt+	-	81%	-	110%	99%	109%

- proportion of analyte extracted is unknown due to aqua regia extraction data being less than the limit of detection or no data being reported by independent analysis.

From the data in Table 5.11, the following observations can be made:

Platinum. There was near-quantitative recovery of Pt from solvent extraction for 3 of the samples, but only for one of these samples (RLM007) did such solvent extraction recovery combine with a good aqua regia recovery to give quantitative extraction by the combined method. Pt was present at low concentrations in the extracts and raffinates of the other samples. The recoveries of Pt by solvent extraction did not appear to be affected by the incomplete extraction of Pt by aqua regia.

Palladium. Further to the typically near-quantitative extraction of Pd by aqua regia, the recovery by solvent extraction was fairly consistent though disappointingly low (c.50%), despite the analytical problems encountered in the determination of this element after solvent extraction (Section 5.5). Pd was present at low concentrations in the extracts and raffinates of the first 2 samples. The combined method, therefore, would not provide quantitative data for this analyte.

Rhodium. There was typically near-quantitative recovery of Rh by solvent extraction. Rh was present at low concentrations in the extracts and raffinates of the first 3 samples. The limiting factor to this element's determination was its incomplete extraction by aqua regia from these samples.

Ruthenium. The variable extraction of Ru by aqua regia was compounded by recovery of 8-81% by solvent extraction. The greatest proportions extracted by aqua regia correlated with the lower recoveries by solvent extraction. Consequently, the combined method seemed unsuited to the determination of this element.

Gold. Apart from the low level of Au in RLM008, the recovery of Au by solvent extraction matched the typically quantitative extraction of this element by aqua regia. The combined method was suitable for the quantitative determination of Au in half of these samples, its suitability to the remainder being restricted by the incomplete extraction of this element by aqua regia.

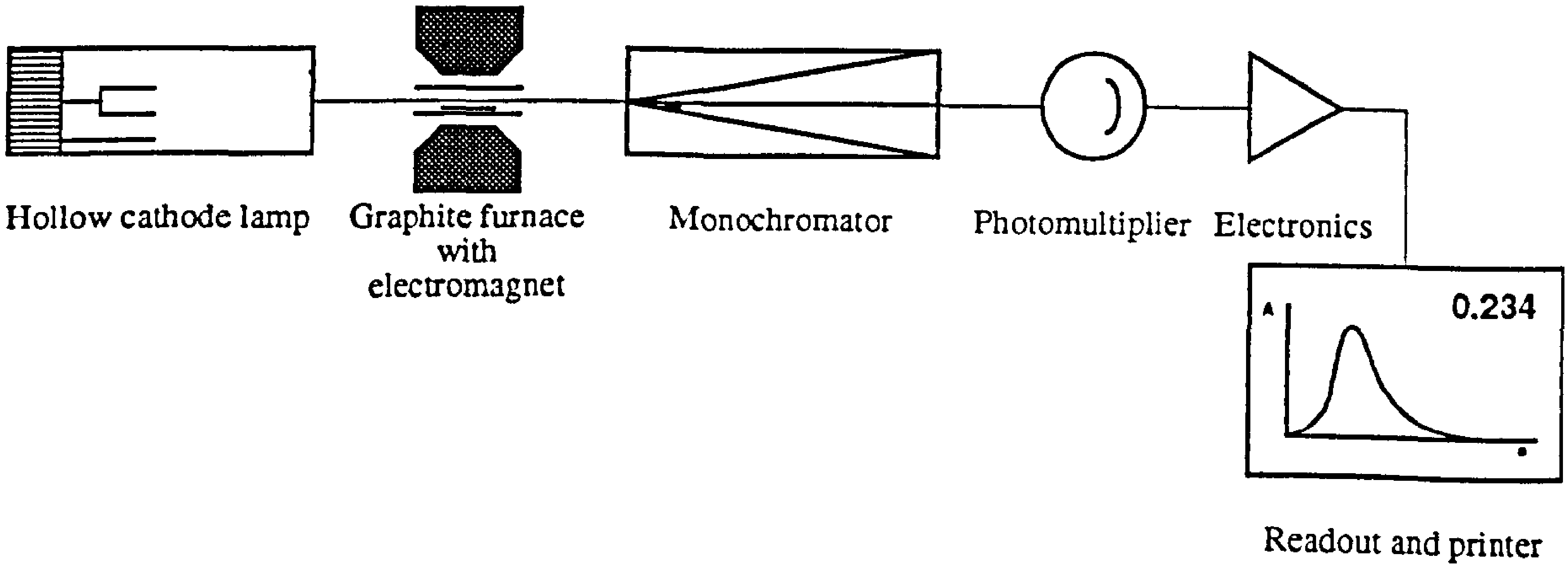
In summary, the combined preparation procedure will be most suitable for Au determination. The solvent extraction efficiency of Pd is disappointing considering the semi-quantitative extraction of Pd by aqua regia. Determination of this element appears to be dependent upon the influence of sample matrix on the success of solvent extraction. Determination of Rh, Pt and Ru is dependent upon both the influence of sample type on the success of the aqua regia dissolution and the effect of sample type on effective solvent extraction. Favourable dissolution of Rh by aqua regia will probably lead to favourable extraction by DPTU/DCE and to a meaningful analysis. Conversely, poor dissolution by aqua regia may be further exacerbated by poor extraction leading to incorrect analysis. Poor dissolution of Ir followed by non-quantitative solvent extraction is to be expected for all samples, consequently, without extensive modification, this sample preparation procedure is not suitable for the isolation and preconcentration of this element.

Chapter 6.
Atomic absorption spectrometric analysis.

6.1 Introduction.

Graphite furnace atomic absorption spectrometry (GFAAS) is one of the high sensitivity techniques available for the analysis of geological materials for the determination of the precious metals. The analytical capabilities of this technique in comparison with other techniques are reviewed in Chapter 3. This chapter describes the work undertaken to optimise the GFAAS techniques using a Perkin Elmer Zeeman 3030 atomic absorption spectrometer equipped with an electrothermal atomiser (Perkin Elmer HGA 500) and Zeeman background correction. A sample was injected into a graphite tube furnace by means of a microlitre pipette autosampler (Perkin Elmer AS-60) and is atomised by programmed heating of this furnace. Intense light from a hollow cathode lamp is directed along the axis of the furnace through the atom cloud. The appropriate atomic line was selected by a monochromator and the change in intensity of the light is caused by atomic absorption is detected by a photomultiplier. Finally, a readout of the absorption is presented on a monitor and a hard copy of the data is printed. This process is summarised in Figure 6.1.

Figure 6.1. Schematic flow diagram of the operation of a graphite furnace atomic absorption spectrometer with Zeeman background correction.



6.1.1 Thermal heating programme.

The route to atomisation is not straightforward in comparison with flame AAS. After injection, the sample must be dried to remove the solvent, then undergo a series of thermal pretreatment steps to remove matrix components that would cause molecular absorption interference and to convert the analyte into a form suitable for atomisation without interference. Only then is the inert purge gas[1] shut off and the tube furnace heated rapidly (2000 °C/s) to atomise the sample. After atomisation the temperature is further increased to 2650 °C (the maximum for pyrolytically coated graphite tubes[2]) or kept at 2650 °C (if atomisation was accomplished at this temperature), and held for a few (more) seconds with a flow of inert purge gas to clean out the furnace and remove any potential source of memory effects. A simplified stepped (ramp and hold) heating procedure is summarised in Figure 6.2.

The duration of each ramp and hold period and the temperature of each step must be optimised for each analyte species and the sample type. For example, refractory elements require a high temperature for atomisation and can withstand relatively high temperatures for thermal pretreatment, whereas more volatile elements do not need

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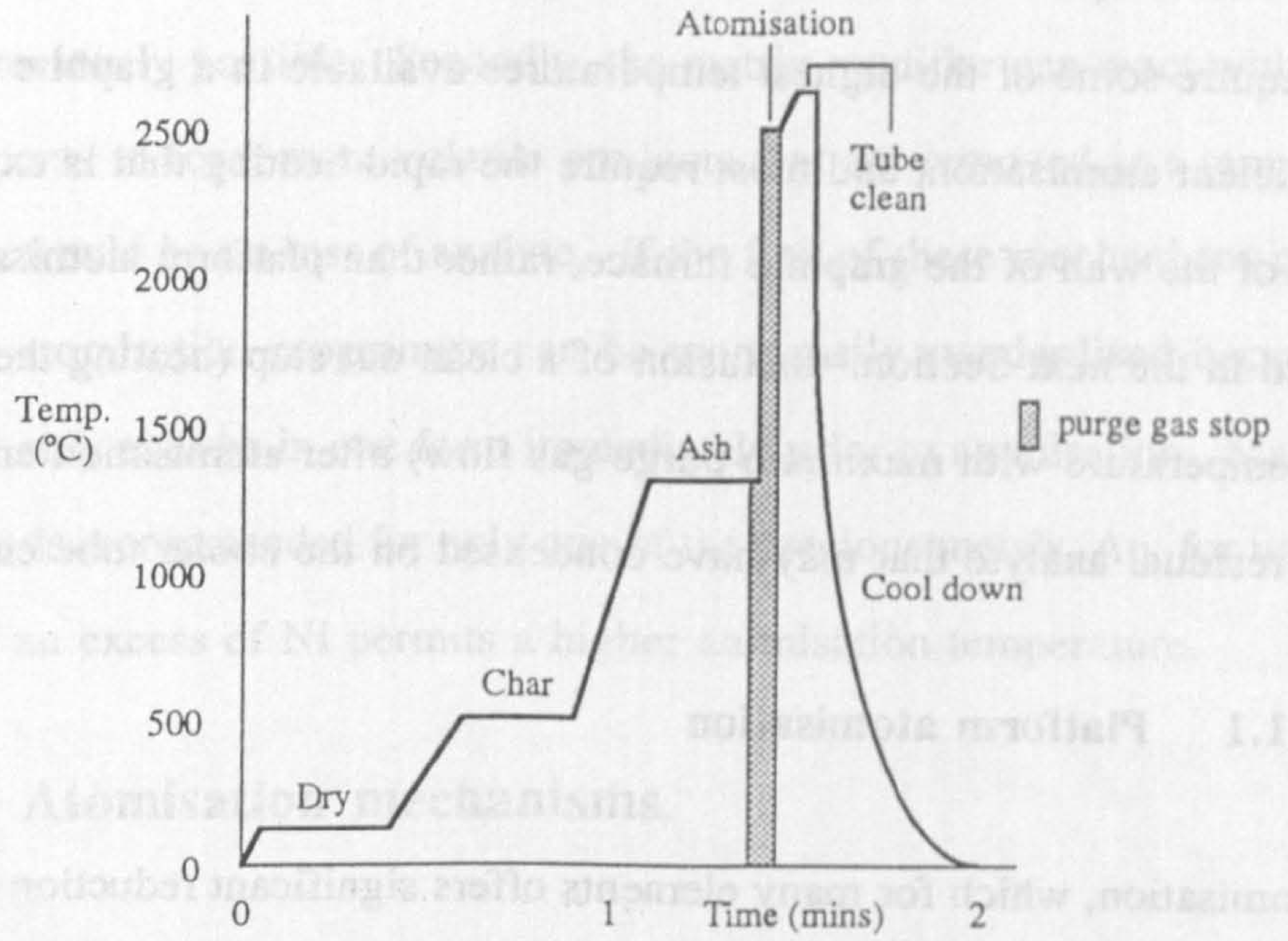
[1] During the drying and thermal pretreatment stages, all surfaces of the graphite furnace are flushed with an inert purge gas, usually argon. This purge gas serves to carry out products released during thermal pretreatment (solvent, matrix components, etc.), to prevent air coming into contact with the hot graphite components (which would lead to a rapid degradation of the tube) and to provide an inert atmosphere into which analyte atoms can be introduced with little risk of vapour phase reactions. However, the flow of this gas through the furnace must be stopped for the few seconds during atomisation to (i) increase the residence time of atoms in the light path, thus avoiding a decrease in sensitivity that would be caused by a gas flow during atomisation and (ii) prevent unwanted cooling of the furnace and atomised sample, which would lead to thermal disequilibrium effects and unwanted interferences

[2] Whereas standard graphite tubes suffer from adsorption of analyte and matrix elements, a thin layer of graphite pyrolytically coated onto the surface of the graphite tube prevents this adsorption and prolongs the life of the tube. The drawback of this coating is that above 2650 °C the pyrocoating tends to break away for the tube, dramatically reducing the tube life. This maximum temperature is required for the efficient atomisation of many of the precious metals.

such high atomisation temperatures and may suffer premature atomisation if too high an ashing temperature is selected.

Figure 6.2. Diagrammatic representation of the stepped thermal atomisation programme showing the drying, charring, ashing, atomisation and cleaning stages of the heating cycle.



The temperature of the drying stage depends on the nature of the solvent such that temperatures close to the boiling point of the solvent are chosen to ensure rapid evaporation. However boiling must be avoided, as this would cause spattering of the analyte, which in turn would lead to poor precision. Rather than maintaining a constant drying temperature, the furnace temperature can be ramped through the boiling point of the solvent to compensate for any increase in the boiling point of the analyte solution due to high amounts of dissolved solids.

In this work, the subsequent thermal pretreatment has been split into two stages, hereafter referred to as the char and the ash stages. The char stage (typically 500 °C) was included on advice from the instrument manufacturers as the temperature at which most organic constituents/interferents could be removed. However, the principal stage for analyte conditioning was the second ash stage, the temperature of which was element dependent. The char stage was retained unaltered and no effort was made to refine its parameters during subsequent optimisation work, the more critical stage being ashing (Section 6.1.2).

The atomisation temperature is also element dependent. The PGE, being refractory elements, require some of the highest temperatures available in a graphite furnace to promote efficient atomisation, and most require the rapid heating that is experienced by atomisation of the wall of the graphite furnace, rather than platform atomisation which is considered in the next Section. Inclusion of a clean out step (heating the furnace at maximum temperature with maximum purge gas flow) after atomisation ensured the removal of residual analyte that may have condensed on the cooler tube ends.

6.1.1.1 Platform atomisation

Platform atomisation, which for many elements offers significant reduction of interferent effects is an alternative to wall atomisation for only two of the precious metals, namely Au and Pd. Because the L'vov platform is heated primarily by radiative effects, and very little by conduction, its temperature lags behind that of the furnace wall, with the consequence that the furnace heating programme requires slight adaptation to allow the platform to reach thermal stability. This adaptation usually involves the extension of hold times for some of the stages and an increase in the ashing and atomisation temperatures, to ensure that these steps have the desired conditioning effects. L'vov (1987) reported that use of platform atomisation enhanced the sensitivity of Au (x2.2) and Pd (x1.4). He credited the enhancement to an increase in vapour density at the optical axis. The sensitivity of Au was additionally improved by an enhanced degree of gaseous carbide dissociation.

6.1.1.2 Matrix modification.

The thermal atomisation procedure can be further adapted to prevent the premature loss of a volatile analyte during thermal pretreatment by addition of an excess of another metal or salt. This process is called matrix modification and operates by one of two mechanisms. Firstly, the presence of a matrix modifier can stabilise the analyte by converting it into a less volatile compound. Since this compound dissociates at a higher temperature, there is opportunity for a greater proportion of the matrix to be removed than was previously possible. Secondly, the matrix modifier can react with concomitant matrix elements to form more volatile products that are removed at a temperature at which there would be no loss of analyte. If the first of these mechanisms occurs, then the thermal atomisation programme can be more easily standardised because the analyte will only ever be in one form immediately prior to atomisation. Matrix modification is recommended for only one of the precious metals, Au, for which the presence of an excess of Ni permits a higher atomisation temperature.

6.1.2 Atomisation mechanisms.

The stepped heating programme is designed to create an easily atomisable form of the analyte after the ashing step. In the case of the precious metals, this final form is usually the metal itself. Akman et al. (1991) reported that Pt and Ir are atomised via sublimation of the pure metal. Considering the thermochemical properties of Cu and relating them to Pt, Akman et al. (1991) proposed the following reaction scheme (Equ. 6.1):

$$H_2PtCl_6 \longrightarrow Pt_{(s)} \xrightarrow[\text{relatively low T}]{\text{fast}} Pt_{(g)} \longrightarrow Pt_{2(g)} \qquad \text{(Equ. 6.1)}$$

$$\underline{\uparrow \text{ relatively high T } |}$$

If the melting point of an analyte metal oxide is less than the ashing temperature then the element will be reduced to the metal or carbide before noticeable volatilisation of the oxide has occurred. Because this criterion is met for the precious metals, Akman et al. (1991) concluded that Au and the PGE would all atomise by the process of sublimation.

Thermal pretreatment to generate the analyte element in metallic form has been considered by many workers. Much of the early work was undertaken using a carbon rod atomiser (CRA) (Aggett and Sprott, 1974; Campbell and Ottaway, 1974) or a heated graphite atomiser (HGA)[3] (Sturgeon et al., 1976; Rowston and Ottaway, 1979). The influence of graphite on the thermal pretreatment of the analyte can be regarded as consistent in both cases and thus applicable to GFAAS as used in this work. Aggett and Sprott (1974) reported that graphite was responsible for the reduction of Co, Fe, Ni and Sn during atomisation. This reduction was not observed when the graphite was coated with tantalum foil. They concluded that, in the absence of graphite, the metal atoms were produced by thermal dissociation of a salt or metal oxide. Campbell and Ottaway (1974) recognised that graphite played an important role in the production of atoms and presented a mechanism in which reduction of an elemental oxide by carbon led to direct liberation of gaseous atoms, assuming that sufficient energy was released on the formation of CO to produce metal atoms directly into the gaseous state.

Rowston and Ottaway (1979) extended this work into the analysis of the precious metals and found that chloride salts of Ru, Rh, Pd, Ir, Pt and Au were reduced to the metal at temperatures below those at which their atoms appeared (Os was not determined); this appearance temperature was lower than the melting points of all the precious metals except Pt. They reported similar appearance temperatures for atoms derived from either HCl or HNO_3 solutions, which indicated a common atomisation procedure. They showed that Pd and Au were reduced to the metal prior to atomisation and reported indirect evidence of reduction for the other PGE. They proposed a mechanism involving the atomisation of the free metal at and above the

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[3] Early designs of instruments used the CRA, a graphite rod with a grove machined into the top such that the atom cloud was ultimately produced in the atmosphere directly above the rod, often the purge gas used was nitrogen. Later designs of instruments incorporated a hollow graphite tube into which the sample was injected and the atom cloud was ultimately generated within the enclosed space within the tube and the purge gas was usually argon. Both atomisers were heated by their inherent resistance to an electric current and atomisation mechanisms are likely to be similar. The purpose of briefly describing the types of atomiser is to draw attention to and to specify that there are similarities and differences between them.

appearance temperature (Au: 1020 °C, Pd: 1210 °C, Rh: 1640 °C, Pt: 1800 °C, Ir: 2020 °C, Ru: 2160 °C).[4] Sturgeon and Falk (1988) reported that no decomposition products of Au (i.e. oxides) were evident during atomisation from single element solutions and they, too, suggested that decomposition of Au oxides was complete prior to atomisation. Hamid (1989) showed that Ru atoms were formed by carbon reduction of Ru oxides. Rowston and Ottaway (1979) also reported temperatures at which conversion from the chloride to the metal was complete (Au: 280 °C, Pt: 590 °C, Ru: 680 °C, Pd: 710 °C, Rh: 760 °C, Ir: 820 °C). As an example, the atomisation scheme proposed by Rowston and Ottaway (1979) for Pt is shown below (Equ. 6.2):

$$H_2PtCl_6 \xrightarrow[\text{130 °C}]{} PtCl_2 \xrightarrow[\text{590 °C}]{} Pt_{(s)} \xrightarrow[\text{1800 °C}]{} Pt_{(g)}. \quad \text{(Equ. 6.2)}$$

Chakrabarti et al. (1981) summarised four possible atomisation mechanisms for metals, depicted below:

(a) thermal decomposition of the solid oxide

$$M_xO_{y(s)} \longrightarrow x\,M_{(g)} + \tfrac{y}{2}O_{2(g)} \qquad \text{(Equ. 6.3)}$$

(b) dissociation of the oxide vapour

$$M_xO_{y(s)} \longrightarrow M_xO_{y(g)} \longrightarrow x\,M_{(g)} + y\,O_{(g)} \qquad \text{(Equ. 6.4)}$$

(c) dissociation of the halide vapour

$$MX_{n(s/l)} \longrightarrow MX_{n(g)} \longrightarrow M_{(g)} + n\,X_{(g)} \qquad \text{(Equ. 6.5)}$$

(d) reduction of the solid oxide by graphite

$$M_xO_{y(s)} + y\,C_{(s)} \longrightarrow x\,M_{(s/l)} + y\,CO_{(g)}$$

$$x\,M_{(s/l)} \longrightarrow \tfrac{x}{2}M_{2(g)} \longrightarrow x\,M_{(g)} \qquad \text{(Equ. 6.6)}$$

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[4] These appearance temperatures concur with the maximum ashing temperatures recommended by Haines and Robért (1984) (Pd: 1200 °C, Rh: 1600 °C, Pt: 1700 °C, Ir: >2000 °C, Ru: 1700 °C) and , except for Pd, by Everett (1976) (Pd: 1450 °C, Rh: 1450 °C, Pt: 1730 °C, Ir: 1730 °C, Ru: 1730 °C).

From these mechanisms and the above work on the PGE it can be inferred that, during charing and ashing, precious metal compounds are reduced to the metal (finely dispersed in either the solid or perhaps liquid state) either by thermal decomposition or by carbon reduction and that atomisation occurs by the simple process of sublimation (or the boiling off) of gaseous metal atoms. Knowledge of the atomisation mechanisms aids the understanding and optimising of thermal atomisation programmes by indicating the ranges of temperatures that should be studied to ensure efficient thermal pretreatment and atom formation.

6.1.3 Interference effects.

Under ideal circumstances, an analytical signal is directly proportional to the quantity of analyte atoms that absorb light at the selected atomic absorption wavelength. In practice, however, deviations from this ideal are encountered. These deviations are caused by a number of factors, collectively referred to as interferences.

Spectral interferences arise from (i) molecular (or more rarely atomic) absorption of interfering species at the selected wavelength; (ii) scattering of light by non-volatilised particles formed by concomitants; (iii) emission of light from the incandescent walls of the furnace. Farago and Parsons (1982) reported that tube wall emission was most significant in the near infra-red region of the spectrum and rapidly tailed off towards shorter wavelengths. Thus, the effect of tube wall emission at wavelengths used for precious metal analysis (242.8 - 349.9 nm) is not likely to be significant.

Non-spectral interferences arise from the effects that variable amounts of concomitant elements have on the analyte, which cause changes in analyte sensitivity according to sample matrix. For example, loss of analyte during thermal pretreatment, different atomisation rates or different degrees of ionisation may result from variations in the concentrations of particular concomitant elements.

Table 6.1. Maximum and minimum degrees of interferences on precious metal analytes (reported as percentage change in AA signal) caused by varying concentrations of precious metals and concomitant elements. The general trend of interference is indicated when no value has been published.

	Au			Pd			Pt		
Interferent	min	max	References	min	max	References	min	max	References
Au				-40	+35	1,4,8,10	-40	0	4,8,10
Pd	-40	-10	1,11				-20	0	4
Pt	-20	+30	11	-30	+25	1,4,15			
Rh				+20	+50	4	-65	0	1,3,4
Ru				0	+10	4	-30	+5	1,4,9
Ir				+5	+30	4	-80	0	3,4,9
Os									
Mg	-		2,12	-		2	-		2
Ca	-		12						
V				-		4			
Cr							-		2
Fe	-12		2,5,12	-63	-20,+	2,5,8,16	-40	-20,+	2,5,8,16
Co							-		2
Ni	-26	+25	2,5,6,10	-40	-20	2,8	-40	-20	1,2,8,10
Cu	-46	+30	5,6,10	-40	+20	1,5,8,16	-45	-18,+	2,5,8,10,16
Zn	-10	+118	1,5						
As	-		12						
Sn				+40		1	+50		1,2
Sb	-20		12						
La				-		4,9	-		9
U				-		4,9	-		9

	Rh			Ru			Ir		
Interferent	min	max	References	min	max	References	min	max	References
Au	-40	0	4,9	-60	-10	4,9	-45	-10	4,9
Pd	-5	0	4	-30	0	4,7	-50	-10	4,7,9
Pt	<-50	+15	3,4,9,15	<-70	+20	4,7,15	-45	-9	3,4,7,15
Rh				-20	+5	4	-40	0	4,9
Ru	-40	+5	1,4,9				-75	-10	1,4,9,14
Ir	-40	0	1,4,9	-90	0	1,4,9,14			
Os				-10		1	-40		1
Mg	-		2	-		4,9			
Ca									
V									
Cr	-		2	-15		2,13			
Fe	-		2	-20		7,13	-90		1,7
Co	-		2	-26		7	-		7
Ni	-		2	-26		7,13	-40	-10	7,9
Cu	-3	+10	2,7,14	-10		1,7	-		7
Zn									
As									
Sn	0	+300*	1,2	-		2,7	-		7
Sb									
La	-		9	-		9	-		9
U	-		9	-		9	-100		9

Footnotes: The values in the min. and max columns refer to the increase percentage (+) or decrease (-) in AA signal due to the presence of the particular interferent on the specified analyte. Simply "-" refers to a negative interference of unspecified magnitude. * The high positive interference of Sn on Rh (+300%) is time dependent, attributed to a very fine colloidal suspension of a reduced rhodium complex in solution. The numbers in the references column refer to the following references: 1: Guerin (1972), 2: Mallet et al. (1972), 3: Adriaenssens and Knoop (1973), 4: Everett (1976), 5: Fishkova and Vilenkin (1978), 6: Savel'eva and Agapova (1979), 7: L'vov et al. (1979), 8: Samchuk and Latysch (1982), 9: Haines and Robert (1984), 10: Sighinolfi et al. (1984), 11: Brajter and Slonawska (1987), 12: Stafilov and Todorovski (1987), 13: Hamid (1989), 14: Aneva et al. (1990), 15: Arpadjan et al. (1990), 16: Terashima (1991).

Vapour phase interferences can occur when the analyte is atomised from a hot surface directly into a cooler atmosphere, resulting in various recombination reactions which lead to the formation of molecular species when the analyte condenses on cooler parts of the furnace. Many of the potential sources of interferences can be controlled by matrix matching standards and/or removing concomitant elements or minimised by correct alignment of the instrument coupled with judicious optimisation of thermal atomisation programmes, with or without matrix modification (to control the chemical environment of thermal pretreatment).

Various degrees of mutual interference between all the precious metals and interferences of excess concentrations of 14 concomitant elements, particularly Fe, Ni and Cu, on each of the precious metals have been observed by a number of workers (Table 6.1). The data on interferences reported in Table 6.1 were obtained from either heated graphite atomisers (HGA) or carbon rod atomisers (CRA), which were used to analyse solutions containing different proportions of analyte and concomitant elements. The intention of presenting the data in Table 6.1 is to identify the diversity of interfering elements and the variable extent of their interferences and it must be remembered that the data was derived from solutions with a range of different analyte concentrations.

6.1.3.1 Compensating for interference effects.

Interferences in flame AAS can by compensated by the use of releasing agents, however, it is not possible to use such releasing agents in GFAAS. Indeed, the three releasing agents commonly used for PGE determination by flame AAS (La, U and V) have been shown to have a depressive interference on Pd determination by GFAAS (Everett, 1976; Haines and Robért, 1984). Consequently, several investigations have been undertaken to characterise GFAAS interference effects in the determination of the PGE.

Brajter and Slonawska (1987) concluded that the best method to deal with complicated interferences was to avoid them by removing the matrix prior to analysis. Terashima (1991) overcame variable interferences in the determination of Pt and Pd by addition of excess Cu and Fe to solutions prior to analysis. He then found that the enhancement of Cu and Fe was constant for all samples. However, the addition of Cu and Fe had to be controlled carefully because the presence of these elements in large amounts led to suppressive interferences on Pt and Pd. Everett (1976) noted that the degree of mutual interferences on all analyte precious metals except Pd was reduced by dilution, supporting the theory that the degree of interference was proportional to the absolute concentration of the interferent and not on the relative concentration, as had been previously proposed (Ebdon, 1972). Everett (1976) thus concluded that dilution of the samples was the best method of reducing and removing mutual precious metal interferences, subject to the instrument sensitivity.

To quantify the mutual interferences expected in aqua regia solutions or organic extracts used in this thesis, the procedures of Everett (1976)[5] were repeated and further tests were carried out on solutions of the precious metals in water, dilute HCl and dilute HNO_3. Another series of tests were carried out with and without excess concentrations of Ni, Fe, Cu, Cr and As (potential concomitants, co-extracted by aqua regia from chromitite samples). The ultimate intention was to determine the precious metals by direct analysis of organic solvent extracts which were free from a large proportion of the co-extracted elements. This separation procedure should lead to the removal of both concomitant elements and the high concentration of acids, so avoiding the corresponding interference effects. Any mutual interference effects caused by the presence of other precious metals in solution could be largely compensated by the use

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[5] The most complete suite of mutual interference studies was reported by Everett (1976) using a CRA with nitrogen as a purge gas. This work was based upon older instrumentation which did not accommodate Zeeman background correction, so it was considered essential to repeat this work on the modern instrumentation used in this thesis, generating a comparable data set.

of standards containing similar concentrations of all the precious metals – a crude form of matrix matching the standards.

6.1.3.2 Osmium.

Os was not determined in any of the samples for a variety of reasons, not the least of which being that Os hollow cathode lamps are no longer manufactured due to the high toxicity of the tetroxide. Also, Os extraction from geological samples by aqua regia was expected to be highly variable owing to the volatility of the tetroxide that would be formed in the prevailing highly oxidising condition. Furthermore, Os has the lowest sensitivity of the precious metals in determination by GFAAS and Everett (1976) reported that, when attempting to determine Os in artificial solutions, approximately 60% of the metal remained unatomised.

6.1.4 Calibration.

No formal calibration was performed in the optimisation and characterisation work described in this chapter (Sections 6.2 and 6.4, respectively), rather the relative change in absorbance between selected test solutions was measured. Before commencing the characterisation work (Section 6.4), preliminary measurements were made on a series of sequential dilutions of test solutions to ensure that the instrument would be operating within its linear working range. Deviations from linearity are expected at high concentrations of all analytes owing to deviations from ideal Beer's Law behaviour (Section 3.2.1).

6.2 Optimisation of furnace thermal programmes.

Analysis of solutions in simple aqueous or dilute acidic media was achieved by use of thermal atomisation programmes recommended by the manufacturer. The ashing temperature was selected to be sufficiently high to ensure full decomposition of chloride species to the free metal but not so high that atoms of the analyte element start to appear (for example, Rowston and Ottaway, 1979). Atomisation of these relatively refractory elements was aided by selecting the maximum heating rate capability of the Perkin Elmer HGA. Thermal stability of Pd and Au was increased in some applications by the use of platform atomisation (Sections 6.1.1.1 and 6.2.2). The manufacturer's recommended values of various instrumental parameters are detailed in Table 6.2.

Table 6.2. *Perkin-Elmer recommended operating parameters.*

Parameter	Pt	Ir	Pd	Pd	Ru	Rh	Au	Au
Atomisation surface	wall	wall	wall	platform	wall	wall	wall	platform
Ashing temperature (°C)	1300	1300	900	900	1400	1300	600	1000
Atomisation temperature (°C)	2650	2650	2300	2650	2500	2400	1600	2200
Wavelength (nm)	265.9	264.0	247.6	247.6	349.9	343.5	242.8	242.8
HCL operating current (mA)	30	30	30	30	30	30	10	10
Slit width (nm)	0.7	0.2	0.7	0.7	0.2	0.2	0.7	0.7
Characteristic mass (pg)	115	250	12	24	36	12	11	13

6.2.1 Atomisation from the furnace wall.

This section considers only wall atomisation for all the precious metal elements. The use of platform atomisation as an alternative to wall atomisation for the determination of Au and Pd will be discussed in Section 6.2.2. The optimum AA signal sought during all the optimisation work was judged to be that with the largest peak area and/or peak height with an additional constraint of reasonable peak shape/conformation. Optimisation of drying conditions was monitored by observation of what happened in the furnace during the drying stages.

6.2.1.1 Drying the sample.

The manufacturer's recommended drying conditions consisted of a 10 s ramp to 90 °C to be retained for 10 s, to allow the furnace to equilibrate, followed by a ramp to 130 °C to be retained for 1s/μl + 5 s (ie 25 s for a 20 μl aliquot) to allow complete drying of the sample. However, Halls (1984) reported that a programmed ramp to the first drying stage was unnecessary as the initial rate of heating would be controlled by the thermal inertia of the graphite furnace itself. Consequently the recommended conditions were altered by removing the first drying step and reducing the hold time of the second drying stage. However, direct heating to 130 °C caused most samples to boil, with a potential spattering of analyte down the tube. To protect against this, a preliminary drying step was re-introduced, with minimum ramp and hold time before a relatively slow ramp up to 130 °C (as recommended). Most samples were evaporated to dryness by the end of the 10 s ramp to 130 °C.

After a circulating water chiller was installed (which defined the minimum furnace temperature at the start of each stepped heating cycle as 45±5 °C) many samples of 20 µl had evaporated to dryness by the end of the first drying step. The second drying stage was retained, however, to allow for changes in the heating rates caused by differences in the nature of samples within an analysis batch. Holding the second drying temperature for 15 s ensured complete removal of the solvent.

6.2.1.2 Subsequent thermal pretreatment and atomisation.

A char stage with a hold time of 15 s after a ramp of 10 s from 130 °C was sufficient for all elements. Ramping up to the ashing temperature over 10 s and holding for a further 15 s proved to be adequate for all elements except Pd with wall atomisation, for which a hold time of 25 s was required to optimise the AA signal. Maximum heating (2000 °C/s) from the ashing temperature to the atomisation temperature, with purge gas stop, enabled efficient atomisation to occur. For all elements, the absorption peak trace had returned to the baseline after 3 s (Au peaks had generally returned to the baseline after 2 s). A clean out stage of 4 s at 2650 °C with a flow of purge gas ensured the absence of residual memory effects.

Throughout the course of this work, the thermal atomisation programmes were continually refined. The parameters most often studied were the ashing and atomisation temperatures and the monochromator slit width (Ir and Ru). The application of matrix modification was not considered in this work with atomisation from the furnace wall The manufacturer's recommended values for these parameters, as presented in Table 6.2, were used as starting points in the optimisation procedures.. The work done on such refinement will be considered by element below:

Platinum: Increasing the ashing temperature above 1400 °C resulted in a decrease in the absorbance, possibly associated with premature loss of analyte. Increasing or decreasing the ashing times had no effect on the absorbance. The maximum temperature permitted by the graphite furnace was required for Pt atomisation.

Iridium: Increasing or decreasing the ashing temperature had no discernible influence on the absorbance. The maximum temperature permitted by the graphite furnace was required for Ir atomisation. Later in the project, the influence of changing the slit width was considered. A slit width of 0.2 nm is recommended for Ir and absorbance data obtained with this slit setting was compared with that obtained with a slit width of 0.7 nm. Use of a 0.2 nm slit led to a larger absorption peak, although the data was less precise than that obtained with the 0.7 nm slit. A 0.2 nm slit was used for all Ir determinations in this thesis except for the optimisation of chemical parameters in solvent extraction, when the increased precision, lower sample blanks and greater peak profile similarity between peaks of solutions of different concentrations led to the use of a 0.7 nm slit.

Palladium: Because the maximum atomisation temperature (2650 °C) was advised for platform atomisation of Pd, atomisation at this temperature was attempted from the tube wall. The heights of the absorption peaks obtained by wall atomisation were independent of atomisation temperature (at those temperatures studied), but peak area was greater after atomisation at 2650 °C. It was interesting to note that a new tube permitted more rapid and efficient atomisation.

Ruthenium: Varying the ashing and atomisation temperatures between 1300-1500 °C and 2400-2650 °C, respectively, did not effect significantly the atomisation of Ru. Ashing at 1400 °C and atomisation at 2500 °C, the recommended conditions, was a good combination to optimise the AA signal. Use of a 0.7 nm slit, rather than the recommended 0.2 nm slit, resulted in a smaller absorption peak, the precision of the analyses were comparable and the precision of the peak area data was greater than that of the peak height data. Analysis of blank 20% aqua regia solutions with a 0.7 nm slit produced very much smaller peaks than those obtained with a slit of 0.2 nm. Measurement of peak height with a slit width of 0.2 nm was used for all the work in this thesis except optimisation of chemical parameters in the solvent extraction when a slit of 0.7 nm was used with peak area integration.

Rhodium: Increasing the atomisation temperature when ashing at 1300 °C showed that the largest absorption peak was achieved with maximum atomisation temperature, although the peak heights were rather erratic and showed a trend towards taller peak with higher atomisation temperature. Subsequent reduction of the ashing temperature below 1300 °C with atomisation at 2400 °C showed an increase in peak height, though not in peak area. Reappraisal of the atomisation temperature with ashing at 1000 °C showed the same pattern as above, when compared with ashing at 1300 °C. Because peak height was being monitored, the recommended atomisation temperature (2400 °C) was retained for all analyses, but the lower ashing temperature (1000 °C) was used for the optimisation of chemical parameters for solvent extraction. Although peak height data was less precise than peak area data in these experiments, the opposite was found in experiments prior to the optimisation of chemical parameters for solvent extraction, so the recommended parameter, peak height, was measured in those instances.

Gold: Increase of the atomisation temperature from the recommended 1600 °C resulted in atomisation peaks that returned to the baseline more rapidly, hence increasing the precision of analysis and giving lower background absorbances. However, this increase was accompanied by a decrease in peak area. A compromise between these factors was reached with atomisation at 2000 °C. Increasing the ashing temperature to 1000 °C was possible with no appreciable loss of sensitivity. Wall atomisation for Au was not often used, atomisation from the platform being preferred (see Section 6.2.2).

The parameters used for the thermal heating programmes are summarised in Table 6.3.

Table 6.3. Optimised thermal heating programmes with wall atomisation for Zeeman 3030 GFAAS.

Heating stage	parameter	Pt	Ir	Pd	Ru	Rh	Au
Drying 1	Temperature	90	90	90	90	90	90
	ramp time	1	1	1	1	1	1
	hold time	9	9	9	9	9	9
Drying 2	Temperature	130	130	130	130	130	130
	ramp time	10	10	10	10	10	10
	hold time	15	15	15	15	15	15
Char .	Temperature	500	500	500	500	500	500
	ramp time	10	10	10	10	10	10
	hold time	15	15	10	15	15	15
Ash	Temperature	1300	1300	800	1400	1000	1000
	ramp time	10	10	10	10	10	10
	hold time	15	15	25	15	15	15
Atomisation	Temperature	2650	2650	2650	2500	2400	2000
	ramp time	0	0	0	0	0	0
no gas flow	hold time	3	3	3	3	3	2
Clean out	Temperature	2650	2650	2650	2650	2650	2650
	ramp time	1	1	1	1	1	1
	hold time	4	4	4	4	4	4

Units for temperature (°C), ramp and hold times (s). Note purge gas stop during atomisation.
A ramp of 0 s denotes maximum heating rate (2000°C/s).

6.2.1.3 Concentration ranges for linear calibration curves.

The relationship between absorption and concentration deviates from linearity at high concentration (non-ideal adherence to Beer's Law). An attempt was made to determine the maximum concentration of each element that could be analysed to define the upper limit of the linear working curve. Analyte solutions were prepared by dilution of Aldrich atomic absorption standard solutions into 20% aqua regia. Approximate maximum concentrations were calculated from manufacturer's literature and the single element solutions were prepared as 200 µg/l (Au, Pd, Rh), 400 µg/l (Ru) and 2000 µg/l (Pt, Ir). Successive dilutions of these solutions were analysed to identify the linear region of the analyte calibration curve. Triplicate analyses were then made on two dilutions within this range. All solution concentrations are reported using 20 µl injections into the graphite furnace. The concentrations of the solutions studied and the triplicate analyses are presented in Table 6.4.

Table 6.4: Results of measurements to determine the upper limit of the linear region of the absorbance/ concentration analyte "calibration" curve. Data from wall atomisation experiments.

Element		Pt		Ir		Ru
	conc	absorbance	conc	absorbance	conc	absorbance
conc A	2000	521	2000	564*	400	1235
conc B	1000	309	1000	340	200	654
conc C	500	169	500	197	100	376
triplicate 1	500	148, 152, 149	500	181, 178, 172	100	275, 328, 286
triplicate 2	1000	283, 292, 287	1000	320, 322, 309	200	628, 576, 602
mean 1 (CV)	500	150 (1.27%)	500	177 (2.61%)	100	296 (9.41%)
mean 2 (CV)	1000	287 (1.50%)	1000	317 (2.21%)	200	602 (4.39%)

Element		Rh		Pd		Au
	conc	absorbance	conc	absorbance	conc	absorbance
conc A	200	1564*	50	263	200	757
conc B	100	852	25	156	100	316
conc C	50	466	12.5	76	50	162
triplicate 1	50	470, 487, 488	15	96, 96, 99	100	266, 271, 265
triplicate 2	80	746, 717, 699	30	187, 184, 179	150	393, 398, 402
triplicate 3	100	873, 877, 895				
mean 1 (CV)	50	482 (2.09%)	15	97 (1.67%)	100	267 (1.16%)
mean 2 (CV)	80	721 (3.25%)	30	183 (2.24%)	150	398 (1.19%)
mean 3 (CV)	100	881 (1.36%)				

*: rollover occurred.
Atomisation temperature for Au was 1600 °C (linear curve location) or 2000 °C (triplicate analyses).
Concentrations in µg/l.

From examination of the data presented in Table 6.4, it was reasoned that, when 20 µl aliquots were used, sample concentrations should be less than the following concentrations: Pt (1000 µg/l), Ir (500 µg/l), Ru (400 µg/l), Rh (100 µg/l), Pd (30 µg/l) and Au (150 µg/l).

6.2.2 Platform atomisation for Pd and Au.

The benefits of atomisation from a graphite platform inserted into the graphite tube furnace compared with atomisation from the wall of the furnace have been discussed earlier (Sections 3.2 and 6.1). Platform atomisation is recommended for the determination of Pd and Au. Thermal programmes were examined for the atomisation of these two metals in a similar way to that used for wall atomisation (Section 6.2.1). A comparison was made between the effects of wall and platform atomisation.

Drying times needed to be extended to allow for the delayed heating of the platform. A hold time of 25 s at the second drying temperature (130 °C) was sufficient to ensure removal of the solvent. The char and clean out stages were the same as those used with wall atomisation. Study of ashing and atomisation stages will be considered for each element below:

Palladium: An increase of the ashing time may have been necessary to account for the delay in heating the sample. However, it was found that increasing this time beyond 15 s caused very little improvement, so the hold time of 15 s was retained, as used in the wall atomisation programme. A decrease of the ashing temperature below the recommended 900 °C made no difference to the final peak area reading. Increasing this temperature, however, causes a decline in the peak area reading. The recommended ashing temperature (900 °C) was selected. The maximum atomisation temperature (2650 °C) was selected as recommended.

Gold: An increase of the ashing time beyond 15 s caused a decrease in the size of the absorption peak, and a 15 s ashing stage gave rise to a taller peak than that generated after a 20 s stage. Increasing the ashing temperature above 900 °C led to significant loss of analyte. A change in the atomisation temperature from the recommended 2200 °C (but without using a matrix modifier) while analysing 20 % aqua regia solutions resulted in irregular atomisation peaks, and some profiles even had two distinct peaks. Addition of an excess of Ni, to act as matrix modifier, served to (i) delay the start of the peak by more than 0.5 s, (ii) broaden significantly the absorption peak and (iii) to eliminate the double peak nature of earlier samples, indicating that Ni stabilised Au in thermal pretreatment prior to atomisation.

The effects of adding different amounts of Ni to the Au sample aliquots were studied before the optimisation of the thermal atomisation programmes. The additional volume did not necessitate an extended drying stage. Higher concentrations of Ni accentuated the delay in peak appearance, peak broadening, and resulted in a slower decline of the absorption peak. These observations substantiate the conclusions drawn above (i.e. that Ni stabilises Au prior to atomisation). The recommended mass of Ni that should be added to the sample aliquot was 50 μg, nevertheless, 10 μg was found to give optimal peak area for 20 μl of a standard solution containing 200 μg/l Au.

An ashing temperature of 900 °C produced maximum peak area, the peak being considerably larger than one generated with an ashing temperature of 1100 °C or even when the ashing stage was omitted. In a second study of Ni matrix modifier concentration, using a new graphite tube and atomisation at 1900 °C, the absorption peak appeared earlier than when atomisation was achieved with an old tube and there was a rise on the tail of the peak during the clean out stage. Again, increasing the mass of Ni added to the furnace resulted in a decrease in size of the first of the 2 distinct peaks and, with addition of 100 μg Ni, the entire absorbance was attributed to the second peak, which itself increased in size in proportion to the amount of Ni added.

Increasing the atomisation temperature caused a more rapid decline of this peak, although the appearance of the peak was not delayed. The maximum area under the absorption peak occurred with an atomisation temperature of 2200 °C. Atomisation at 1900 °C, however, provided a slightly larger peak when only 10 μg Ni was used. The mass of Ni matrix modifier added was 10 µg, the atomisation temperature was thus set at 1900 °C. An atomisation hold time of 5 s was often required to allow the absorption peak to return to the baseline, in contrast to the 2 s period required during wall atomisation.

The optimum parameters selected for the thermal heating programmes are summarised in Table 6.5.

Table 6.5. Optimised thermal heating programmes with platform atomisation for Zeeman 3030 GFAAS. The parameters relating to the determination of Au are when 10 µg Ni is used as a matrix modifier.

Heating stage	parameter	Pd	Au (+Ni)
Drying 1	Temperature	90	90
	ramp time	1	1
	hold time	9	9
Drying 2	Temperature	130	130
	ramp time	10	10
	hold time	25	25
Char	Temperature	500	500
	ramp time	10	10
	hold time	10	15
Ash	Temperature	900	1000
	ramp time	10	10
	hold time	10	15
Atomisation	Temperature	2650	1900
	ramp time	0	0
no gas flow	hold time	4	5
Clean out	Temperature	2650	2650
	ramp time	1	1
	hold time	4	4

Units for: temperature (°C), ramp and hold times (s).
Note purge gas stop during atomisation.
A ramp of 0 s denotes maximum heating rate (2000°C/s).

6.2.2.1 Concentration ranges for linear calibration curves.

The linear working curves for Au and Pd using platform atomisation were determined by a similar method to that used with wall atomisation, by identification of the linear region of the curve followed by triplicate analyses to confirm the region. Platform atomisation with Ni matrix modification stabilised Au atomisation to such a degree that a new working standard solution had to be prepared at 2000 µg/l. The concentrations of the solutions studied and the triplicate analyses are presented in Table 6.6.

Table 6.6. Results of measurements to determine the upper limit of the linear region of the absorbance/ concentration analyte "calibration" curve of Pd and Au with atomisation from the L'vov platform.

Element		Pd		Au (+Ni)		Au (+Ni)
	conc	absorbance	conc	absorbance	conc	absorbance
conc A	200	559	1000	3738*	200	907
conc B	150	472	800	3308*	300	1352
conc C	100	321	500	2250	400	1755
conc D	50	172			500	2151
conc E					600	2519*
triplicate 1	70	230, 235, 234	500	2148, 2119, 2147	-	-
triplicate 2	100	332, 343, 334	800	3145*, 3108*, 3101*	-	-
mean 1 (CV)	70	233 (1.07%)	500	2138 (0.77%)	-	-
mean 2 (CV)	100	336 (1.70%)	800	3118 (0.76%)	-	-

*: rollover occurred.
Au: linear location @ 25 µg Ni, triplicates @ 50 µg Ni.
Concentrations in µg/l.

Although triplicate analyses were performed on Au solutions at 800 µg/l, it was apparent that this concentration was too high, generating absorbances that were above the rollover limit[6] of the spectrometer. More recent examination of analytical data of

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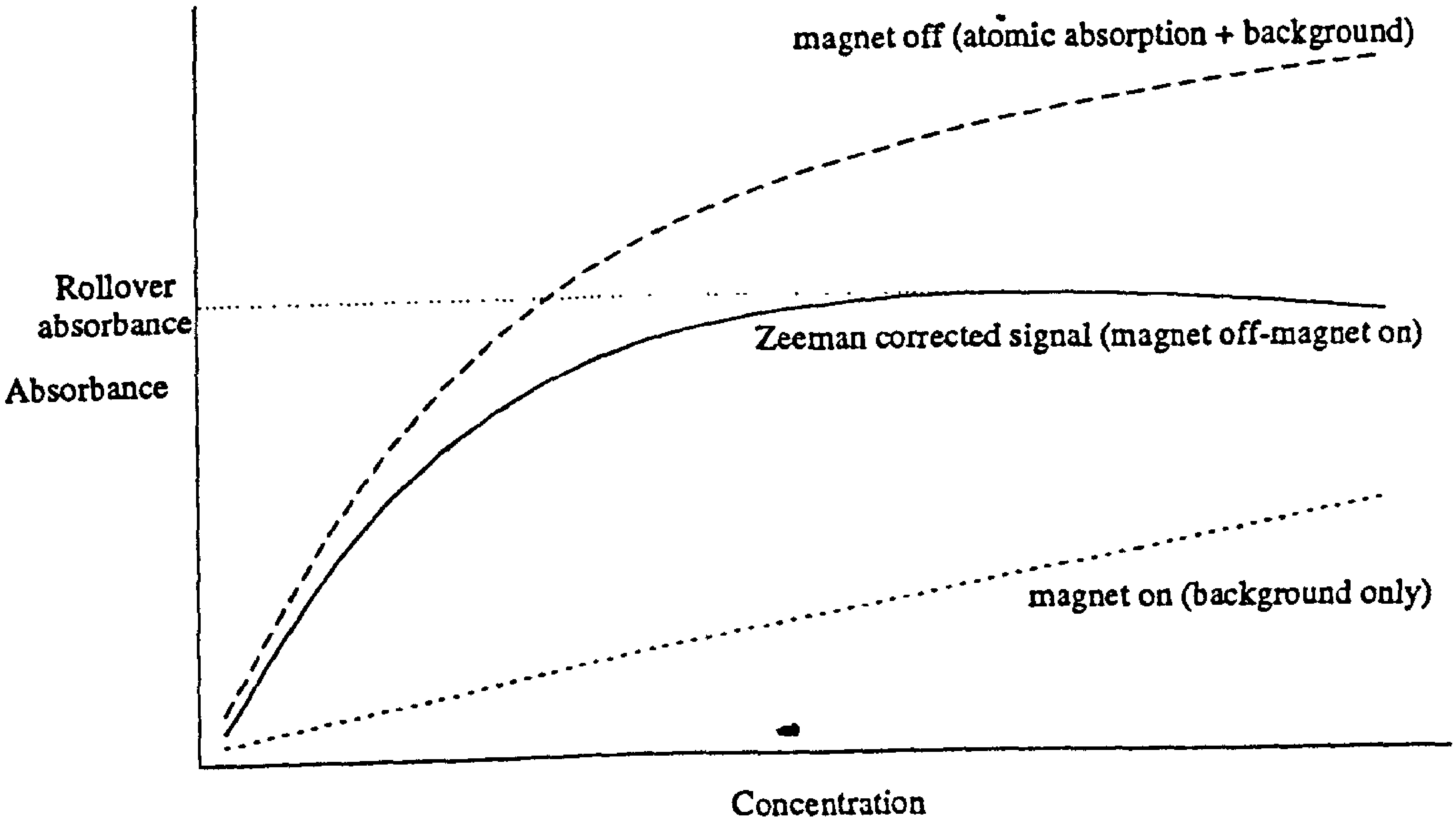
[6] As mentioned above, the absorbance vs. concentration curve deviates from linearity, bending down towards the concentration axis at high concentrations. (This effect is accentuated by the Zeeman background correction line splitting effects at high analyte concentrations (Section 3.2.2.1)). However, the detected background absorbance increases linearly with analyte concentration (when the Zeeman magnet is powered on and components of the analytical lines are either shifted to higher and lower wavelengths or removed by polarisation). Subtraction of the background from the total absorbance gives rise to a curve that is linear at low analyte concentrations, deviates from linearity at higher concentrations and the slope becomes negative above a particular concentration. This is pictured diagrammatically in the figure below, which has been drawn to highlight the rollover effect (it is unfortunate that the linear working range is not so readily identified in this figure).

less concentrated solutions has indicated that rollover threshold was exceeded even with a solution concentration of 600 µg/l. Indeed, the linear working curve can be regarded as extending to just 300 µg/l. The linear working curve for Pd extended to 100 µg/l. These concentrations compare favourably with those permitted by wall atomisation (Au: 150 µg/l and Pd: 30 µg/l) and show that platform atomisation allowed analysis of solutions over a wider concentration range.

6.2.3 Choice of atomisation surface.

Solutions analysed for the determination of Pt, Ir, Ru and Rh were atomised from the wall of the furnace. Solutions analysed for the determination of Pd and Au were atomised from the L'vov platform. Ni matrix modifier (10 µg) was used in the determination of Au with platform atomisation.



The instrument warns the analyst when the absorbance value reaches 90% of the rollover absorbance. A sample that generates an absorbance that is identified as being close to the rollover absorbance should be diluted to ensure that actual concentrations can be deduced from an absorbance in the linear working range. It can be seen from the figure above that an absorbance close to the rollover absorbance would be ambiguous, indicating one of two different concentrations.

6.2.4 Adaption of thermal atomisation programmes for the analysis of organic solutions.

Solvent extraction of precious metal complexes into 1,2-dichloroethane (DCE) or chloroform (Chapter 5) was used as a method of separating analytes away from interfering elements co-extracted by the aqua regia leach. The form of the precious metals in these solutions (as chlorocomplex species) was different to that in aqueous solutions. These different species may have stabilised the analyte during thermal pretreatment such that the analyte was not reduced to the metal at the same temperature used for ashing aqueous solutions. Alternatively, this new species may have been more volatile than the analyte itself, which would lead to loss of analyte if thermal pretreatment was carried out at a too high temperature. Consequently, consideration must be given as to whether it may be necessary to adapt the thermal atomisation programmes.

To account for the different volatilities of the solvents used, the drying temperatures were reduced and the drying times extended. The parameters used are presented in Table 6.7.

Table 6.7. Lengths of drying times and drying temperatures used for the 3 solvents examined (aqueous, 1,2-dichloroethane (DCE) and chloroform).

Heating stage	parameter	solvent aqueous	solvent DCE	solvent chloroform
Drying 1	Temperature / °C	90	70	50
	ramp time / s	1	1	1
	hold time / s	9	9	9
Drying 2	Temperature / °C	130	90	60
	ramp time / s	10	10	10
	hold time / s	15	20	20

Absorption profiles similar to those obtained from aqueous solutions were generated from the analysis of both DCE and chloroform using thermal atomisation programmes that had had only the drying stages altered. No further optimisation of the programmes was attempted because it was found that a satisfactory comparison of absorbances between organic extracts, aqueous raffinates and aqueous standards could be made by using the same thermal pretreatment and atomisation programmes. The only exception to this was the determination of Au from organic extracts.

Atomisation of Au at 1600 °C from solutions containing containing excess Fe, Ni and Cu resulted in no appreciable absorption; the presence of one or more of these metals prevented the atomisation of Au at this temperature or had caused near-total removal of the Au during ashing. However, a well defined atomic absorption peak was produced with atomisation above 2000 °C. Maximum peak area was observed at different temperatures in different sets of runs, but, atomisation at 2300 °C produced optimum signal for analysis of the DCE extracts of these solutions. The aqueous standards and raffinates were then re-analysed with atomisation at 2300 °C to permit a comparison of absorbances and an estimation the degree of extraction.

6.3 Long-term precision.

Long-term precision of the Zeeman instrument was monitored by running one standard solution (prepared in 1987) before most day's analytical run and immediately after the tube conditioning heating cycles. This solution was a simple dilution of 2.5 ml (1000 µg/ml) AAS standard stock solution of Pt (BDH Spectrosol AAS solution in 0.2% HNO_3) into 500 ml with deionised water with no interferents; the concentration was 5 µg/l. This solution was analysed at quarter dilution, i.e. 1.25 µg/l by mixing 5 µl with 15 µl deionised water in the graphite furnace.

The programme used for analysis of the simple Pt solution remained the same throughout its use, comprising of the manufacturer's recommendations for slow drying steps with ashing at 1300°C and atomisation at 2650°C. The reproducibility test was run on nearly all the tubes immediately after tube conditioning and before most analytical batches. Figure 6.3 shows the absorbances derived from these measurements plotted against the number of heating cycles that each tube had undergone., The distribution of these.data is depicted in the histogram shown in Figure 6.4.

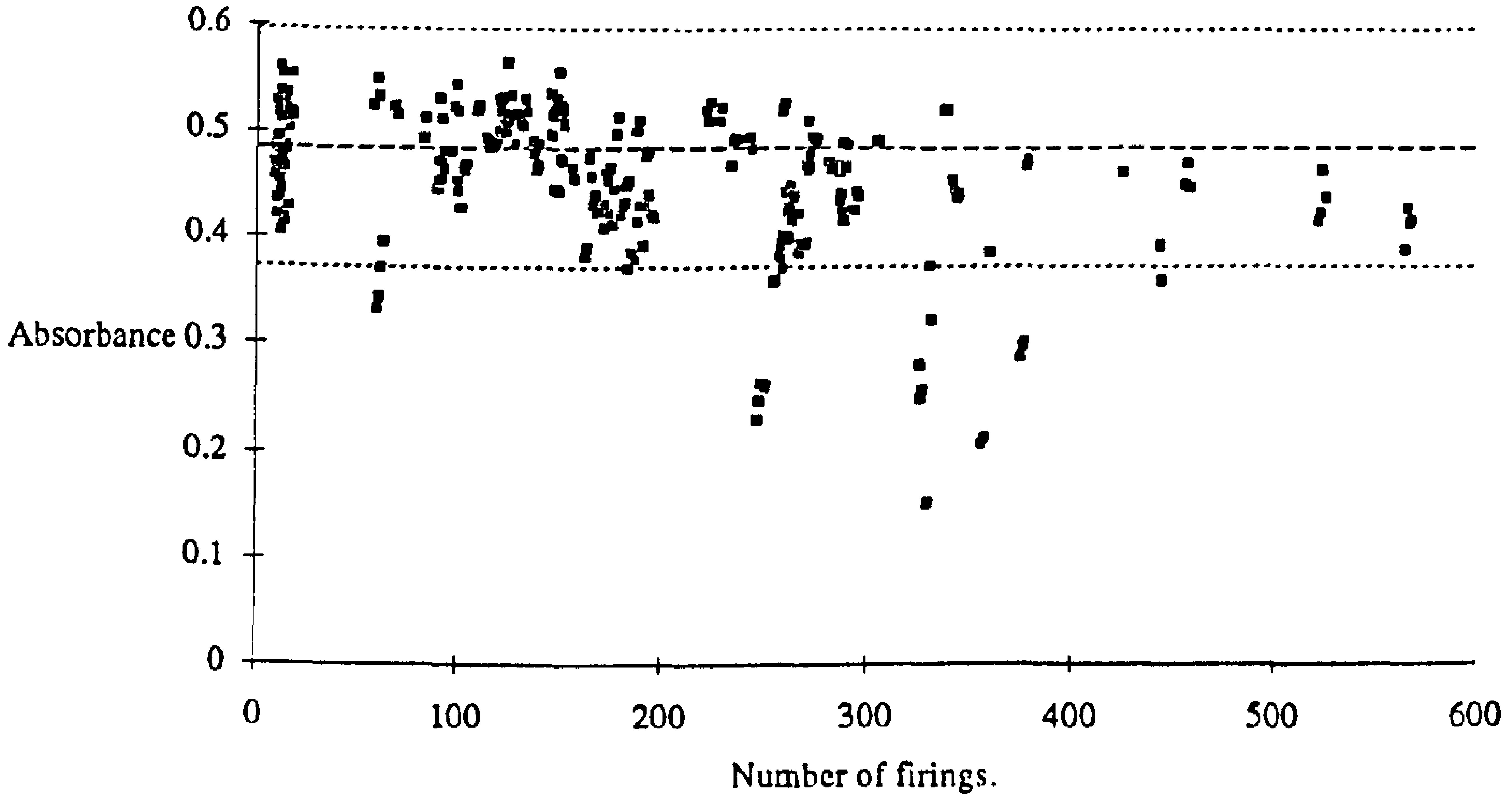


Figure 6.3. Plot of absorbance of the Pt solution against number of tube firing cycles. Data from 20 tubes are plotted onto the same axis. The dashed line represents the mean and the dotted lines the mean ± 3 standard deviation limits derived from the cycles<20 data sub-set.

From Figure 6.3 it can be seen that instrument sensitivity decreased gradually with increased tube age and that this decrease became more rapid after 300-350 heating cycles. Indeed, rarely was analysis attempted with a tube that had undergone more than 300 cycles.

To test the significance of the gradual decrease in sensitivity with time and to identify the reproducibility of data generated form different tubes, a statistical examination of the data generated from the tubes with <300 heating cycles was made to test for normality of the data set and to compare the variability in absorbance data generated from each tube with those generated from different tubes. Within this data set there is a sub-set of data generated from tubes that had undergone <20 heating cycles, i.e. those analyses made immediately after tube conditioning. This sub-set was examined in the same way as the larger data set. The distribution of both these data sets are depicted in Figure 6.4, superimposed upon the histogram of the whole data set. The black-coloured, <20 firings data set is superimposed upon the grey-coloured, <300 firings data set which is superimposed upon the white shaded complete data set.

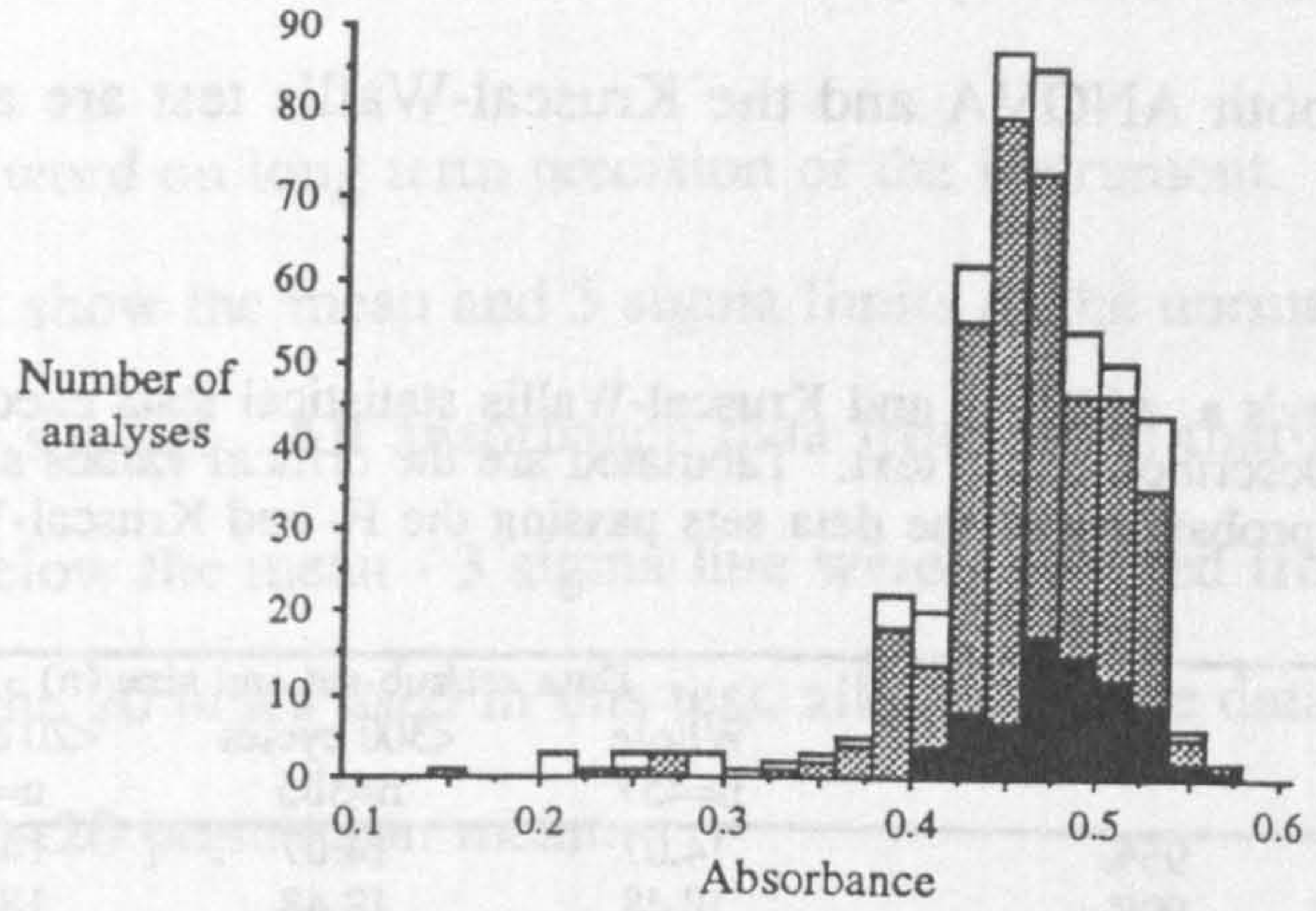


Figure 6.4. Histograms of Pt reproducibility data; all analyses (white), analyses when the tube had undergone <300 firings (grey), and analyses when the tube had undergone <20 firings (black). The three histograms are superimposed upon each other.

6.3.1 Statistical tests used in the examination of data.

These statistical tests and their usage are further explained in Section 8.3.2. The data was first tested by the chi-square test and Geary's a-Test for normality and secondly by Analysis of Variance (ANOVA) followed by the F-test or the Kruscal-Wallis test to examine the variability of the data. Results of the statistical tests are shown in Table 6.8.

Application of the chi square test using 8 categories showed that χ^2 was less than the critical value at the 95% confidence limit for 7 degrees of freedom only for the cycles <20 data set, but χ^2 was less than the 99% confidence limit for 7 degrees of freedom for the cycles <300 data set. Application of Geary's test identified non-normality at the 99% confidence level for the cycles <300 data set. One of the prerequisites of ANOVA is a normally distributed data set (see Section 8.3.2), so the F-ratio was calculated only for the cycles <20 and cycles<300 data set. A non-parametric test, analogous to ANOVA, was performed on the entire data set and, due to its possible non-normal nature, the cycles <300 data set. The F-value and the associated probability of there being no difference between the variability of data from each tube and the variability of data between the tubes for both ANOVA and the Kruscal-Wallis test are also presented in Table 6.8.

Table 6.8. Chi square (X^2), Geary's a, ANOVA and Kruscal-Wallis statistical tests executed on the three different data sets/sub-sets described in the text. Tabulated are the critical values and calculated values of the parameters and the probability of the data sets passing the F- and Kruscal-Wallis tests.

			Data set/sub-set and size (n)		
			Whole n=457	<300 cycles n=385	<20 cycles n=75
Chi squared test	critical values	95%	14.07	14.07	14.07
		99%	18.48	18.48	18.48
	calculated χ^2		52.0	145	11.1
Geary's test	critical values	upper 1%	-	0.823	0.854
		upper 5%	-	0.816	0.839
		lower 5%	-	0.780	0.759
		lower 1%	-	0.773	0.741
	calculated Geary's a		-	0.742	0.804
ANOVA	critical value	95%	-	$F_{(365,19)} = 1.9$	$F_{(57,17)} = 2.06$
	calculated F-value		-	30.5	1.27
	calculated Probability		-	0.0001	0.243
Kruscal-Wallis	calculated Probability		0.0001	0.0001	-

Critical values were obtained from from statistical tables (Pearson and Hartley, 1966).

It can be seen from Figure 6.4 and Table 6.8 that the data obtained with fresh tubes (i.e. cycles<20) form a normal population with mean 0.481 and a standard deviation of 0.037 (CV=1.5%) and that there is no significant difference between the variability of data from each tube compared to the variability between the different tubes. This indicates that, at the 95% confidence level, there was no systematic error introduced into the analysis by using different tubes. However, there was extremely low probability of there being no such difference when the large data sets were considered; the variance between the tubes was approximately 30 times the variance of analyses from each tube.

Thus, the differences in the rates at which and the degrees to which each of the tubes deteriorated was great enough to render highly unsatisfactory the comparison of data obtained by different tubes. It is also concluded that use of tubes that had undergone 300 firings should be avoided.

6.3.2 Long term precision of the instrument.

Finally, a word on long term precision of the instrument. The horizontal lines drawn on Figure 6.3 show the mean and 3 sigma limits of the normal population defined by the cycles<20 sub-set. All absorbance data from tubes that had undergone <300 cycles that fall below the mean - 3 sigma line were measured from just one tube. Therefore, for 19 of the 20 tubes used in this test, all absorbance data fall within mean ± 3 sigma of the cycles <20 population mean.

6.4 Characterisation of interference effects.

References in the literature to interferences in precious metal determination caused by the presence of other elements show considerable variation in the degrees of enhancement or suppression (Table 6.1). Indeed, it appears that the severity of interferences may be both matrix and instrument dependent. Therefore, work was carried out to characterise interferences in this application relevant to the Perkin-Elmer Zeeman 3030 atomic absorption spectrometer. Firstly, the mutual interferences caused by the presence of the precious metals upon one another will be described. Secondly, the effects of other concomitant elements and different acids, particularly aqua regia, will be considered.

6.4.1 Mutual interference effects.

Mutual interference effects were studied from two perspectives. Firstly in comparison to work by Everett (1976), using the same concentrations of analyte and interferent elements. Secondly using solutions of the precious metals approximating to natural chondrite abundances: chondrite approximating to ratios that are found in actual geological samples. The concentration of analyte in each of the solutions was adjusted to be approximately in the middle of the linear working range of the atomic absorption spectrometer. The solutions were prepared in three different solutions; deionised water, 0.29% v/v HNO_3 and 0.56% v/v HCl.[7] The differences between the effects of these solutions will be discussed in this section, the effects of each solvent on the analyte elements will be discussed in Section 6.4.3.

6.4.1.1 Comparison with previous work.

Single element solutions were prepared for Au, Pd, Pt, Rh, Ru and Ir at 250, 50, 10 and 2 µg/ml, these solutions will be referred to as the interferent solutions. Also solutions were prepared for Pt and Ir at 5 and 1 µg/ml, Ru at 1 and 0.2 µg/ml and Pd and Rh at 0.2 and 0.04 µg/ml, these solutions will be referred to as the analyte solutions. The solutions containing Pt and Au were prepared as dilutions of Spectrosol AAS standard solutions (BDH). Water soluble Specpure powders (JMC) were used to prepare stock solutions of the other elements by dissolving the required mass of each powder in 50 ml deionised water to form 250 µg/ml solutions (Pd: 0.0334 g $(NH_4)_2PdCl_4$, Rh: 0.0482 g $(NH_4)_3RhCl_6.1\frac{1}{2}H_2O$, Ru: 0.0411 g $(NH_4)_2Ru(H_2O)Cl_5$, Ir: 0.292 g $(NH_4)_2IrCl_6$). The more concentrated, interferent, solutions were prepared before the analytical run and, because of the fear of solution degradation, the analyte solution dilutions were made during the analytical run of the previous analyte.

To permit drift correction during each analytical run, the analyte solutions without interferents were analysed before and after the sets of five samples that had added

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[7] These vol/vol concentrations correspond to mass/vol concentrations of 0.2%.

interferents. In fact drift was significant for only Ir (5 ng). Analyte solutions (5 µl) were analysed with added interferent solutions (10 µl) and the total volume of analyte sample solution was made up to 20 µl with deionised water (5 µl).

Table 6.9. Absorbance values of precious metal analyte solutions at two different concentrations compared with the degree of interference caused by a 100-fold excess of other precious metals. Also reported, for comparison, are the relative interferences reported by Everett (1976) who used a carbon rod atomiser and the same solution concentrations.

Interferent	Analyte .	Pd	Pd	Pt	Pt	Rh	Rh	Ru	Ru	Ir	Ir
	conc. (ng/5µl)	1	0.2	25	5	1	0.2	5	1	25	5
None	Abs.	142	25	451	94	221	44	388	79	293	56
Au	Abs.	167	31	446	102	262	51	354	49	332	64
	rel. intf.	+18%	+25%	-1%	+8%	+19%	+16%	-9%	-38%	+13%	+14%
	E76	0%	+35%	-35%	0%	-10%	0%	-60%	-15%	-45%	-30%
Pd	Abs.	–	–	470	103	242	48	411	68	306	73
	rel. intf.	–	–	+4%	+9%	+9%	+9%	+6%	-14%	+4%	+30%
	E76	–	–	-20%	0%	-5%	0%	-30%	0%	-50%	-10%
Pt	Abs.	147	25	–	–	265	54	459	68	266	66
	rel. intf.	+4%	-2%	–	–	+20%	+22%	+18%	-14%	-9%	+17%
	E76	0%	+25%	–	–	-35%	+10%	-30%	+20%	-25%	-10%
Rh	Abs.	153	27	419	90	–	–	387	46	334	66
	rel. intf.	+8%	+7%	-7%	-4%	–	–	0%	-42%	+14%	+18%
	E76	+20%	+40%	-65%	0%	–	–	-20%	+5%	-20%	0%
Ru	Abs.	139	26	433	99	233	44	–	–	292	55
	rel. intf.	-2%	+5%	-4%	+6%	+5%	+1%	–	–	-1%	-2%
	E76	0%	+10%	-70%	-30%	-30%	+5%	–	–	-75%	-10%
Ir	Abs.	133	22	460	99	293	51	206	47	–	–
	rel. intf.	-6%	-12%	+2%	+6%	+32%	+15%	-47%	-40%	–	–
	E76	+5%	+30%	-80%	0%	-40%	0%	-55%	0%	–	–

Abs.: drift corrected absorbance reading from GFAAS (this work).
rel. intf.: relative interference compared to interference-free solution.
E76: relative interference reported by Everett (1976).

Wall atomisation was used for all elements, peak height was monitored for Pd, Rh and Ru and peak area for Pt and Ir. The mass of analyte introduced into the furnace, the absorbances of the sample solutions and the relative interferences are reported in Table 6.9. Evaluation of GFAAS results is shown by element below, a comparison to results from Everett (1976) is made at the end of this section:

Palladium: The presence of Au enhanced the signal of Pd at both concentrations studied. Interference from the other metals was <10%. The value tabulated for the Ir interference (-12%) may have been accentuated by the uncertainties in the low absorbance readings.

Platinum: The determination of Pt seemed to be unaffected to a significant extent by the presence of the other elements at the concentrations studied.

Rhodium: The presence of Au, Pt and Ir presented a positive interference (signal enhancement) on the determination of Rh, the positive interference due to the presence of Pd and Ru was not much smaller. There is good agreement in the degree of interference between the two analyte concentrations studied.

Ruthenium: The presence of Au, Rh and Ir resulted in a negative interference (depression of signal) on the determination of Ru, the magnitude of the interference being greater for the less concentrated of the two analyte solutions. The effects of Pd and Pt were more confusing: the presence of these elements appeared to enhance the atomic absorption signal at the higher concentration and to depress the signal at the lower analyte concentration studied.

Iridium: The presence of Au, Pd and Rh resulted in a positive interference in the determination of Ir, the effect of Pd was more pronounced at the lower concentration studied. Interference by Pt was positive at the lower analyte concentration and slightly negative at the higher analyte concentration. Ru did not interfere in the determination of Ir.

There is very poor correlation between these results and those of Everett (1976). Only one pair of results showed similarity (Ru interference on Pd). Only three individual results show a degree of similarity (Au on Pd, Pt on Rh, Ir on Ru). There are a number of results for the lower analyte concentration samples, that show minimal interference effects. It is of note that the large negative interferences reported by Everett (1976) in the determination of Pt were absent under the studied conditions and that a number of the interferences observed had a different effect to those previously reported (e.g. Au on Ir).

Everett (1976) noted that a reduction in the absolute concentration of interferent resulted in the removal of large negative interferences observed with the more concentrated analyte solutions. This pattern is present in the results obtained here for only one combination (Pt on Ir) and is absent for most of the other pairings. This pattern is reversed for Au, Pd, Rh and Pt on Ru, where a reduction in the absolute concentration of interferents led to a more severe negative interference, although this result may have been influenced by the fact that the mass of Ru used in the analysis (1.0 ng) was close to the detection limit for Ru. In these circumstances the presence of interferents in the sample solutions would lead to a significantly increased background, which might swamp the analytical signal.

The differences between these results and those reported by Everett (1976) could be due to different graphite atomisers (HGA vs CRA), different sheath gases (Ar vs N_2), different thermal atomisation programmes and/or different interference reactions. In terms of analysis of geological materials, the 100-fold excess examined here was largely academic as it is extremely unlikely to encounter a situation where, for example, Rh concentration is 100 times that of Pd. However, there are significant similarities between this work with that of Everett (1976), in particular the positive interferences of Au on Rh and Ir, Pd on Ir and Pt on Rh and the negative interference of Au on Ru. Such combinations, and all other combinations at more realistic relevant concentrations have been studied further and will be discussed below.

6.4.1.2 Mutual interferences at relative chondrite abundance levels.

Stock solutions were prepared in the same way as above, Au and Pt as dilutions of SpectrosoL AAS standard solutions and Pd, Rh, Ru and Ir as dissolutions of JMC Specpure powders in deionised water. The concentrations of the analyte solutions are given in Table 6.10 together with the interferent element solution concentrations used for each analyte and the natural chondrite abundance levels (Naldrett and Duke, 1980). Each analyte solution had added to it every combination of the other five precious metals, from single element solutions up to an interferent solution containing all five elements. Interferent solutions prepared for Ru and Rh were respectively $\frac{2}{25}$ and $\frac{1}{10}$ dilutions of the solutions prepared for Ir, likewise, Pd and Au solutions were respectively $\frac{1}{5}$ and $\frac{1}{2}$ dilutions of the solutions prepared for Pt. Thus, the interferent solutions used in the determination of Ir and Pt were always freshly prepared, those used for the determination of Ru and Pd were generally 6-24 hours old and those used in the determination of Rh and Au were over 24 hours old.

Table 6.10. Concentration of analyte solutions (µg/l) and the concentrations of interferent elements (µg/l). Natural chondrite abundance levels (Naldrett and Duke, 1980) are also reported. In each analysis, the analyte was at the concentration specified in the first row of data and each interferent was used at the concentration specified in the corresponding row in the lower part of the table. The interferent was at a different concentration for each analyte, but the ratio of interferent-to-analyte was always the same as that observed in chondrite. The concentrations of the analytes were selected to be within the linear concentration range for each analyte.

	Ir	Ru	Rh	Pt	Pd	Au
Analyte concentration	1590	204	48	1000	106	75

Interferent concentration for each analyte	analyte Ir	analyte Ru	analyte Rh	analyte Pt	analyte Pd	analyte Au	Chondrite abundance (ppb)
Ir	–	159	127	530	106	270	540
Ru	2040	–	163	680	136	340	690
Rh	600	60	–	200	40	100	200
Pt	3000	300	240	–	200	500	1020
Pd	1590	159	127	530	–	270	545
Au	450	45	36	150	30	–	152

The analyte solution, sans interferents, was analysed regularly throughout each analytical run to monitor drift in instrument sensitivity and possible evaporation of solvent from the sample cups. Each of the samples was analysed in duplicate. If agreement between duplicate analyses was not acceptable, the relevant combination of interferents was re-analysed after the full run. The analyte solution (10 µl) was analysed together with the relevant interferent solution (10 µl). Both peak height and peak area were monitored for all elements to to allow full interpretation of the interference effects. Platform atomisation was used for the determination of Pd and Au, although Au was determined without the aid of a matrix modifier.

The mutual interference effects of the precious metals will be considered by analyte below, together with comments on the effects of an acid matrix. In the associated tables (Tables 6.11-6.16), the mean absorbance values of the duplicate analyses are shown together with the relative interference of each the of combinations.

Table 6.11. Mean absorbance values (Abs.) and the relative interference (R.I.), due to all combinations of the other precious metals, of duplicate analyses (both peak height and peak area data) for the determination of Ir in 3 different solution matrices (H_2O, HNO_3 and HCl). The concentration of each interferent is presented in Table 6.10.

	H_2O	H_2O	H_2O	H_2O	HNO_3	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl
	area	area	height	height	area	area	height	height	area	area	height	height
Interferent	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.
none	287		384		242		384		251		345	
Ru	280	-2%	369	-4%	233	-4%	415	8%	242	-4%	336	-3%
Rh	284	-1%	460	20%	249	3%	443	15%	248	-1%	479	39%
Pt	281	-2%	447	16%	246	2%	420	9%	242	-4%	513	49%
Pd	289	1%	431	12%	250	3%	427	11%	246	-2%	543	57%
Au	286	0%	379	-1%	246	2%	402	5%	257	2%	417	21%
Ru Rh	274	-5%	448	17%	233	-4%	419	9%	245	-2%	385	11%
Ru Pt	273	-5%	397	3%	227	-6%	413	7%	236	-6%	480	39%
Ru Pd	279	-3%	471	23%	229	-6%	418	9%	241	-4%	511	48%
Ru Au	280	-2%	382	-1%	224	-8%	408	6%	242	-4%	414	20%
Rh Pt	279	-3%	432	13%	229	-5%	399	4%	245	-2%	492	43%
Rh Pd	289	1%	451	17%	244	1%	408	6%	252	0%	524	52%
Rh Au	285	-1%	446	16%	238	-2%	413	8%	251	0%	501	45%
Pt Pd	279	-3%	450	17%	234	-3%	400	4%	247	-2%	502	46%
Pt Au	283	-1%	429	12%	231	-5%	391	2%	248	-1%	488	41%
Pd Au	287	0%	434	13%.	239	-1%	395	3%	254	1%	497	44%
Ru Rh Pt	282	-2%	445	16%	224	-7%	385	0%	236	-6%	450	30%
Ru Rh Pd	278	-3%	467	22%	231	-5%	400	4%	244	-3%	500	45%
Ru Rh Au	294	2%	407	6%	226	-6%	395	3%	245	-3%	441	28%
Ru Pt Pd	283	-1%	453	18%	224	-8%	395	3%	233	-7%	473	37%
Ru Pt Au	288	0%	421	10%	226	-7%	389	1%	239	-5%	459	33%
Ru Pd Au	283	-1%	452	18%	227	-6%	387	1%	246	-2%	507	47%
Rh Pt Pd	281	-2%	460	20%	235	-3%	381	-1%	245	-2%	484	40%
Rh Pt Au	278	-3%	432	13%	235	-3%	388	1%	246	-2%	467	35%
Rh Pd Au	284	-1%	467	22%	239	-1%	385	0%	247	-2%	496	44%
Pt Pd Au	278	-3%	457	19%	234	-3%	378	-2%	247	-1%	477	38%
Ru Rh Pt Pd	281	-2%	487	27%	228	-6%	387	1%	232	-8%	483	40%
Ru Rh Pt Au	276	-4%	452	18%	232	-4%	400	4%	241	-4%	469	36%
Ru Rh Pd Au	278	-3%	473	23%	226	-7%	383	0%	241	-4%	512	49%
Ru Pt Pd Au	276	-4%	465	21%	219	-9%	378	-1%	235	-6%	485	41%
Rh Pt Pd Au	272	-5%	443	15%	227	-6%	367	-4%	244	-3%	485	40%
Ru Rh Pt Pd Au	270	-6%	457	19%	223	-8%	391	2%	234	-7%	486	41%

Iridium (Table 6.11). The presence of other precious metals on the determination of Ir resulted in a minimal decrease in the area of the absorption peak, the maximum value being 6% decrease of absorbance signal when all the interferents were present. The height of the absorbance peak was more susceptible to the effect of the various elements upon Ir. Most combinations of elements resulted in an enhancement of peak height of 10-25%. Notably, neither Ru nor Au offered an increased peak height and combinations of interferents containing both these elements showed the least increase in heights. The presence of Pd was associated with the greatest increases in peak heights, often eliminating the negative effects of Ru and Au.

With a dilute HNO_3 matrix the negative effect of all combinations of interferents except individual elements (Rh, Pt, Pd, Au) either remained the same or was slightly accentuated. The peak height did not show such a significant enhancement as was found with the water solutions of the mixed interferents and there was no significant enhancement/depression of the signal from solutions containing more than two interferents. The single element interferent solutions demonstrated some enhancement of peak height, Rh, Pd and Pt showing less of an enhancement than in the water matrix. Most notably, the Ru and Au interference seemed to enhance the peak height rather than to depress it and the depressive effects of these elements on the signal were less apparent when all the mixtures are considered.

The effects of the interfering elements upon Ir in a dilute HCl matrix was very similar to that in the water solution although Ru and Pt and their combination arguably caused slightly more severe depression of signal. The interferents in an HCl matrix caused significantly greater enhancement of the peak height with the sole exception of Ru alone. The enhancing effect of Pd is further stressed and the depressive effects of Ru and Au is again evident, although to a lesser extent.

In summary, the presence of HCl and Pd in a solution to be analysed for Ir was beneficial in terms of increasing the sensitivity and promoting a more rapid atomisation Ir (a significantly taller peak with no change in peak area). Solutions without Pd and a higher concentration of Au or, particularly, Ru may lead to incorrectly low results.

However, to minimise the influence of these interferences, it is advisable to use peak area measurements as these are much less susceptible to the interference effects that are so apparent in peak height measurements.

Table 6.12. Mean absorbance values (Abs.) and the relative interference (R.I.), due to all combinations of the other precious metals, of duplicate analyses (both peak height and peak area data) for the determination of Ru in 3 different solution matrices (H_2O, HNO_3 and HCl). The concentration of each interferent is presented in Table 6.10.

	H_2O	H_2O	H_2O	H_2O	HNO_3	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl
	area	area	height	height	area	area	height	height	area	area	height	height
Interferent	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.
none	137		152		224		335		234		317	
Ir	132	-3%	152	0%	219	-2%	342	2%	232	-1%	319	1%
Rh	133	-3%	149	-2%	218	-3%	328	-2%	233	0%	318	0%
Pt	136	-1%	154	1%	228	2%	343	3%	230	-2%	315	-1%
Pd	136	-1%	150	-1%	225	1%	335	0%	236	1%	328	3%
Au	136	-1%	153	1%	227	2%	334	0%	235	0%	334	5%
Ir Rh	139	2%	154	1%	222	-1%	330	-2%	237	1%	349	10%
Ir Pt	140	2%	154	1%	233	4%	362	8%	236	1%	331	4%
Ir Pd	138	1%	149	-2%	224	0%	340	2%	235	1%	327	3%
Ir Au	140	2%	157	3%	229	2%	351	5%	235	0%	319	1%
Rh Pt	139	2%	153	1%	233	4%	353	5%	238	2%	338	7%
Rh Pd	137	0%	153	1%	221	-1%	329	-2%	237	1%	329	4%
Rh Au	138	1%	151	0%	230	3%	342	2%	236	1%	323	2%
Pt Pd	140	2%	155	2%	210	-6%	313	-6%	235	0%	321	1%
Pt Au	138	1%	153	1%	229	2%	346	3%	233	0%	312	-2%
Pd Au	139	1%	152	0%	213	-5%	317	-5%	232	-1%	310	-2%
Ir Rh Pt	141	3%	152	0%	229	2%	340	1%	232	-1%	315	0%
Ir Rh Pd	139	1%	155	2%	221	-1%	328	-2%	230	-2%	302	-5%
Ir Rh Au	141	3%	154	1%	232	4%	334	0%	232	-1%	317	0%
Ir Pt Pd	142	4%	162	6%	231	3%	339	1%	236	1%	311	-2%
Ir Pt Au	143	5%	156	3%	225	1%	342	2%	238	2%	320	1%
Ir Pd Au	144	5%	160	6%	221	-1%	315	-6%	234	0%	325	2%
Rh Pt Pd	144	5%	162	6%	214	-5%	314	-6%	231	-1%	323	2%
Rh Pt Au	146	7%	162	6%	220	-2%	313	-7%	236	1%	324	2%
Rh Pd Au	145	6%	161	6%	222	-1%	329	-2%	234	0%	327	3%
Pt Pd Au	145	6%	158	4%	200	-11%	284	-15%	233	0%	326	3%
Ir Rh Pt Pd	143	5%	161	6%	208	-7%	299	-11%	229	-2%	312	-1%
Ir Rh Pt Au	138	1%	151	-1%	226	1%	330	-2%	231	-1%	313	-1%
Ir Rh Pd Au	141	3%	162	6%	228	2%	326	-3%	236	1%	329	4%
Ir Pt Pd Au	138	1%	152	0%	210	-6%	314	-6%	234	0%	332	5%
Rh Pt Pd Au	139	2%	150	-2%	201	-10%	298	-11%	238	2%	339	7%
Ir Rh Pt Pd Au	139	1%	151	0%	209	-7%	223	-33%	236	1%	329	4%

Ruthenium (Table 6.12). The greatest enhancement of the absorption signal of Ru was 6-7%, exhibited by a few of the triple interferent combinations but there seems to be no associated enhancement of the signals with the four or all five interferent elements. The presence of any other precious metal has an insignificant effect on the absorption of Ru. The effects of the other precious metals, when in a matrix of HNO_3, on the absorption of Ru was not too different except that the combination of Pt and Pd with or without Au and/or Rh caused slight depression of signal. This depression of peak height is most significant when all five precious metals were present. None of the previously described interferences were observed when the matrix was HCl, the only outstanding result being the 10% height enhancement of signal with Ir and Rh. This enhancement was not corroborated by either of the single element tests nor by any of the triple element combinations.

In summary, determination of Ru appeared to be independent of matrix, although care should be taken when analysing solutions enriched in Pd and Pt in HNO_3. It was noticeable that the influence on both peak area and height is generally similar. This observation indicated that the interference mechanism controlling the rate of atomisation involved in Ir determination was not evident in Ru determination.

Rhodium (Table 6.13). The only outstanding interference on Rh in sample aqueous solutions was that caused by Ru and Pt on the peak height (7%). This interference was not apparent in any of the other combinations including Ru and Pt. The presence of HNO_3 increased the depressive interference effect of virtually all combinations of interfering elements. This interference was greatest when the combination of interfering elements were Ru + Pt, Ir + Pd, Pt + Pd and Ir + Pt + Pd and especially all five of the precious metals. None of the interferences due to the above or any combination of interfering elements were apparent when analysing solutions with a matrix of HCl.

Table 6.13. Mean absorbance values (Abs.) and the relative interference (R.I.), due to all combinations of the other precious metals, of duplicate analyses (both peak height and peak area data) for the determination of Rh in 3 different solution matrices (H_2O, HNO_3 and HCl). The concentration of each interferent is presented in Table 6.10.

	H_2O	H_2O	H_2O	H_2O	HNO_3	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl
	area	area	height	height	area	area	height	height	area	area	height	height
Interferent	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.
none	167		281		139		207		125		169	
Ir	163	-2%	279	-1%	132	-5%	199	-4%	126	1%	172	2%
Ru	165	-1%	284	1%	138	-1%	208	0%	127	2%	171	1%
Pt	164	-2%	280	0%	135	-3%	200	-4%	125	0%	167	-1%
Pd	166	-1%	281	0%	133	-4%	199	-4%	124	-1%	168	0%
Au	164	-2%	279	-1%	135	-3%	197	-5%	122	-2%	169	0%
Ir Ru	165	-1%	291	4%	139	0%	208	1%	125	0%	170	1%
Ir Pt	166	-1%	288	2%	135	-3%	195	-6%	125	0%	169	0%
Ir Pd	165	-1%	288	2%	130	-7%	194	-6%	126	1%	169	0%
Ir Au	167	0%	291	4%	143	3%	206	0%	126	1%	168	-1%
Ru Pt	170	2%	301	7%	130	-6%	193	-7%	125	0%	166	-2%
Ru Pd	167	0%	289	3%	133	-4%	200	-3%	127	2%	170	0%
Ru Au	167	0%	285	2%	136	-2%	199	-4%	125	0%	168	-1%
Pt Pd	164	-2%	280	0%	132	-5%	193	-7%	124	-1%	163	-4%
Pt Au	164	-2%	277	-1%	140	1%	204	-2%	125	0%	169	0%
Pd Au	166	-1%	285	1%	135	-3%	199	-4%	125	0%	163	-3%
Ir Ru Pt	165	-1%	285	2%	140	1%	201	-3%	124	-1%	171	1%
Ir Ru Pd	168	1%	287	2%	135	-3%	203	-2%	126	0%	167	-1%
Ir Ru Au	165	-1%	283	1%	137	-2%	204	-1%	127	1%	170	1%
Ir Pt Pd	164	-2%	282	0%	131	-6%	192	-7%	126	0%	168	-1%
Ir Pt Au	165	-1%	280	0%	137	-1%	201	-3%	126	1%	170	1%
Ir Pd Au	164	-2%	276	-2%	136	-2%	205	-1%	125	0%	172	2%
Ru Pt Pd	163	-3%	279	-1%	133	-4%	196	-5%	127	2%	171	1%
Ru Pt Au	164	-2%	277	-2%	135	-3%	197	-5%	128	2%	175	4%
Ru Pd Au	165	-1%	284	1%	133	-5%	201	-3%	126	0%	171	1%
Pt Pd Au	165	-1%	276	-2%	136	-2%	205	-1%	126	1%	168	0%
Ir Ru Pt Pd	167	0%	281	0%	133	-4%	200	-3%	127	1%	172	2%
Ir Ru Pt Au	166	-1%	284	1%	137	-1%	209	1%	125	0%	176	4%
Ir Ru Pd Au	165	-1%	281	0%	134	-3%	202	-2%	127	2%	169	0%
Ir Pt Pd Au	166	-1%	279	-1%	136	-2%	204	-2%	128	3%	167	-1%
Ru Pt Pd Au	164	-2%	275	-2%	132	-5%	195	-6%	124	-1%	162	-4%
Ir Ru Pt Pd Au	164	-2%	278	-1%	129	-7%	192	-7%	124	-1%	165	-2%

In summary, determination of Rh by AAS seemed to be influenced to only a very small extent by interference due to the other precious metals. Care should be taken when analysing solutions in HNO_3, it being preferable to determine Rh from HCl solution.

Table 6.14. Mean absorbance values (Abs.) and the relative interference (R.I.), due to all combinations of the other precious metals, of duplicate analyses (both peak height and peak area data) for the determination of Pt in 3 different solution matrices (H_2O, HNO_3 and HCl). The concentration of each interferent is presented in Table 6.10.

	H_2O	H_2O	H_2O	H_2O	HNO_3	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl
	area	area	height	height	area	area	height	height	area	area	height	height
Interferent	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.
none	241		476		206		399		143		246	
Ir	239	-1%	479	1%	205	-1%	403	1%	143	0%	243	-1%
Ru	234	-3%	483	2%	199	-3%	399	0%	147	3%	251	2%
Rh	234	-3%	471	-1%	196	-5%	394	-1%	145	2%	252	2%
Pd	238	-1%	468	-2%	206	0%	400	0%	152	6%	264	7%
Au	240	0%	468	-2%	206	0%	402	1%	144	0%	249	1%
Ir Ru	238	-1%	485	2%	203	-1%	400	0%	144	1%	305	24%
Ir Rh	236	-2%	465	-2%	204	-1%	403	1%	149	4%	305	24%
Ir Pd	239	-1%	471	-1%	203	-1%	397	0%	152	6%	301	22%
Ir Au	238	-1%	468	-2%	205	-1%	404	1%	151	6%	296	20%
Ru Rh	235	-3%	470	-1%	201	-2%	399	0%	149	4%	285	16%
Ru Pd	236	-2%	469	-1%	203	-2%	405	2%	151	6%	285	16%
Ru Au	237	-2%	469	-1%	202	-2%	395	-1%	150	5%	279	13%
Rh Pd	239	-1%	473	-1%	202	-2%	396	-1%	149	4%	267	9%
Rh Au	239	-1%	475	0%	206	0%	402	1%	145	1%	267	9%
Pd Au	241	0%	472	-1%	201	-2%	389	-3%	144	1%	256	4%
Ir Ru Rh	238	-1%	476	0%	202	-2%	395	-1%	145	1%	257	5%
Ir Ru Pd	238	-1%	473	-1%	198	-4%	386	-3%	149	4%	261	6%
Ir Ru Au	239	-1%	474	0%	198	-4%	388	-3%	148	4%	262	7%
Ir Rh Pd	238	-1%	475	0%	200	-3%	389	-3%	158	10%	272	11%
Ir Rh Au	239	-1%	482	1%	205	0%	390	-2%	157	10%	274	11%
Ir Pd Au	240	0%	482	1%	199	-3%	392	-2%	161	12%	272	11%
Ru Rh Pd	239	-1%	479	1%	199	-3%	389	-2%	158	10%	274	11%
Ru Rh Au	239	-1%	474	0%	197	-4%	377	-5%	152	7%	263	7%
Ru Pd Au	239	-1%	474	0%	203	-1%	396	-1%	158	10%	272	10%
Rh Pd Au	240	-1%	470	-1%	207	0%	401	1%	166	16%	285	16%
Ir Ru Rh Pd	240	0%	478	0%	207	1%	398	0%	155	8%	265	8%
Ir Ru Rh Au	239	-1%	478	0%	198	-4%	393	-2%	143	0%	249	1%
Ir Ru Pd Au	242	0%	487	2%	202	-2%	399	0%	156	9%	271	10%
Ir Rh Pd Au	241	0%	489	3%	202	-2%	391	-2%	157	10%	270	10%
Ru Rh Pd Au	240	0%	486	2%	199	-3%	393	-2%	149	5%	257	4%
Ir Ru Rh Pd Au	240	0%	485	2%	204	-1%	402	1%	148	4%	256	4%

Platinum (Table 6.14). Determination of Pt in aqueous solution did not appear to be subject to any significant interferences. Interferences in the determination of Pt from HNO_3 solution were also minimal although a slight tendency for depressive effects was observed in comparison with simple aqueous solutions. Interferences in the determination of Pt from HCl solution, however, were far more significant than those in the other two matrices. The peak area was increased by 10% for combinations of four interfering elements, except notably, that without Pd, and for combinations of three interfering elements containing Pd with Au or Rh. The peak area was not significantly increased for any of the single or double interferent combinations, nor when all five precious metals were present. Similarly, peak height increased following the same pattern as that observed from peak area for all combination of interferents, except for the pairs of interfering elements. Although the increase in peak area was not apparent when Ir and Ru were present as interfering elements, the presence of these elements caused a significantly taller peak, suggesting that Ir and/or Ru might promote the atomisation of Pt. However the enhanced peak heights were not apparent in multiple interferent solutions containing these two elements.

In summary, determination of Pt should ideally be made in HNO_3 solution to minimise the occurrence of unexpected interferences.

Table 6.15. Mean absorbance values (Abs.) and the relative interference (R.I.), due to all combinations of the other precious metals, of duplicate analyses (both peak height and peak area data) for the determination of Pd in 3 different solution matrices (H_2O, HNO_3 and HCl). The concentration of each interferent is presented in Table 6.10.

	H_2O	H_2O	H_2O	H_2O	HNO_3	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl
	area	area	height	height	area	area	height	height	area	area	height	height
Interferent	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.
none	93		75		149		110		122		93	
Ir	91	-2%	74	-1%	149	0%	111	1%	125	2%	93	0%
Ru	92	-1%	73	-2%	151	1%	111	1%	121	-1%	91	-2%
Rh	93	0%	75	-1%	150	1%	113	2%	122	0%	94	1%
Pt	101	8%	79	6%	153	3%	113	3%	122	0%	93	0%
Au	96	3%	78	4%	153	3%	112	2%	123	1%	94	1%
Ir Ru	91	-2%	75	-1%	149	0%	112	1%	122	0%	93	0%
Ir Rh	93	0%	77	2%	158	6%	116	5%	122	0%	91	-3%
Ir Pt	193	108%	147	96%	173	16%	127	16%	120	-2%	92	-1%
Ir Au	93	0%	78	4%	152	2%	111	1%	123	1%	94	1%
Ru Rh	91	-2%	74	-1%	149	0%	111	1%	120	-2%	92	-1%
Ru Pt	116	24%	91	22%	148	-1%	108	-2%	124	1%	91	-2%
Ru Au	94	1%	78	4%	148	-1%	109	-1%	121	-1%	92	-1%
Rh Pt	144	55%	112	50%	148	-1%	108	-2%	122	0%	91	-2%
Rh Au	96	3%	77	3%	149	0%	109	-1%	121	-1%	92	-1%
Pt Au	122	31%	92	23%	150	1%	111	1%	123	1%	94	1%
Ir Ru Rh	94	1%	76	1%	146	-2%	107	-2%	122	0%	93	0%
Ir Ru Pt	122	31%	95	27%	147	-1%	108	-1%	122	0%	92	-1%
Ir Ru Au	95	3%	76	1%	148	0%	110	0%	121	0%	93	0%
Ir Rh Pt	128	37%	99	33%	149	0%	110	0%	123	1%	92	-1%
Ir Rh Au	96	4%	79	5%	150	1%	110	0%	121	-1%	91	-2%
Ir Pt Au	116	25%	92	23%	148	-1%	109	-1%	123	1%	94	1%
Ru Rh Pt	123	32%	96	28%	147	-1%	110	0%	122	0%	92	-1%
Ru Rh Au	100	7%	79	5%	147	-1%	109	-1%	122	0%	92	-1%
Ru Pt Au	102	9%	80	7%	147	-2%	110	0%	123	1%	92	-1%
Rh Pt Au	109	17%	86	14%	147	-1%	109	-1%	123	1%	93	0%
Ir Ru Rh Pt	117	26%	92	22%	150	1%	110	0%	122	0%	93	0%
Ir Ru Rh Au	91	-2%	74	-2%	151	2%	111	1%	124	2%	93	0%
Ir Ru Pt Au	95	2%	77	3%	150	1%	112	2%	124	1%	93	0%
Ir Rh Pt Au	163	75%	125	67%	150	0%	112	2%	123	1%	93	0%
Ru Rh Pt Au	107	15%	86	15%	159	6%	115	5%	124	2%	92	-1%
Ir Ru Rh Pt Au	171	84%	130	73%	149	0%	112	2%	123	1%	94	1%

Palladium (Table 6.15). All significant interferences on Pd arose from combinations of interfering elements that contained Pt. There was an increase in peak size for all these interfering combinations from <20% to 108% for the combination Ir and Pt. All previous interferents containing Pt showed a positive interference with magnitude Ir > Rh > Au > Ru and this pattern was largely evident throughout the other multiple combinations, the one exception being Ir + Ru + Pt + Au which showed no significant increase in peak size. Most notably, the presence of all five precious metals resulted in a significant increase peak size.

When HNO_3 solutions were analysed, significant interference effect with combinations of precious metals including Pt was apparently only for Ir and Pt and then to a much reduced extent. None of the combinations of interfering elements exhibited any interference when HCl solutions were analysed. The presence of Pt seemed to stabilise Pd during thermal pretreatment and prevented pre-atomisation losses of the analyte from aqueous solutions. The presence of either HNO_3 or HCl also seemed to stabilise Pd in a similar way to that of Pt, such that the presence of Pt did not invoke the large increase in peak size described above.

In summary, HCl was the better acid matrix, in terms of permitting interference-free determination of Pd. Perhaps a Pd-chloro species was formed in solution that was thermally more stable than the hydrated Pd species which is present in simple aqueous solutions. Similarly a Pt-Pd species formed in aqueous solution may be more stable than the Pd species alone. The Pd-chloro species appeared to be more thermally stable, premature atomisation being avoided with or without the presence of Pt.

Table 6.16. Mean absorbance values (Abs.) and the relative interference (R.I.), due to all combinations of the other precious metals, of duplicate analyses (both peak height and peak area data) for the determination of Au in 3 different solution matrices (H_2O, HNO_3 and HCl). The concentration of each interferent is presented in Table 6.10.

	H_2O	H_2O	H_2O	H_2O	HNO_3	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl
	area	area	height	height	area	area	height	height	area	area	height	height
Interferent	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.	Abs.	R.I.
none	93		219		39		70		123		325	
Ir	109	17%	271	24%	63	61%	137	96%	257	109%	643	98%
Ru	117	26%	256	17%	59	52%	101	44%	232	89%	533	64%
Rh	119	28%	271	24%	93	139%	194	178%	216	76%	496	53%
Pt	130	40%	361	65%	136	248%	318	355%	171	39%	422	30%
Pd	88	-5%	193	-12%	66	69%	134	91%	142	16%	344	6%
Ir Ru	101	8%	279	27%	82	110%	160	129%	228	86%	553	70%
Ir Rh	116	25%	290	32%	106	171%	220	214%	244	98%	601	85%
Ir Pt	121	30%	357	63%	133	240%	317	353%	166	35%	425	31%
Ir Pd	105	13%	277	27%	100	157%	219	213%	179	45%	483	49%
Ru Rh	113	21%	277	26%	106	171%	200	186%	210	70%	557	71%
Ru Pt	117	26%	353	61%	149	281%	341	386%	167	36%	405	25%
Ru Pd	105	13%	271	24%	84	116%	135	92%	162	31%	382	18%
Rh Pt	129	38%	360	64%	153	291%	377	438%	137	11%	314	-4%
Rh Pd	113	21%	289	32%	114	192%	255	265%	141	14%	347	7%
Pt Pd	131	41%	364	66%	217	455%	422	502%	154	25%	356	9%
Ir Ru Rh	113	21%	291	33%	143	268%	269	285%	198	61%	499	54%
Ir Ru Pt	120	29%	347	58%	151	287%	347	396%	145	18%	392	21%
Ir Ru Pd	116	25%	307	40%	123	216%	269	285%	128	4%	315	-3%
Ir Rh Pt	121	30%	335	53%	161	313%	366	423%	200	63%	527	62%
Ir Rh Pd	120	29%	309	41%	127	227%	287	310%	128	4%	320	-2%
Ir Pt Pd	245	164%	433	98%	161	312%	384	449%	217	76%	518	60%
Ru Rh Pt	115	24%	319	46%	178	357%	402	475%	131	7%	316	-3%
Ru Rh Pd	121	30%	292	33%	130	234%	243	247%	133	8%	309	-5%
Ru Pt Pd	132	42%	353	61%	153	292%	365	422%	126	3%	319	-2%
Rh Pt Pd	131	41%	351	60%	139	256%	336	380%	124	1%	311	-4%
Ir Ru Rh Pt	127	36%	348	59%	143	266%	326	365%	146	19%	355	9%
Ir Ru Rh Pd	120	29%	317	45%	124	219%	265	279%	144	17%	355	9%
Ir Ru Pt Pd	122	31%	341	56%	144	269%	334	377%	155	26%	401	23%
Ir Rh Pt Pd	171	84%	468	114%	146	275%	367	425%	159	30%	411	26%
Ru Rh Pt Pd	142	52%	347	58%	143	268%	336	380%	174	41%	434	34%
Ir Ru Rh Pt Pd	126	36%	339	55%	149	282%	348	397%	194	57%	493	52%

Gold (Table 6.16). A positive interference of 17-40% was observed in the presence of any of the other precious metals except Pd which leads to a negative interference. A positive interference was shown for all combinations of two of the other elements, the most significant being those pairs that include Pt. A positive interference was shown for all multiple interferent combinations, with Ir + Pt + Pd and Ir + Rh + Pt + Pd being the most significant for the groups of three and four elements, respectively.

Analysis of solutions with HNO_3 matrix showed that the presence of all the precious metals and combinations of precious metals resulted in significant enhancement of peak size. The presence of Pt in any combination of interfering elements caused the most significant signal enhancement, and particularly Pt + Pd. The presence of the other precious metals (Ir, Ru, Rh and Pd) significantly increased the peak size although there was no correlation between the various combinations and the magnitude of the effects.

The magnitude of the enhancements caused by the precious metals in HCl solution was less than that in HNO_3 and about the same as that in water. The difference observed with HCl, however, showed that the effect of Pt was much less pronounced and that Ir, Ru and Rh and combinations of these elements showed the larger interferences. The presence of Pd in combinations with other interfering elements tended to decrease the enhancements induced by those other elements with the exception of Ir + Pt, Ir + Ru + Pt, Ru + Rh + Pt and Ir + Ru + Rh + Pt, when the presence of Pd further enhanced the effects of the other elements.

In summary, the presence of any of the other precious metals helped to stabilise Au during the thermal pretreatment, although Pd could have a negative effect, in direct contrast to its reported benefit as a "universal" matrix modifier for many other analytes (e.g. Schlemmer and Welz, 1986). The presence of HNO_3 could have beneficial effects on the Au signal, although Au can be lost from HNO_3 solution over time. The presence of Pt in solution was beneficial in terms of enhancing the Au signal, but the use of HCl solutions may reduce the benefits of Pt.

There will be a significant signal enhancement in the determination of Au from digests of natural samples. These enhancement effects will probably be due to stabilisation of Au by other metals in solution during thermal pretreatment. The addition of one metal, preferably not another analyte, in excess to act as a matrix modifier should saturate the potential enhancement of the other precious metal elements such that each analysis should be free of unquantifiable interferences. In fact, it was found that the addition of Ni as a matrix modifier (as recommended by the manufacturer) significantly enhanced the determination of Au (Section 6.2.2).

6.4.1.3 Comparison of the two mutual interference studies.

Table 6.18 reproduces the data for the relative interference of the single interferents on each analyte derived from the two mutual interference studies, described above, specifying the concentrations of the analyte elements. The annotation "cf E76" refers to work described in Section 6.4.1.1 and "chondrite" refers to work described in Section 6.4.1.2. The main difference between the two data sets, that must be taken into account before any comparison can be made, is that "cf E76" data was obtained with 100-fold excess interferent over analyte and "chondrite" data was obtained with interferent to analyte ratios approximating to chondrite ratios. These ratios are tabulated in Table 6.17. The overall trend evident from the data in Table 6.18 is that there is a minimal interference of single precious metal elements upon each other at the relative concentrations that are likely to be found in geological samples, the most significant being +6% interference of Pt on Pd.

Table 6.17. Interferent-to-analyte ratios (approximating to chondrite ratios) used in "chondrite" analyses.

	Analyte				
Interferent	Pd	Pt	Rh	Ru	Ir
Au	0.28	0.15	0.75	0.22	0.28
Pd	-	0.53	2.6	0.78	1.0
Pt	1.9	-	5.0	1.5	1.9
Rh	0.38	0.20	-	0.29	0.38
Ru	1.3	0.68	3.4	-	1.3
Ir	1.0	0.53	2.6	0.78	-

The 100-fold excess interferent data may prove useful in assessing mutual interference effects in the analysis of PGE ore materials. However in routine exploration work, an ore will often be identified by the element that is in anomalously high concentrations. Determination of this element will be, by definition, virtually unaffected by the presence of very much smaller concentrations of potentially interfering precious metal elements. Once high levels of one or two of the elements have been identified, their interference on elements present at lower levels can be quantified more fully. It must also be considered that some ores are likely to have relative PGE patterns related to chondrite ratios. Consequently, the mutual interference studies described in Section 6.4.1.2 will be of great assistance in the interpretation of analyses of such materials.

Table 6.18. Comparison of the relative interference effects between pairs of precious metals, using data taken from the two studies reported in Sections 6.4.1.1 and 6.4.1.2.

	Analyte	Pd	Pd	Pt	Pt	Rh	Rh	Ru	Ru	Ir	Ir
Analyte conc. (ng/5μl)	cf. E76	1	0.2	25	5	1	0.2	5	1	25	5
	chondrite	0.53	0.53	5.0	5.0	0.24	0.24	1.02	1.02	7.95	7.95
Interferent											
Au	cf. E76	+18%	+25%	-1%	+8%	+19%	+16%	-9%	-38%	+13%	+14%
	chondrite	+4%	+4%	0%	0%	-1%	-1%	+1%	+1%	0%	0%
Pd	cf. E76	–	–	+4%	+9%	+9%	+9%	+6%	-14%	+4%	+30%
	chondrite	–	–	-1%	-1%	0%	0%	-1%	-1%	+1%	+1%
Pt	cf. E76	+4%	-2%	–	–	+20%	+22%	+18%	-14%	-9%	+17%
	chondrite	+6%	+6%	–	–	0%	0%	+1%	+1%	-2%	-2%
Rh	cf. E76	+8%	+7%	-7%	-4%	–	–	0%	-42%	+14%	+18%
	chondrite	-1%	-1%	-3%	-3%	–	–	-2%	-2%	-1%	-1%
Ru	cf. E76	-2%	+5%	-4%	+6%	+5%	+1%	–	–	-1%	-2%
	chondrite	-2%	-2%	-3%	-3%	+1%	+1%	–	–	-2%	-2%
Ir	cf. E76	-6%	-12%	+2%	+6%	+32%	+15%	-47%	-40%	–	–
	chondrite	-1%	-1%	-1%	-1%	-1%	-1%	0%	0%	–	–

6.4.2 Matrix element-precious metal interference effects.

The effects on the AAS determination of Ir, Rh, Pt, Pd and Au of five matrix elements (Ni, Fe, Cr, Cu and As) that may be co-extracted by aqua regia were examined. Analyte solutions were prepared to the following concentrations by the method described in Section 6.4.1.1: Ir (500 µg/ml), Rh (150 µg/ml),Pt (2200 µg/ml), Pd (300 µg/ml) and Au (220 µg/ml). Interferent element solutions were prepared by successive dilutions of the Spectrosol AAS standard solutions (BDH) with deionised water, to concentrations tabulated in Table 6.19. The concentrations of interferent elements used cover a range of concentrations that might be expected in digests of mineralised Shetland chromitites.

Table 6.19. Concentrations of interferent elements and acids used in the assessment of interferences.

		Interference concentration number.					
Interferent	Analyte	Intf conc 0	Intf conc 1	Intf conc 2	Intf conc 3	Intf conc 4	Intf conc 5
Ni	Ir	0	200	400	800	-	-
	Rh Pt Au	0	100	200	400	1000	-
	Pd	0	10	20	40	100	-
Fe	Ir	0	-	400	800	-	-
	Rh Pt Au	0	-	200	400	1000	-
	Pd	0	-	20	40	100	-
Cr	Ir	0	70	140	280	700	-
	Rh Pt Au	0	35	70	140	350	700
	Pd	0	3.5	7	14	35	70
Cu	Ir	0	12	24	48	120	240
	Rh Pt Au	0	6	12	24	60	120
	Pd	0	0.6	1.2	2.4	6	12
As	Ir	0	7	14	28	70	140
	Rh Pt Au	0	3.5	7	14	35	70
	Pd	0	0.35	0.7	1.4	3.5	7
HCl	Ir Rh Pt Pd Au	0	-	-	2%	5%	10%
HNO_3	Ir Rh Pt Pd Au	0	-	-	2%	5%	10%

Interferent element concentrations in µg/ml. Acid concentrations in % v/v.
Ir is present at the lowest concentrations in Shetland chromitites and its determination has the lowest sensitivity by GFAAS and Pd is present at the highest concentrations in Shetland chromitites and its determination has the highest sensitivity by GFAAS. Consequently, the concentrations of the interferent solutions had to be increased (Ir) or decreased (Pd) to maintain consistant interferent-to-analyte ratios at the particular analyte concentrationsused in these experiments. The concentrations of interferents used in the experiments will be referred to as Intf conc n in subsequent Tables.

An aliquot of the interferent (10 µl for Ir, Rh and Pt determination or 5 µl interferent plus 5 µl of deionised water for Pd and Au determination) was injected into the furnace then the same volume of the analyte solution was added to the furnace to allow mixing before the start of the thermal programme. The order of the interferent element studies was Ni, Fe, Cr, Cu then As. A control (i.e. analyte with no interference) was analysed between each element and the data was drift corrected to these analyses. The lowest concentration of interferent element was analysed first rising to the most concentrated just before a control sample. These experiments were repeated after an interval of a few months to confirm the results. In the second set of experiments, only Rh, Pt and Au were studied and one set of interferent solutions prepared. All solutions were prepared in the same way as above and the same thermal programmes were used for the analyses.

Table 6.20. Data from Ni, Fe, Cr, Cu, As interference experiments; analytes Ir, Rh and Pd.

		Ir		Rh.1		Rh.2		Pd	
Interferent	concentration No.	abs.	rel abs.	abs.	rel abs.	abs.	rel abs.	abs.	rel abs.
Ni	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 1	72	94%	830	117%	489	90%	421	138%
	Intf conc 2	73	95%	830	117%	477	87%	438	144%
	Intf conc 3	70	91%	596	84%	426	78%	465	152%
	Intf conc 4	-	-	297	42%	279	51%	523	171%
Fe	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 2	72	94%	700	99%	453	83%	336	110%
	Intf conc 3	44	57%	742	105%	415	76%	387	127%
	Intf conc 4	-	-	289	41%	223	41%	407	133%
Cr	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 1	72	94%	763	108%	604	111%	303	99%
	Intf conc 2	73	95%	706	100%	544	100%	305	100%
	Intf conc 3	64	83%	737	104%	541	99%	352	115%
	Intf conc 4	48	62%	846	120%	504	92%	313	103%
	Intf conc 5	-	-	615	87%	414	76%	331	109%
Cu	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 1	74	96%	689	97%	568	104%	294	96%
	Intf conc 2	71	92%	698	99%	579	106%	297	97%
	Intf conc 3	73	95%	685	97%	548	100%	305	100%
	Intf conc 4	72	94%	712	101%	526	96%	310	102%
	Intf conc 5	77	100%	700	99%	442	81%	320	105%
As	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 1	79	103%	717	101%	569	104%	325	107%
	Intf conc 2	78	101%	713	101%	567	104%	326	107%
	Intf conc 3	78	101%	720	102%	559	102%	335	110%
	Intf conc 4	80	104%	718	102%	567	104%	326	107%
	Intf conc 5	81	105%	711	101%	598	109%	325	107%

The results for both experiments are shown in Table 6.20 and 6.21. The suffix .1 refers to the first set of experiments and the suffix .2 to the repeat experiments. The results will be discussed by analyte below:

Iridium (Table 6.20). The presence of As did not significantly affect the absorption signal. Excess Ni or Cu caused a suppression of the signal by up to 10%. Cr and Fe caused significant suppression of signal. The suppression caused by the presence of Fe must be taken into consideration, although Cr is not likely to be leached from natural geological samples by aqua regia.

Table 6.21. Data from Ni, Fe, Cr, Cu, As interference experiments; analytes Pt and Au.

Interferent	concentration No.	Pt.1 abs.	rel abs.	Pt.2 abs.	rel abs.	Au.1 abs.	rel abs.	Au.2 abs.	rel abs.
Ni	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 1	265	84%	325	91%	578	44%	293	26%
	Intf conc 2	262	83%	313	88%	463	35%	223	20%
	Intf conc 3	236	75%	295	82%	351	27%	164	15%
	Intf conc 4	181	57%	270	75%	234	18%	80	7%
Fe	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 2	220	70%	304	85%	450	34%	317	29%
	Intf conc 3	204	65%	277	78%	346	26%	191	17%
	Intf conc 4	191	60%	236	66%	420	32%	114	10%
Cr	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 1	283	90%	344	96%	1333	101%	1031	93%
	Intf conc 2	322	102%	344	96%	1198	91%	930	84%
	Intf conc 3	315	100%	322	90%	963	73%	840	76%
	Intf conc 4	314	99%	302	84%	970	74%	710	64%
	Intf conc 5	311	98%	271	76%	859	65%	594	54%
Cu	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 1	300	95%	353	99%	1385	105%	1111	100%
	Intf conc 2	241	76%	355	99%	1323	100%	1153	104%
	Intf conc 3	234	74%	353	99%	1164	88%	1103	99%
	Intf conc 4	234	74%	347	97%	1058	80%	889	80%
	Intf conc 5	245	78%	341	95%	999	76%	728	66%
As	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 1	311	98%	356	100%	1294	98%	1147	103%
	Intf conc 2	306	97%	357	100%	1314	100%	1139	103%
	Intf conc 3	318	101%	354	99%	1384	105%	1154	104%
	Intf conc 4	311	98%	356	100%	1330	101%	1135	102%
	Intf conc 5	331	105%	360	101%	1316	100%	1131	102%

Rhodium (Table 6.20). The presence of As did not cause suppression, indeed its presence arguably enhanced the Rh signal. The presence of Cr or Cu caused 10-20% suppression of the Rh signal. The presence of Fe or Ni caused the most significant depression of signal (up to 60%). The presence of these elements in the quantitative determination of Rh should be avoided.

Platinum (Table 6.21). The behaviour of Pt to these interferents closely matched that of Rh. As has an insignificant effect on the absorption signal of Pt. Cr and Cu caused significant suppression of signal (up to 20-25%). Ni and Fe caused the most significant interferences, suppressing the signal by 30-40%.

Palladium (Table 6.20). The presence of Cu had little effect on on the absorption signal of Pd. As and Cr arguably enhanced the signal by 5-15%. Ni and Fe enhanced the Pd signal by 40-70% and 10-30%, respectively. The presence of Ni and Fe may have served to stabilise Pd during thermal pretreatment, thus preventing premature atomisation.

Gold (Table 6.21). The behaviour of Au towards these interferents mirrored that of Rh and Pt, differing in that the degree of interference tailed off at the higher interferent element concentrations. As had minimal effect on the absorption signal. The presence of Cr and Cu caused a 20-40% signal suppression. Fe and Ni caused a signal suppression of >80% and it was noticeable that these large suppressions occurred at much lower relative concentrations than other interferents for the other analytes.

In summary, the presence of As should not cause concern in the determination of these elements; As itself was likely to have been volatilised during the thermal pretreatment and any variation shown in Tables 6.20 and 6.21 was probably due to analytical imprecision. Cr was not extracted to any appreciable extent by aqua regia and its interference effects are not, therefore, likely to have any influence in this application. The suppression effects of Cu must be taken into account, especially when analytical samples have high concentrations of this element. Ni and especially Fe caused the greatest suppression of analytical signal and the influence of these elements must be compensated in the development of a satisfactory analytical procedure.

6.4.3 Attempts to control matrix element interferences.

An attempt was made to suppress the interferences described above by investigating the effect of adding to the analysis solution an extra element to act as a matrix modifier. The effect of the matrix modifier was evaluated on the following 3 systems: the interference of Fe on Pt, Fe on Au and Ru on Ir. Fe was identified as causing a major suppression problem with regards to interference in the analysis of the precious metals

(Section 6.4.2). Pt and Au were selected as analytes to be studied because the effects of Fe on their determination and because Spectrosol solutions of these elements were readily available. The interference of Ru on Ir was studied because sample solutions to be analysed for the determination of Ir will usually contain larger concentrations of Ru. Also, the unexpected interference of Ru on Ir, identified in Section 6.4.1.2, suggested that this system was worthy of further investigation.

Potential matrix modifiers selected for investigation were those elements that have been used in other applications (i.e. Pd, Mg) or that have an affinity for the PGE in classical wet chemistry (i.e. As, Cu, Pb, Sn, Te) The effects of these elements on each of the 3 systems will be described below.

6.4.3.1 Interference of Fe on Pt.

The solutions containing Pt, Fe, Cu and As were prepared as detailed in Section 6.4.2. Pb, Sn, Te, Mg and Pd solutions were prepared at concentrations of 10, 40, 100, 400 and 1000 µg/ml. Solutions of Pb, Sn and Te were prepared by successive dilutions of the Spectrosol AAS standard solutions (BDH). The top concentration solution of Pd was prepared by dissolving 0.0534 g Specpure $(NH_4)_2PdCl_4$ (JMC) in 20 ml 0.2% HNO_3 and that of Mg by dissolving 0.1734 g $MgCO_3$ (laboratory reagent grade for chromatographic adsorption analysis, BDH) in 10 ml 20% HNO_3 and diluting to 50 ml. Lower concentration solutions of Pd and Mg were prepared by successive dilution of the stock solution.

1 ml Pt solution was added to 1 ml of the interferent solution in the autosampler cups. Aliquots of 10 µl of Fe solution at 1000 or 400 µg/ml were added to 10 µl of the analyte solution inside the graphite furnace. The results from these studies are shown in Table 6.22.

Table 6.22. Effects of the presence of different potential matrix modifiers on the Fe interference on Pt. All Pt absorbances have been drift corrected against an absorbance value generated with no matrix modification (that value relating to a matrix modifier concentration of 0). The relative absorbance was calculated by comparison to an interference-free absorbance value (that value relating to 'no additional elements).

potential matrix modifier	Matrix modifier conc.	Fe concentration 400 µg/l Pt abs.	400 µg/l rel Pt abs.	1000 µg/l Pt abs.	1000 µg/l rel Pt abs.
no additional	elements	245	100%	244	100%
Pb	0	202	83%	183	75%
	10	196	80%	198	81%
	40	206	84%	195	80%
	100	201	82%	194	80%
	400	187	76%	167	68%
	1000	157	64%	155	64%
Sn	0	202	83%	183	75%
	10	198	81%	183	75%
	40	205	84%	183	75%
	100	198	81%	181	74%
	400	185	76%	184	76%
	1000	153	63%	164	67%
Te	0	202	83%	183	75%
	10	205	84%	183	75%
	40	205	84%	181	74%
	100	203	83%	182	74%
	400	201	82%	183	75%
	1000	207	85%	179	73%
Mg	0	202	83%	183	75%
	10	196	80%	180	74%
	40	197	81%	183	75%
	100	195	79%	184	75%
	400	195	79%	173	71%
	1000	202	83%	187	76%
Pd	0	202	83%	183	75%
	10	211	86%	185	76%
	40	211	86%	188	77%
	100	205	84%	186	76%
	400	215	88%	184	75%
	1000	197	80%	179	74%
As	Intf Conc 0	202	83%	183	75%
	Intf Conc 1	211	86%	189	77%
	Intf Conc 2	218	89%	198	81%
	Intf Conc 3	213	87%	191	78%
	Intf Conc 4	225	92%	205	84%
	Intf Conc 5	215	88%	198	81%
Cu	Intf Conc 0	202	83%	183	75%
	Intf Conc 1	213	87%	194	80%
	Intf Conc 2	226	92%	201	82%
	Intf Conc 3	225	92%	201	82%
	Intf Conc 4	210	86%	209	86%
	Intf Conc 5	237	97%	193	79%
As+Cu	Intf Conc 0	202	83%	183	75%
	Intf Conc 1	225	92%	170	70%
	Intf Conc 2	224	91%	166	68%
	Intf Conc 3	225	92%	150	62%
	Intf Conc 4	229	93%	155	64%
	Intf Conc 5	217	89%	148	61%

rel. abs. is the relative absorbance compared with an interference-free Pt solution.
Intf Conc N refers to the concentration detailed in Table 6.19.

It can be seen from Table 6.22 that Pd, Mg and Te did not affect the interference of Fe on Pt. Sn and Pb caused increased suppression of the Pt signal as their concentration increased. Cu, Cu + As and, to a lesser extent, As caused a reduction of the Fe interference as their concentration increased. The effect of As was slight, but that of Cu nearly fully restored the Pt absorbance to its initial value, indicating that Cu largely compensated for the suppression caused by Fe, with 0.12 µg Cu eliminating the interference of 4 µg Fe. The effect of Cu on the more concentrated Fe interference was very similar, although a greater mass of Cu was required to compensate the Fe suppression. The effect of As was peculiar in so much as it was postulated that this element would have been lost during thermal pretreatment, indeed, the beneficial effect of As in this application is not consistent.

6.4.3.2 Interference of Fe on Au.

Table 6.23. Effects of the presence of different potential matrix modifiers on the Fe interference on Au. All Au absorbances have been drift corrected against an absorbance value generated with no matrix modification (that value relating to a matrix modifier concentration of 0). The relative absorbance was calculated by comparison to an interference-free absorbance value (that value relating to 'no additional elements).

potential matrix modifier	matrix modifier conc. (mg/l)	Fe concentration			
		400 µg/l Au abs.	400 µg/l rel Au abs.	1000 µg/l Au abs.	1000 µg/l rel Au abs.
no additional	elements	1121	100%	801	100%
Cu	Intf Conc 0	200	18%	128	16%
	Intf Conc 1	108	10%	54	7%
	Intf Conc 2	114	10%	105	13%
	Intf Conc 3	137	12%	102	13%
	Intf Conc 4	143	13%	105	13%
	Intf Conc 5	162	14%	113	14%
As	Intf Conc 0	200	18%	128	16%
	Intf Conc 1	134	12%	100	13%
	Intf Conc 2	135	12%	99	12%
	Intf Conc 3	150	13%	107	13%
	Intf Conc 4	188	17%	119	15%
	Intf Conc 5	176	16%	135	17%
As+Cu	Intf Conc 0	200	18%	128	16%
	Intf Conc 1	150	13%	80	10%
	Intf Conc 2	157	14%	91	11%
	Intf Conc 3	142	13%	108	13%
	Intf Conc 4	127	11%	76	9%
	Intf Conc 5	128	11%	77	10%

rel. abs. is the relative absorbance compared with an interference-free Au solution.
Intf Conc N refers to the concentration detailed in Table 6.19.

The solutions containing Pt, Fe, Cu and As were prepared as detailed in Section 6.4.2. Effects of the other 5 elements were not studied for this interference system owing to their disappointing behaviour in the studies of the interference of Fe on Pt. The interferent and analyte solutions were mixed as described in Section 6.4.3.1.

The results are shown in Table 6.23, from which it can be seen that neither As nor Cu, singly or together, alleviate the suppression effects of Fe, in fact all combinations served to make the suppression even worse.

6.4.3.2 Interference of Ru on Ir.

Interferent solutions were prepared as detailed in Sections 6.4.2 and 6.4.3.1. The Ir and Ru solutions were prepared by dissolution of JMC Specpure powders in water (Ru: 0.0822 g $(NH_4)_2Ru(H_2O)Cl_5$ diluted to 25 ml; Ir: 0.0585 g $(NH_4)_2IrCl_6$ diluted to 50 ml). The analyte solution containing Ir was diluted to 4 µg/ml. Solutions of Ru were prepared at 400 and 40 µg/ml by subsequent dilution of the top concentration solution. The interferent and analyte solutions were mixed as described in Section 6.4.3.1.

The results are shown in Table 6.24, from which it can be seen that Pb, Mg, Pd and Cu caused even greater interference, over and above that of Ru alone and the degree of interference increased with increasing potential modifier concentration. Sn, Te and As appeared to have little effect at high Ru concentrations but the results showed that, at the lower Ru concentration, they could all compensate the interference effects of Ru on Ir.

Table 6.24. Effects of the presence of different potential matrix modifiers on the Ru interference on Ir. All Ir absorbances have been drift corrected against an absorbance value generated with no matrix modification (that value relating to a matrix modifier concentration of 0). The relative absorbance was calculated by comparison to an interference-free absorbance value (that value relating to 'no additional elements).

potential matrix modifier	Matrix modifier conc. (mg/l)	Ru concentration 40 µg/l Ir abs.	40 µg/l rel Ir abs.	400 µg/l Ir abs.	400 µg/l rel Ir abs.
no additional	elements	177	100%	166	100%
Pb	0	169	95%	22	13%
	10	156	88%	22	13%
	40	154	87%	19	11%
	100	150	85%	24	14%
	400	137	77%	24	14%
	1000	114	64%	29	17%
Sn	0	169	95%	22	13%
	10	165	93%	25	15%
	40	167	94%	25	15%
	100	176	99%	23	14%
	400	200	113%	20	12%
	1000	176	99%	28	17%
Te	0	169	95%	22	13%
	10	171	97%	20	12%
	40	175	99%	21	13%
	100	175	99%	20	12%
	400	178	101%	18	11%
	1000	186	105%	27	16%
Mg	0	169	95%	22	13%
	10	166	94%	26	16%
	40	165	93%	28	17%
	100	159	90%	28	17%
	400	159	90%	28	17%
	1000	151	86%	42	25%
Pd	0	169	95%	22	13%
	10	177	100%	21	13%
	40	170	96%	23	14%
	100	165	93%	26	16%
	400	155	87%	24	15%
	1000	157	89%	23	14%
As	Intf Conc 0	169	95%	22	13%
	Intf Conc 1	177	100%	23	14%
	Intf Conc 2	184	104%	24	15%
	Intf Conc 3	192	108%	24	15%
	Intf Conc 4	185	105%	25	15%
	Intf Conc 5	168	95%	25	15%
Cu	Intf Conc 0	169	95%	22	13%
	Intf Conc 1	165	93%	22	13%
	Intf Conc 2	169	95%	26	16%
	Intf Conc 3	169	95%	32	19%
	Intf Conc 4	161	91%	25	15%
	Intf Conc 5	151	85%	28	17%

rel. abs. is the relative absorbance compared with an interference-free Ir solution.
Intf Conc N refers to the concentration detailed in Table 6.19.

6.4.4 Interferences due to acid matrices.

The effects of the 2 acids that will be present in aqua regia extracts (HCl and HNO_3) on determination of the precious metals by AAS were examined. Analyte solutions were prepared as detailed in Section 6.4.2. These experiments were carried out directly after the interference studies described in Section 6.4.2 and the analytical protocol was as described in that Section. The results are shown in Table 6.25 and 6.26.

Table 6.25. Data from HCl and HNO_3 interference experiments; analytes Ir, Rh and Pd.

		Ir		Rh.1		Rh.2		Pd	
Interferent	concentration No.	abs.	rel abs.	abs.	rel abs.	abs.	rel abs.	abs.	rel abs.
HCl	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 3	78	101%	773	109%	550	101%	317	104%
	Intf conc 4	78	101%	682	96%	523	96%	319	105%
	Intf conc 5	72	94%	691	98%	556	102%	338	111%
HNO_3	Intf conc 0	77	100%	707	100%	546	100%	305	100%
	Intf conc 3	67	87%	655	93%	516	95%	309	101%
	Intf conc 4	67	87%	668	94%	507	93%	295	97%
	Intf conc 5	68	88%	571	81%	404	74%	663	217%

Table 6.26. Data from HCl and HNO_3 interference experiments; analytes Pt and Au.

		Pt.1		Pt.2		Au.1		Au.2	
Interferent	concentration No.	abs.	rel abs.	abs.	rel abs.	abs.	rel abs.	abs.	rel abs.
HCl	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 3	249	79%	343	96%	1247	95%	1161	105%
	Intf conc 4	212	67%	340	95%	1384	105%	1149	104%
	Intf conc 5	267	84%	344	96%	*>1600	>120%	1215	110%
HNO_3	Intf conc 0	316	100%	358	100%	1319	100%	1109	100%
	Intf conc 3	333	105%	329	92%	968	73%	940	85%
	Intf conc 4	318	101%	342	96%	956	72%	862	78%
	Intf conc 5	281	89%	336	94%	875	66%	887	80%

*; rollover occurred.

These results will be discussed by analyte below:

<u>Iridium</u> (Table 6.25). The presence of HNO_3 caused a depression of Ir signal by up to 15%. However, the effects of HCl were less severe, causing a depression of only 6%

even at the highest acid concentration studied (10%).

Rhodium (Table 6.25). The presence of HNO_3 caused increasing interference with increasing concentration, suppressing analytical signal by 20-25% with 10% acid. The presence of HCl did not cause significant interference in the determination of Rh.

Platinum (Table 6.26). The presence of HNO_3 did not cause significant interference in the determination of Pt. However the presence of HCl could cause depression of analytical by up to 35%, although the results of the 2 runs were not consistent.

Palladium (Table 6.25). The presence of <10% HNO_3 had little effect on the determination of Pd. However, if this value can be regarded as being real and not spurious (the high value was not supported by a trend up through the lower concentrations of acids), it can be reported that the presence of HNO_3 at the highest concentration studied did cause a doubling in size of the absorption signal. The effect of HCl was very much less significant, causing an enhancement of analytical signal by up to 10%.

Gold (Table 6.26). The presence of HNO_3 caused a depression of analytical signal of 20-30%, even at the lowest acid concentration studied. The presence of 10% HCl could cause an enhancement of analytical signal by 10->20%. The presence of the higher concentration of HCl caused sufficient increase in sensitivity that the absorbance signal exceeded the rollover concentration threshold of the spectrometer. Although no direct comparison of absorbances of the solutions without mutual interferences (Section 6.4.1.2) have been made, it can be seen that the same broad pattern exists for enhancements/suppressions of signal by the acids.

In summary, HNO_3 provided the most stable matrix for Pt, but HCl provided the most stable (least suppressive) matrix for Ir, Rh, Pd and Au. However, account has to be made for the interference caused by the presence of both acids because both will be present in solution after aqua regia attack.

6.4.4.1 AAS analysis of aqua regia extracts.

Preliminary tests were carried out on the atomisation of 20% aqua regia extracts. At the actual atomisation stage an expulsion of white smoke was observed from all openings of the furnace. This smoke gave rise to extreme background signals, above which the detection of analyte absorption signals was extremely difficult. The observed smoke may have been due to the high acid content, the high level of co-extracted elements (e.g. Fe and Ni), or a combination of both these factors. A slow ramp to atomisation (50°C/s) was sufficient to permit smoke-free atomisation, but this long ramp also led to a total or near-total loss of analyte. Presumably the ramp was sufficiently slow to allow the removal of prematurely volatilised analyte along with the ashing products by the Ar sheath gas in the usual way.

6.4.5 Summary of interference effects.

All of the precious metals suffer interference effects caused by the presence of other precious metals, concomitant trace elements or acids within the solution. Despite a detailed and comprehensive investigation, removal or compensation of these interferences has not resulted in any firm recommendations. The most success has been achieved in the determination of Au with platform atomisation, using excess Ni as a matrix modifier. This procedure stabilised to a large degree the Au absorption signal, although some analytical interferences still remained.

It is concluded, therefore that the most reliable way of eliminating interferences caused by the presence of other constituents in a solution is to undertake a preliminary chemical separation to remove the very constituents that cause the interferences. The application of a solvent extraction procedure has been described in Chapter 5. The adaption of thermal programmes to the analysis of organic extract solutions have been discussed in Section 6.2.3. The next Section will combine the observations of these

Sections and assess the suitability of GFAAS to the analysis of organic solutions for the determination of the precious metals.

6.5 Analysis of organic solutions by GFAAS.

The conditions appropriate for the analysis of organic compared to aqueous solutions was influenced by the difference in volatility of the solvents. The lower boiling points of the organic solvents required a lower drying temperature accompanied by a slight increase in length of the drying steps. Thermal pretreatment and atomisation were accomplished using the same temperatures as employed for the analysis of aqueous solutions without deleterious effects, despite concern that the analyte would be present in different forms after thermal pretreatment. Indeed the lack of deleterious effects suggests that the analyte was present as the same or similar species after thermal pretreatment of aqueous or organic samples.

Evaporation of the organic solvent from the sample cups mounted in the AAS sample changer awaiting analysis was a problem when using chloroform, but was less significant when using DCE – the solvent of choice. Any systematic change that might be encountered due to evaporation of the solvent can be compensated for by the periodic analysis of a drift monitor solution prepared in the same way and at the same time as the unknown sample.

Analysis of organic solutions by GFAAS can be accomplished with no more difficulty than that encountered in the analysis of aqueous solutions. Indeed, such analyses can be advantageous because extraction procedure is designed to extract selectively large proportions of the precious metals, thus suppressing interferences that could arise from the presence of matrix elements.

6.6 Summary.

This present chapter has described GFAAS for use in the determination of Au and the PGE. The need for detailed thermal heating programmes for use with both wall and platform atomisation has been evaluated. The use of matrix modification and its application in the determination of Au have been described (the addition of 10 μg Ni to the sample aliquot led to optimal atomic absorption signal for the determination of Au using platform atomisation (Section 6.2.2)). The mechanism of atomisation has been discussed (PGE species are reduced to the metal during thermal pretreatment and atomisation occurs by boiling off gaseous metal atoms (Section 6.1.2)) together with a brief outline of interference effects that might be experienced during analysis. Some spectral and non-spectral interferences are summarised in Section 6.3.1 and Table 6.1.

Detailed optimisation of the thermal heating programmes – drying, thermal pretreatment and atomisation – has been reported (see Tables 6.3, 6.5 and 6.7 for details) together with an assessment of the concentrations of the analytes that would generate absorbances within the linear working range of the instrument (sample solutions should be less than the following concentrations: Pt: 1000 μg/l; Ir: 500 μg/l; Ru: 400 μg/l; Rh: 100 μg/l; Pd: 30 μg/l [wall atomisation], 100 μg/l [platform atomisation]; Au: 150 μg/l [wall atomisation], 300 μg/l [platform atomisation] (Sections 6.2.1 and 6.2.2)). Long-term precision of the instrument has been shown to be very good (the coefficient of variation calculated from the analysis of one solution in new graphite tubes over 3 years was 1.45% (Section 6.3)).

A detailed characterisation of interferences that may be encountered during the analysis of aqua regia leaches of geological materials has been reported, the most serious being the interferences caused on all analytes by Fe and Ni (Tables 6.2 and 6.2.1). Mutual interferences between the precious metals and matrix element interferences on the precious metals have been extensively studied at different relative analyte-to-interferent concentrations. Mutual interferences derived on modern instrumentation are significantly different from results published earlier and show that mutual interferences are not likely to be significant at relative concentrations commonly found in geological samples (Section 6.4.1.3). Attempts to overcome such interference effects by testing the effects of a number of matrix modifiers on known interferent systems have also been reported (the most successful result being the removal of the Fe interference on the Pt in the presence of Cu (Section 6.4.3)) and an assessment has been made of the application of GFAAS in the analysis of organic solutions, showing that GFAAS is well suited to the sensitive analysis of organic extracts generated in the solvent extraction procedure (Section 6.5).

6.6.1 Aqua regia, solvent extraction and GFAAS.

The combination of an aqua regia leach and selective solvent extraction have been discussed in Section 5.6.1, the conclusions from which were (i) the method was suitable (a) for Au and (b) for Rh, Pt and Ru subject to limitations imposed by the sample matrix (e.g. non-quantitative extraction of these elements by aqua regia), (ii) solvent extraction of Pd was disappointingly low considering the near-quantitative extraction of this element in aqua regia, and (iii) determination of Ir was hindered by the insolubility in aqua regia of many Ir-containing phases in aqua regia (it was not possible to determine Os by GFAAS for the reasons outlined in Section 6.1.3.2). The sensitivity of the determination of these elements by GFAAS demonstrates the benefits of this approach. The characteristic masses of the analytes are shown in Table 6.2, from which it can be seen that Au, Rh and Pd can be determined with the greatest sensitivity, closely followed by Ru and the sensitivities of the determination of Pt and Ir are significantly less than those for the previously mentioned elements.

The favourable extraction (by aqua regia and organic solvent) of Au and sometimes Rh and Ru, combined with the high sensitivity of GFAAS means that this technique is well suited to the determination of these elements in organic extracts of aqua regia leachates of geological materials,with some concern about the influence of sample matrix in suppressing extraction efficiency. The high sensitivity of GFAAS can be applied for the determination of Pd in dilutions of the aqua regia leachates; its use in the determination of Pd in the organic extracts is limited by the disappointingly low extraction of Pd by this method. The lower sensitivity of GFAAS towards Pt determination is fortunately offset against the fact that concentrations of Pt in geological materials are typically higher than concentrations of the other precious metals. The low extraction of Ir by aqua regia, coupled with the low sensitivity of GFAAS towards this analyte serve to make this method unsuitable for the determination of Ir. Investigations made to improve extraction of some or all the precious metals are discused in the next chapter.

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Chapter 7.
Limitations to aqua regia dissolution.

7.1 Introduction.

A recognised limitation to the aqua regia dissolution method was the variable and often incomplete recovery of some of the precious metals (Chapter 4), despite expectations that Pt, for example, was soluble in aqua regia (Chapter 2). Some explanations for the low recoveries of the precious metals have been alluded to in Section 4.5.2 which relate the observed low recoveries to sample mineralogy and geochemistry. The PGE may exist in solid solution within insoluble matrix minerals or may be occluded as discrete grains within such insoluble minerals. Alternatively, PGE minerals (PGM) which were exposed to acid attack may be insoluble in aqua regia. The modes of occurrence of the precious metals have been summarised in Sections 1.1.2 and 1.1.3, consideration of which has suggested that some or all of the above hypotheses could be the reasons for incomplete precious metal recovery from the samples tested.

In this chapter, experiments are described that were carried out to test the physical control of sample mineralogy and the chemical control of PGM geochemistry. The incorporation of a roasting step in the scheme of sample preparation was also evaluated as a method of reducing the geochemical limitations to the aqua regia dissolution method.

7.2 Limitations due to sample mineralogy.

Low recoveries of Ir have been purported previously to have been caused by the inclusion of Ir within insoluble chromite grains (Chapter 4). The technique of ß-autoradiography was used to identify the presence of minerals containing, amongst other elements, Au and Ir. Comparison of ß-autoradiographs (ß-maps) before and after aqua regia leaching enabled the identification of grains that had or had not been dissolved.

7.2.1 Beta-autoradiography.

The technique of ß-autoradiography has been fully described by Potts (1984) and, at the simplest level, permits the systematic location in irradiated thin sections of isotopes that decay by beta-emission. After irradiation, the samples are allowed to decay for a suitable period after which time a photographic emulsion, sensitive to ß-particles is placed in contact with the thin section. The film is exposed in the dark for a suitable time, after which it is removed from the thin section and developed to produce an autoradiograph (ß-map). This ß-map delineates the distribution of mineral grains containing significant activities of ß-emitting isotopes formed during neutron activation. Different elements cannot be distinguished directly by ß-autradiography. However, different minerals can usually be identified by comparing autoradiographs recorded after different elapse times after irradiation. Differences caused by the different decay rates of individual isotopes often permits categories of minerals to be distinguished unambiguously. Optimum decay and exposure times for specific elements are given in Potts and Prichard (1986) who showed that optimum exposure times for identifying Au and Ir mineralisation were 12 and 40 days, respectively, after irradiation.

The nature of the chromitite rock is such that a ß-map shows grey shading in the areas of the chromite mineral and light grey, almost colourless, shading in the areas of the serpentine matrix. The positions of minerals containing concentrations of ß-emitting isotopes are identified by black spots on the ß-map. Because of the penetrating characteristics of the ß-particles within the emulsion, the diameter of this spot is larger by 2 orders of magnitude than the mineral containing the ß-emitting isotope (Prichard et al., 1989). This apparent magnification of the grains of interest is helpful in the identification of the textural location of grains of interest, including those grains that contain a concentration of Ir.

Work by Prichard et al. (1989) showed that spots in the lighter areas normally correspond to grains containing Au, Sb or Ir in the serpentinite matrix, some of which may be dissolved in aqua regia, and those in the darker areas would normally correspond to Ir-bearing minerals occluded within the chromite grains (probably Ir-rich laurite within the chromite, Section 1.1.3 (Prichard et al., 1989)). The purpose of this experiment was to seek the textural location of ß-emitters to test the hypothesis that after aqua regia leach of the sample, some of the black spots on the lighter grey areas of a ß-map would not be present (owing to dissolution of Au and/or Sb) and those spots on the darker areas would still be present (Ir).

7.2.2 Experimental.

Thin sections were prepared (by the thin section laboratory at the OU) from 2 selected hand specimens of chromitite from the Cliff quarry, Unst, Shetland (HP 608111), the same locality from which OU-CX, CHR-C and CHR-Pt+ were collected. The glass slides were cut down to fit into a polythene irradiation canister and all surplus glass was cut away (to reduce the background from Na in the glass). A resinous coating routinely applied to thin sections was removed with inhibisol (an industrial solvent) to permit intimate contact between the thin section and the film on which the ß-map would be recorded. The canister containing the 2 cut down slides was then sealed and dispatched for irradiation to the Imperial College Reactor Centre, Ascot (now the Centre for Analytical Research in the Environment (CARE)).

After suitable decay periods, ß-maps were generated using different exposure times to optimise the resolution of the black spots against the "textural grey-scale" image. The following exposure times and decay periods were used: first exposure for 23 hours starting 11 days after irradiation, second exposure for 2 hours and 20 minutes starting

12 days after irradiation, and third exposure for 61.5 hours starting 14 days after irradiation. Comparison of the 3 ß-maps generated for different exposure times revealed that the optimum contrast of black spots against the grey background was obtained after 23 hours exposure. After these ß-maps had been produced, each of the 2 slides was scored across the middle with a diamond pencil and broken in half. One half was immersed in aqua regia and the other would become a control.

17 days after irradiation, the 2 half slides were placed into an evaporating basin and covered with 20 ml 3:1 aqua regia. After 15 minutes the samples were removed from the acid and rinsed with plenty of deionised water before being dried with paper tissue. All pieces of apparatus that had come into contact with the irradiated samples, including the acid and rinse washings, were tested for radioactive contamination. Having found no significant contamination, the liquids were washed to drain with copious amounts of water, the evaporating basin was thoroughly washed and the paper towels were disposed of in the approved manner.

Having dried the samples, ß-maps were again recorded of both halves of the slide with exposure for 23 hours (the optimum exposure time for this application) starting 17 days after irradiation. The film was then developed and the resulting ß-map was compared with generated from the 23 hour exposure, 11 days after irradiation. Having developed the final ß-map and confirmed that it was usable, the irradiated slides were transferred to a dense polythene bag, sealed and stored in a lead safe until their activity had dropped to a sufficiently low level.

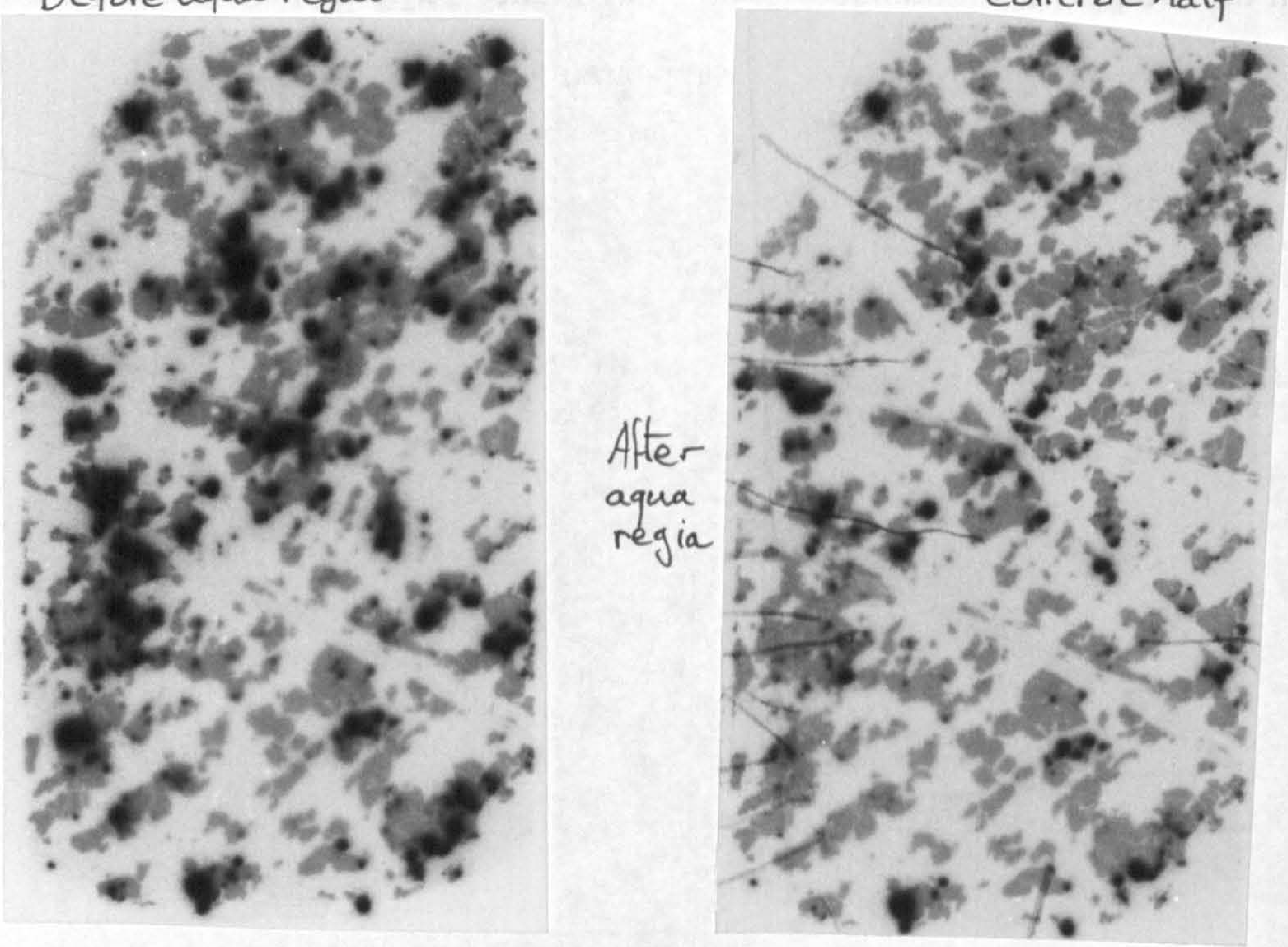
7.2.3 Observations and results.

During the aqua regia attack, the acid turned yellow in the proximity of the slides, this colour was dissipated upon mild agitation. The yellow colour was probably caused by Fe, leached out of the sample matrix.

Images of the 2 ß-maps exposed for 23 hours are shown in Figure 7.1. It can be seen from the ß-maps that a number of spots have faded or disappeared entirely. The number of spots that had faded or disappeared from the leached and control halves of the slides are shown in Table 7.1.

Figure 7.1. Beta-autoradiographs generated from the aqua regia leached and control halfs of 2 irradiated slides.

SLIDE 1.

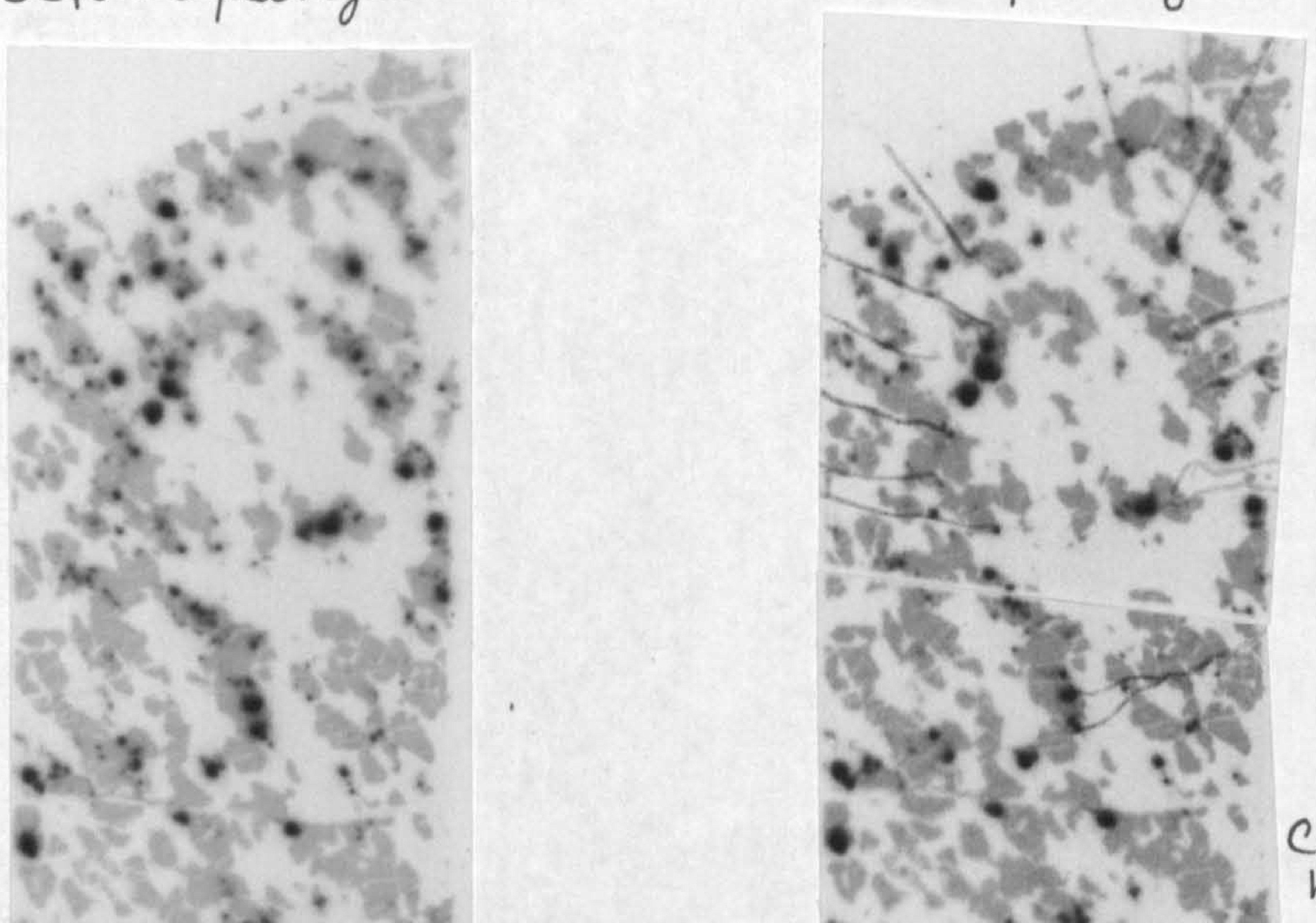


Before aqua regia

Control half

After aqua regia

SLIDE 2.



Before aqua regia

After aqua regia

Control half

Table 7.1. The number of spots that had faded and disappeared from ß-maps of thin sections, one half of which had been leached by aqua regia and the other unleached as a control.

	Leached half of slide		Control half of slide	
	Spots faded	Spots disappeared	Spots faded	Spots disappeared
Slide 1	9	5	2	0
Slide 2	10	5	2	0

Comparison of the ß-maps before and after the aqua regia leach showed that some spots had disappeared entirely from the maps of the leached slides and further spots had faded. The data in Table 7.1 show that, whereas no spots had disappeared from the control slides, 5 had disappeared from each of the leached slides. Furthermore, 9 of the 10 of these spots were originally in the lighter serpentinite areas of the slide rather than the darker chromite areas. A significantly larger number of spots had faded from the leached halves of the slides compared to the control halves. These faded spots were distributed fairly evenly over the whole matrix.

7.2.4 Discussion and conclusions.

The fading and subsequent disappearance of the spots on the ß-maps can be attributed to 2 factors, dissolution of the ß-emitting species by aqua regia or decay of the ß-emitter during the time interval between irradiation and exposure of the ß-map.

The samples under study have a complex mineralogy and have been the subject of a detailed study by Prichard et al. (1989) (Section 1.1.3). The predominant PGM are alloys, sulphides, arsenides and antimonides, (the most common PGM found in samples form Cliff, Shetland are listed in Table 1.4 and reproduced in Table 7.2). The ß-emitting isotopes relevant to this experiment are as follows, together with their half lives: ^{76}As (1.1 days), ^{198}Au (2.7 days), ^{122}Sb (2.7 days), ^{124}Sb (60.2 days) and ^{192}Ir (74.0 days).

The decay time following irradiation before the first autoradiograph was recorded was sufficiently long to ensure that virtually all of the ^{76}As would have decayed (11 days is

10 half lives). However, there will also have been significant decay of ^{198}Au over the 6 days between the 2 exposures. This decay may account for the fading observed for some of the spots. The activity of both ^{124}Sb and ^{192}Ir will have remained virtually unchanged during the experimental period. The fact that a significantly greater number of spots had faded and disappeared from both the attacked samples compared to their controls indicates that the aqua regia was at least partially responsible for the removal of ß-emitters further to the fading attributable to the decay of these species.

It is suggested that (a) the presence of non-faded spots in the darker areas were due to the presence of Ir-rich laurite occluded within the chromite that were not attacked by aqua regia, (b) the presence of non-faded spots in the lighter areas were due to antimonides (including irarsite, IrAsS) which too were not attacked by aqua regia, (c) faded spots across the ß-map were indicative of Sb (and Au) species that suffered degrees of dissolution by aqua regia and Au species that had simply decayed in the time intervening between the exposure of the 2 ß-maps, (d) spots that had disappeared were caused by Au or Sb species that were completely removed by aqua regia dissolution before the second ß-map was recorded. The conclusions help to explain the variable recovery of some of the precious metals and particularly the low recovery of Ir.

7.3 Limitations due to mineral geochemistry.

Low recoveries of Pt and Ru have been purported previously to have been due to the presence of mineral phases, containing these metals, which are insoluble in aqua regia (Chapter 4). Little is known about the solubilities of different PGM in mineral acids; an extensive literature review identified only 3 references containing useful information, Schoeller and Powell (1955, p. 325), Powell (1962, p.672) and Smith (1987, p.426). The information gleaned form these references has been combined with the mineralogical data from Table 1.4 and is presented as Table 7.2.

Table 7.2. PGE mineralogy of a chromitite sample from the Cliff quarry, Unst, Shetland (Prichard et al., 1989) and comment on the aqua regia solubility of these and other PGM where known. The minerals are listed in order of abundance in chromitite, the most frequently observed is listed first. Precise modal abundances are not known and would in fact be technically difficult to measure.

dominant element	mineral *	formula	solubility in aqua regia
Pt	sperrylite	$PtAs_2$	no
	genkinite	$(Pt,Pd)_4Sb_3$	
	hongshiite	$PtCuAs$	
	alloy	Pt-Pd-Cu	
	alloy	Pt-Pd-Au-Cu	
Pd	mertieite	$(Pd,Cu)_8(Sb,As)_3$	
	stibiopalladinite	$(Pd,Cu)_5(Sb,As)_2$	yes
	potarite	$PdHg$	
	alloy	$AuPd$	
Rh	hollingworthite	$(Rh,Pt,Pd)AsS$	
	unidentified	$Rh(Sb,S)$	
	unidentified	$(Rh,Ni)Sb$	
Ir	irarsite	$(Ir,Ru,Rh,Pt)AsS$	
	unidentified	$Ir(Sb,S)$	
Ru	laurite	$(Ru,Os,Ir)S_2$	no
	ruthenian pentlandite	$(Ni,Fe,Ru)_9S_8$	
Os	native metal	Os	
	iridosmine	Os,Ir	no

* Other minerals reported to be soluble in aqua regia: native gold, platinum, palladium. Minerals reported to be insoluble in aqua regia: cooperite (Pt,Pd,Ni)S; braggite (Pt,Pd,Ni)S; osmiridium (Ir,Os); platiniridium (Ir,Pt).

The results which were presented in Table 4.11 indicated good recovery of Pd and Au from OU-CX[1] but only 18% recovery of Pt and Rh and <1% recovery of Ir. The poor recovery of Ir has been approached in the previous Section. The recovery of Ir may also have been hindered by the insolubility of laurite, which was occluded within chromite (no information on the solubility of this irarsite could be found). Quantitative recovery of Au was likely to be due to the presence of Au in soluble alloys. Quantitative recovery of Pd could be attributable to the fact that the second most common Pd mineral, stibiopalladinite, is soluble in aqua regia and the most common Pd mineral, mertieite, is also likely to be soluble taking into account the similarity of its composition

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[1] Sample OU-CX was collected from the same locality as samples whose study permitted the generation of Table 7.2, Cliff quary, Unst, Shetland.

to that of stibiopalladinite. The low recoveries of Pt and Rh may correlate with minor fractions of these elements that are present as minor constituents in other soluble PGM. The highest proportion of the Pt in the sample is present as sperrylite (the most common Pt mineral) which is known to be insoluble in aqua regia. Following similar arguments, it would appear that hollingworthite, the most common Rh mineral, is also insoluble in aqua regia.

Roasting experiments.

Schoeller and Powell (1955, p. 325) reported that sperrylite would decompose to Pt metal upon roasting and would then be soluble in aqua regia. This roasting procedure appeared likely, therefore, to enhance the recoveries of selected PGM by acid attack and so the effect of roasting upon the dissolution of some grains of sperrylite was tested by use of scanning electron microscopy (SEM). SEM photomicrographs were recorded of and secondary x-rays detected (using an energy dispersive system similar to that described in Chapter 4) from sperrylite grains before and after aqua regia attack, with and without roasting pretreatment.

7.3.1 Experimental.

The experiments were carried out using 9 grains of sperrylite, but due to a series of experimental errors and duplication of the conditions,[2] only the results from grains 2, 5 and 8 are presented. The results derived from these grains represent the full range of tests executed on the samples.

Preparation of the samples for SEM. For ease of handling during the SEM analysis, a number of grains were mounted with a pair of tweezers onto an aluminium stub with a

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[2] Grains 1, 4, 6 and 7 disintegrated upon handling after roasting or aqua regia attack. Grain 3 duplicated the conditions experienced by grain 2. Grain 9 was lost during the handling of the small grains with tweezers.

disc of double sided sticky tape. Electrical contact between each grain and stub was achieved by painting a strip of carbon paste from the grain to the edge of the stub and finally by carbon coating the entire stub. Before each application of roasting or aqua regia, the grains were each removed carefully from the stub with a pair of tweezers and washed in acetone to remove carbon paste and the glue from the sticky tape. After cleaning and drying, the grains were placed into small porcelain crucibles awaiting the next stage in the experiment.

Aqua regia attack. 4 ml of 3:1 aqua regia was added to the crucible and the grains were submerged with a PTFE spatula. After 60 minutes the grains were removed, rinsed and dried on filter paper and the acid was discarded. After drying the grains were remounted onto the SEM stub as above preferably in the same orientation such that comparable photomicrographs could be taken.

Roasting. The crucible containing the grains was placed into a furnace set at a sufficiently high temperature to effect the decomposition of sperrylite (700 °C) for 30 minutes. After cooling, the grains were carefully remounted onto the SEM stub as above.

7.3.2 Results and discussion.

Care was required in the sample handling procedures described above as the grains became soft after roasting and clumsy use of the tweezers resulted in squashing the grain. Also the duration of the aqua regia attack on the grains had to be monitored in order to leave some residue for subsequent SEM analysis.

Qualitative results of the scans are shown in Table 7.3. These data indicate that the primary constituents of the grains were, not surprisingly, Pt and As. Other minor constituents may have been impurities in the mineral grain or some contamination from the host rock material that remained on the surface of the grain. After an initial attack of aqua regia these primary constituents remained unchanged. However, it appears that As was lost during roasting, with just Pt remaining in the roasted grain, confirming the observations of Schoeller and Powell (1955, p. 325). After the final aqua regia attack, the residue contained only Pt.

Table 7.3. Elements identified by qualitative scans of secondary x-rays present in grains of sperrylite after specified stages of processing: (1) before any treatment, (2) after an initial aqua regia attack, (3) after the grain had been roasted, and (4) after aqua regia attack of the roasted grain. Results are presented for sperrylite grains 8, 2 and 5. The major constituents are presented on the top line within each cell, the presence of any subsidiary elements is recorded by their inclusion on the lower row in parenthesis.

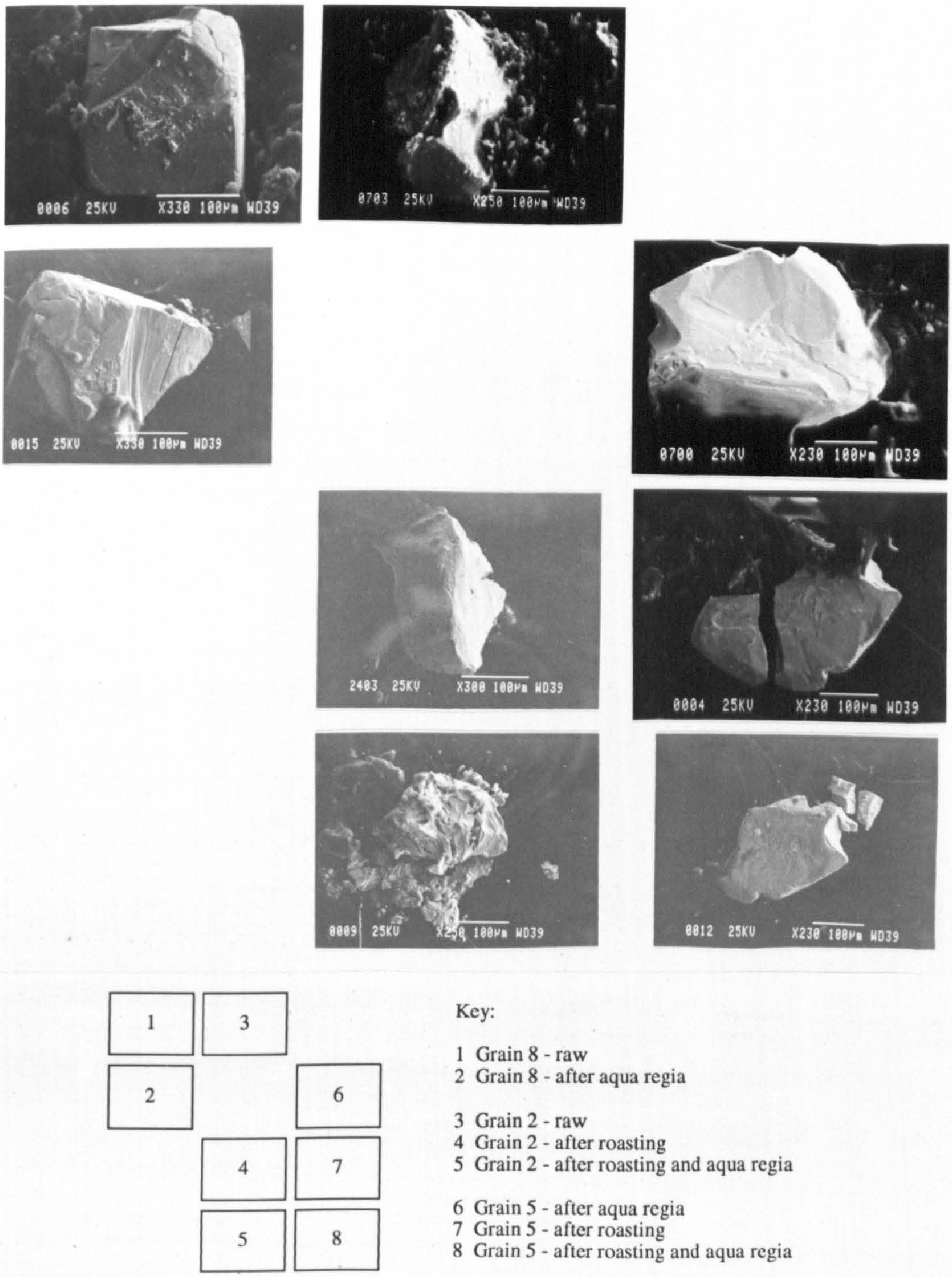
state of the mineral	Grain 8	Grain 2	Grain 5
(1) untreated.	As Pt 0006	As Pt (Fe S Cr Cu) 0703	-
(2) after an initial aqua regia attack	Pt As 0015	-	As Pt 0700
(3) after roasting	-	Pt (Cu) 2403	Pt (Ni Pd Fe) 0004
(4) after aqua regia attack of the roasted mineral	-	Pt (Cu) 0009	Pt 0012

The number in the bottom right hand corner of each cell refers to the number of the corresponding photograph.

Photomicrographs of the grains taken at various stages through the procedure are presented in Figure 7.2. There is little difference in terms of overall form of the grain or rounding of sharp grain boundaries between the 2 photographs of grain 8, 0006 (before initial aqua regia attack) and 0015 (after initial aqua regia attack) which indicates that the initial aqua regia attack had minimal effect on sperrylite

From comparisons of photographs of grain 2, 0703 (before roasting) and 2403 (after roasting), it can be seen that the edges of the grains had become less well defined and some of the surface detail was lost (perhaps to leave a honeycomb residue) during the roasting process. From comparison of photographs 2403 (after roasting) and 0009 (after roasting and final aqua regia attack), it can be seen that all structure of the grain has been lost, indeed the aqua regia residue was quite plastic in nature.

Figure 7.2. Photomicrographs produced with the aid of SEM of 3 different grains of sperrylite at different stages during an experiment to determine the effect of roasting on the aqua regia solubility of the mineral. The different stages of the grains in the procedure are detailed in the attached key.



Key:

1 Grain 8 - raw
2 Grain 8 - after aqua regia

3 Grain 2 - raw
4 Grain 2 - after roasting
5 Grain 2 - after roasting and aqua regia

6 Grain 5 - after aqua regia
7 Grain 5 - after roasting
8 Grain 5 - after roasting and aqua regia

Comparison of photographs of grain 5, 0700 (after initial aqua regia attack) and 0004 (after initial aqua regia attack and roasting),[3] also show a slight loss of surface detail upon roasting although the edges of grain 5 in photograph 0004 seem to be better defined than the edges of grain 2 at the same stage (2403). Comparison of photographs 0004 (after initial aqua regia attack and roasting) and 0012 (after initial aqua regia attack, roasting and final aqua regia attack) show that the grain has become more friable after roasting and the overall grain size has decreased during the aqua regia attack. Like grain 2, the aqua residue was softer than the initial sperrylite grain, but a greater effort was made to handle this grain carefully, with the consequence that the the overall shape was better retained.

7.3.3 Conclusions.

Aqua regia does not attack sperrylite. Roasting sperrylite causes a loss of As with an associated breakdown of the rigid crystal structure of the mineral grain. The loss of As from insoluble sperrylite leaves a residue of disseminated Pt, which is then soluble in aqua regia (the aqua regia attack was prematurely curtailed so as to leave a residue that could be analysed by SEM). This scheme can be represented by the following reaction:

$$\underset{\text{insoluble}}{PtAs_{2\,(s)}} \xrightarrow{700\,^{\circ}C} \underset{\text{driven off}}{2\,As_{(g)}} + \underset{\text{soluble.}}{Pt_{(s)}}$$

7.4 Roasting as a sample pretreatment step.

The introduction of a roasting step prior to the aqua regia dissolution of a geological sample should lead to the decomposition of sperrylite (and many other arsenides and

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[3] This grain (5) had flipped over during its remounting, so photograph 0004 effectively shows the underside of the grain depicted in photograph 0700.

sulphides) which may then lead to increased recovery of Pt, other PGE but also matrix elements. The beneficial effects of roasting to increase Pt recovery must therefore be balanced against the potential increased analytical problems that might arise through increased levels of Fe, Ni, Cu and other metals that may have also been present in insoluble phases such as base metal sulphides and arsenides, prior to roasting.

To test the benefits of roasting, a selection of samples for which independent analyses are available were analysed by the aqua regia extraction/ICP-MS finish method described in Section 4.4 with the addition of a roasting stage prior to acid attack. The samples used are listed in Table 7.4 and they are described in Section 4.5. Also listed in Table 7.4 are the previous analytical results obtained by an independent laboratory using NiS-fire assay/ICP-MS and the analytical results derived in this work by the aqua regia/ICP-MS technique without roasting, both sets of data have been presented previously in Table 4.11. The aqua regia dissolution of the roasted samples took place contemporaneously with the analysis of the unroasted samples.

7.4.1 Experimental.

The powders were roasted in batches of 6 as this number of beakers neatly fitted into the furnace. About 25 g of sample powder was weighed into a silica beaker. Six beakers were then placed into a furnace at room temperature which was then set to heat up to 700 °C (see Section 7.4.3). This temperature was attained after about 20 minutes. After a further 30 minutes, the beakers were removed in turn and the powders were agitated to prevent a crust forming on the surface and to aid the release of decomposition products. The beakers were then returned to the furnace for a further 60 minutes before being removed and allowed to cool. Two 10 g sub-samples of roasted powder were then taken from the roasted mass and treated in the same manner as the unroasted samples. The aqua regia dissolution and analysis of the subsequent leachates has been fully described in Chapter 4.

7.4.2 Results.

Concentrations of the precious metals in the 11 materials studied by 3 different methods are presented in Table 7.4. The 3 methods are: NiS-fire assay/ICP-MS (independent analysis), aqua regia attack/ICP-MS (without roasting) and aqua regia attack after roasting followed by ICP-MS (roasting included). The aqua regia/ICP-MS data with and without roasting are directly comparable. The NiS-fire assay data obtained by an independent external laboratory is included to give an indication of the extent of recovery attained by the aqua regia techniques used in this work.

Effects of roasting will be considered by analyte below.

Platinum. Roasting served to increase recovery of Pt from all samples except RLM007, for which the difference between the 2 aqua regia methods was not significant. Furthermore there was an increase in recovery of an order of magnitude for samples 14/75, 2/77, Brag71 and MR16 and an increase up to quantitative recovery in MR65.

Palladium. Roasting led to improved recovery of Pd in only 3 of the samples and was detrimental to Pd recovery from twice that number. Furthermore, near-quantitative recovery observed without roasting was not evident in the roasted samples of CMR292, MR65, RLM007 and RLM098.

Rhodium. Roasting was detrimental to the recovery of Rh from 6 samples and arguably increased recovery in only 1 sample.

Ruthenium. Roasting improved the recovery of Ru from 4 samples and was detrimental to its recovery in the same number of samples. Any changes in recovery efficiency seem to be dramatic. For example there was >60% recovery from Brag71 and Brag78 compared to Ru concentrations below detection limit without roasting. Conversely, quantitative recovery of Ru from RLM098 was no longer observed when roasting was included in the sample preparation procedure.

Table 7.4. Concentrations of the precious metals determined by aqua regia leach/ICP-MS, with and without a roasting pretreatment step. The samples are 11 of those independently analysed by NiS-fire assay/ICP-MS and reported in Table 4.11

Sample		Pt	Pd	Rh	Ru	Os	Ir	Au
<u>chromitites</u>								
14/75	independent analysis	2800	1300	470	960	-	380	70
	without roasting	200	730	216	85	5	30	30
	roasting included	1740	500	7	27	<	0.7	31
2/77	independent analysis	3110	1670	610	1200	-	<200	50
	without roasting	110	490	191	76	<	16	13
	roasting included	2200	630	18	260	<	28	14
Brag71	independent analysis	16	11	9	45	24	25	-
	without roasting	<2	<	1	<	<	<	<
	roasting included	5	8	1	40	18	<	1.6
Brag78	independent analysis	51	18	46	310	160	180	-
	without roasting	8	<	4	<	<	2	<
	roasting included	17	<	2	210	150	30	<
CMR292	independent analysis	500	520	55	190	50	97	6
	without roasting	130	450	6	35	6	3	2
	roasting included	400	240	9	115	25	29	10
RLM007	independent analysis	870	2100	110	190	98	120	130
	without roasting	1140	2200	87	290	45	17	155
	roasting included	1040	1540	28	120	22	19	138
RLM098	independent analysis	9	10	5.5	44	12	14	2
	without roasting	6	8	1	74	<	<	<
	roasting included	35	<	<	<	<	<	2
<u>pyroxenites</u>								
CMR163	independent analysis	110	4	6	26	4	4.5	8
	without roasting	120	<	<	<	<	<	16
	roasting included	150	<	<	<	<	<	7
MR63	independent analysis	44	62	3	4	4	2.5	6
	without roasting	29	40	<	<	<	<	<
	roasting included	34	27	<	<	<	<	<
MR65	independent analysis	100	220	9.5	13	6	5.5	28
	without roasting	65	180	3	12	<	<	34
	roasting included	106	85	<	6	<	0.3	23
<u>wehrlite</u>								
MR16	independent analysis	48	18	4	19	2	5	-
	without roasting	<	22	<	<	<	<	<
	roasting included	32	30	<	<	<	<	<

All data listed as ppb (whole rock).
- not determined by NiS-fire assay.
< below detection limit.

<u>Osmium.</u> Recovery of Os was increased with the inclusion of a roasting step in 3 of the samples and decreased in 2. The most noticeable changes in recovery were the

significant increases observed in the analysis of Brag71 and Brag78.

Iridium. Recovery of Ir was slightly increased by the inclusion of roasting in 4 of the samples and was decreased in only one sample.

Gold. Inclusion of a roasting step had little effect on the recovery of Au. Three of the samples showed increased recovery and 3 arguably showed decreased recovery of Au.

7.4.3 Discussion and conclusions.

Roasting appeared to be beneficial in increasing the recovery of Pt. Roasting was beneficial to the recovery of Ru and Os in some samples, but not in others. That roasting was beneficial at all in the determination of Ru and Os is surprising regarding their volatile nature when present as tetroxides, perhaps the breakdown of arsenides and sulphides ensured that a reducing atmosphere was prevalent above the sample powder at the high temperatures that one might expect loss of oxides of these elements. The effect of roasting upon the determination of Ir and Au was ambiguous and did not cause dramatic increases or decreases in their recoveries from the samples studied. Roasting appeared to be detrimental to the recovery of Pd and Rh. The decline in recovery efficiency of Pd was of particular concern, considering the near-quantitative recoveries of this element from most samples reported in Section 4.5.

The roasting temperature (700 °C) was selected to be below the decomposition temperature of some associated matrix sulphides and arsenides, e.g. millerite (NiS) and nickeline (NiAs). However this temperature may also have been too low to quantitatively effect the decomposition of some PGM that were the target for such a process. Equally, common base metal sulphides, such as pyrite (FeS) and chalcopyrite ($FeCuAs_2$), will decompose at and below 700 °C, resulting in the presence of increased levels of more easily solubilised species of transition elements which in turn may lead to increased analytical interferences. These interferences may account for the poor results for, particularly, Pd and Rh.

Little is known about the behaviour of PGE oxides or other products of decomposition that may form at the elevated temperatures encountered in the roasting step. The presence of these unknown decomposition products may also give rise to further difficulties in the sample preparation or subsequent analysis. For example, a decomposition product may be less soluble than the arsenide or sulphide from which it was derived. Such problems may also account for some of the observed decreased recoveries.

7.5 Summary.

It was recognised that limitations in the aqua regia dissolution method exist. Although mineralogical control over the accuracy of analytical results are not often considered, an attempt has been made in this chapter to to study the physical controls of sample mineralogy and the chemical controls of mineral geochemistry. There is a very real probability that an element of interest will be survive aqua regia leaching unattacked due to its occlusion within in soluble matrix material (e.g. Ir in laurite occluded within grains of chromite, Section 7.2). Having produced a sample with all the PGE species available for attack, there still remains the possibility that some species will be insoluble in aqua regia (e.g. sperrylite, Section 7.3). Conversion of insoluble species into a soluble forms of the metal can be effected with consequential improved recovery (e.g. roasting to improve the recovery of Pt, Section 7.4).

This chapter can be seen to represent preliminary investigation into some of the causes of variable and incomplete PGE recovery from geological materials. Further work may permit the study of the solubilities of common PGM and alloys to characterise more fully the limitations imposed by PGE mineralogy to the more general application of the aqua regia leach method for the determination of the precious metals, particularly in ophiolitic samples.

Chapter 8.
Testing the homogeneity of candidate reference materials: an application of aqua regia selective extraction.

8.1 Introduction.

Reference materials provide the standards against which the accuracy of new and existing analytical techniques can be evaluated in the analysis of unknown samples and may be used to resolve differences in results between analysts. The concentration of the element is determined in the reference material and compared to a certified value for that element. To claim that the technique is accurate, the difference between analysed and certified values must fall below a certain limit, such that this difference has no practical significance (Sutarno and Steger, 1985). Reference materials (RMs) should contain the elements of interest at a concentration consistent with that expected in unknown samples. Furthermore, because analytical intereferences are dependent upon the presence and relative concentration of other matrix elements, the relative concentration of analyte to concomitant elements should closely resemble that in unknown samples (Watters, 1991). It is important, therefore, that the concentration of a range of analyte elements in any candidate reference material should be well characterised.

There are few available RMs with certified values for Au and the PGE and none of these represent chromite-rich matrices, which are commonly found to host these elements. To redress this situation (partly as a requirement of on-going research on mineralisation in chromitites undertaken at the OU) and to increase the available range of RMs, two chromitite samples were prepared as candidate reference materials. The Geological Survey of Canada has also realised the need for a greater representation of RMs for Au and the PGE and, in a joint programme with the Canadian Centre for

Mineral and Energy Technology (CANMET), are preparing six rock samples for certification in these elements (Hall et al., 1989a).

The preparation was carried out in conjunction with the Groupe International de Travail-International Working Group (GIT-IWG), under the direction of K.Govindaraju (CRPG, Nancy, France). The homogeneity of the samples was assessed at the OU and 35 laboratories worldwide contributed analyses of the samples. The samples were collected in May 1986, reduced to crushate in October 1987 and transferred to France for further crushing, milling and further mixing and splitting in October 1988. Testing for homogeneity was carried out in the Spring of 1989 and the samples were released for distribution later that Summer. The cooperating laboratories contributed data throughout 1990 and 1991. This data has been compiled and, together with the results of the homogeneity testing, has been published (Potts et al., 1992).

Due to the size and nature of the project, many workers were involved, accreditation is as follows. Sample collection was carried out by P.J. Potts and J.R. Holbrook under the field guidance of H.M. Prichard and R.A. Lord (all of the OU), sample preparation by C.J.B.G. and J.S. Watson (OU), homogenisation and distribution by J.-P. Blanchard and K. Govindaraju (Centre de Recherches Petrographique et Geologique (CRPG), Vandœuvre-lès-Nancy, France), homogeneity testing by C.J.B.G. (aqua regia/ICP-MS under the supervision of K.E. Jarvis, NERC/ICP-MS unit), J.S.W. and P.C. Webb (OU) (ED-XRF) and P.J.P. and N.W. Rogers (OU) (INAA), statistical analysis of homogeneity testing data by C.J.B.G., interpretation of statistical data by C.J.B.G. and P.J.P. (with statistical advice from T. Lambert (OU)), compilation of analytical results from 35 contributing laboratories by K.G. and the project was supervised by P.J.P. The following sections summarise those steps undertaken in the preparation of the two new reference materials, emphasising the work carried out by myself.

The selective aqua regia extraction technique developed as part of this thesis (Chapter

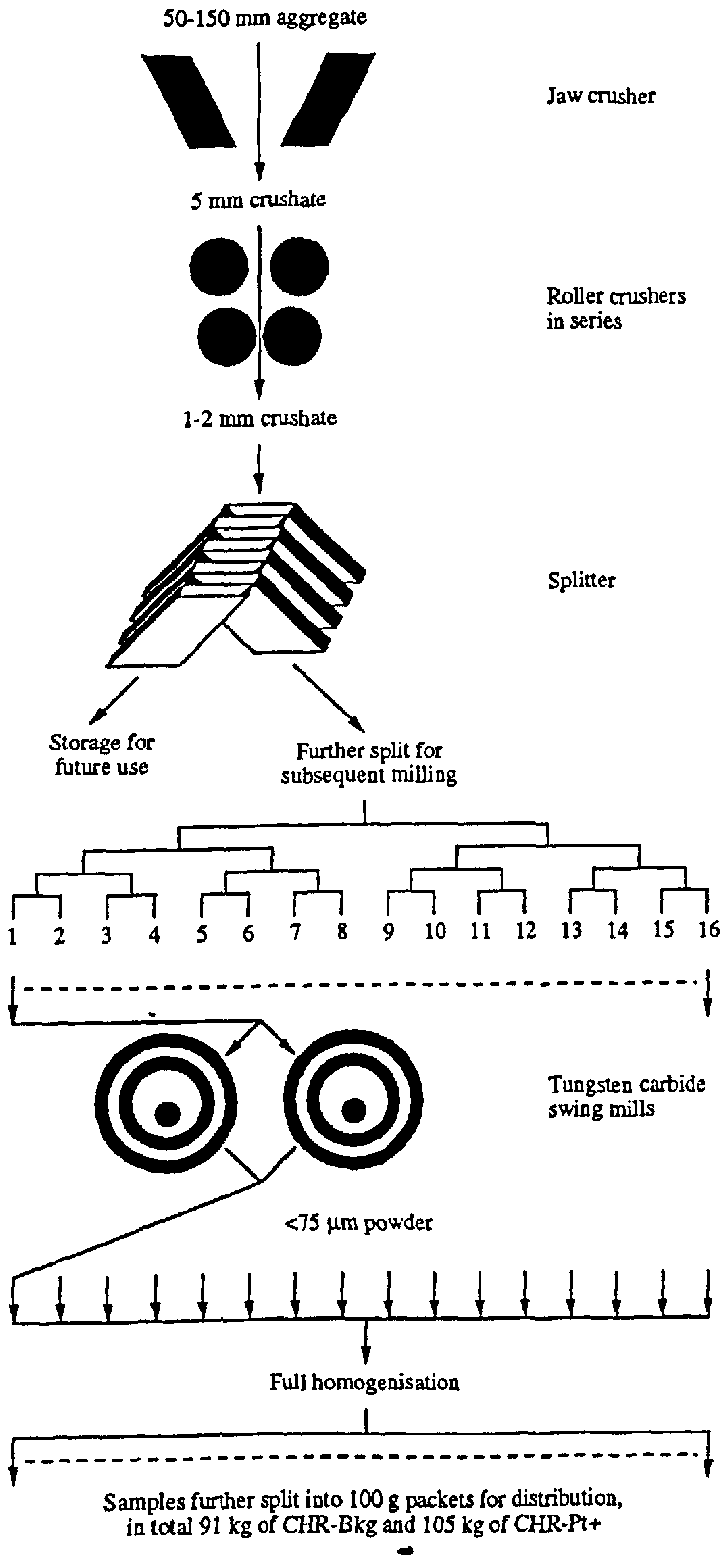
4) was considered to be an excellent method for characterising the homogeneity of Au and the PGE as required by this study.

8.2 Sample preparation.

Two chromitite samples were collected from Unst, Shetland, one from a site known to be particularly enriched in PGE and Au (Prichard et al., 1989) and the other from a site of similar host rock with no reported presence of PGMs, but likely to contain PGE and Au at ng/g concentration levels. The enriched sample was referred to as CHR-Pt+ and the less mineralised one as CHR-Bkg. About 200 kg of each of the two samples were collected from quarries of serpentinised chromite-bearing dunite from the Shetland Ophiolite complex (Prichard, 1985). An advantage of collecting the samples from this location was that a detailed study of the geology of the area has been undertaken and the mineralogy of PGE and Au has been well documented (Prichard et al., 1989). Observations from the homogeneity testing data could then be interpreted in relation to sample mineralogy.

The samples were reduced in size from the 50-150 mm hand specimens collected to 5 mm crushate by passing through a jaw crusher at the OU. This crushate was then mixed by coning before being stored in 20 kg lots in nylon sack reinforced dustbin liners for transport to the CRPG laboratories for further processing. During this subsequent processing, note was made of the changes in the physical character of the samples that might affect sample homogeneity.

Figure 8.1. Flow diagram of sample preparation procedure.



The crushate was further reduced to 0.3-0.5 mm by passing through two roller crushers operated in tandem then passed over a Jones Riffle Splitter to form two equivalent portions. One of these splits was set aside and stored for future use and the other was further split into sixteen identical working samples. Each of these sixteen working samples was then dried in an oven for at least six hours and, when cool, reduced to typically <75 µm by passing through one of two tungsten carbide swing mills in measures of 50-55 g. After full homogenisation by repeated coning, quartering and mixing, the samples were flat packed and sealed into 100 g polythene bags for distribution.[1] A total of 91 kg of CHR-Bkg and 105 kg of CHR-Pt+ was prepared in this way for distribution. The sample preparation procedure is summarised in Figure 8.1. Throughout the procedure, CHR-Bkg was prepared first to prevent contamination from the enriched sample, CHR-Pt+.

During roller crushing both samples tended to aggregate into platelets 1-2 cm in diameter. These platelets generally comprised only serpentinised fractions but some contained fine grains of chromite. The platelets decreased in size (<7 mm) during splitting. This aggregation is not thought to have had a significant effect on the overall sample homogeneity. As the swing mills became warmer, so the powders tended to cake onto the sides of the mill barrels. A few soft balls (2-3 mm in diameter) were noticed to have formed during the milling of two of the working samples which were rather damp prior to milling. Most of these masses were broken up by the brushes used to clean out the mill barrels. Any residual aggregate was so soft that it would break down during subsequent mixing and homogenisation and was expected to have no detrimental effect effect on sample homogeneity.

8.3 Testing the homogeneity of the samples.

Apart from the property of matching the matrix of unknown samples, the aliquot of a RM taken for analysis must be representative in composition of the whole sample. For this to be the case, each of the elements of interest must be distributed uniformly

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[1] Less sample separation by mineral settling was expected using flat plastic bags for long term storage rather than upright bottles or jars as is the more usual practice for RMs.

throughout the sample. If this situation is true, the sample is said to be homogeneous in that particular element at a specified mass aliquot. However, by their mineralogical nature rock samples are inhomogeneous at the particulate level. It is essential, therefore, to test the homogeneity of any candidate reference material to confirm that it is suitable for its intended use.

Some homogeneity testing programs have relied on the determination of a limited number of elements (e.g. Lister, 1982). However, bearing in mind the complex mineralogy of these chromitite samples, it is more prudent to determine directly the whole suite of PGE and Au to characterise the homogeneity of each element. Rather than distributing the samples to a number of external laboratories (e.g. Kane et al., 1990), the homogeneity testing programme was conducted at the OU for all samples, using one method with one operator for each suite of elements. This procedure eliminated the effects of inter-laboratory and inter-method bias and permitted a more accurate evaluation of sample inhomogeneity by identifying variations associated with the sample rather than the analytical method. The method chosen for determination of the precious metals was the selective aqua regia dissolution (as described in Chapter 4) followed by ICP-MS. Two complementary techniques were employed for the determination of some precious metals and other trace and major elements: INAA (for Ir, Au, As, Sb, Fe, Co and Zn) and ED-XRF (for Fe, Cr, Ni, Cu, Zn, Ga and As).

To undertake homogeneity testing, a number of the packets were selected at random from the whole collection prepared for distribution. The selected packets were regarded as being representative of the whole set. In this study, twenty-four 100 g packets of each sample were selected at random for homogeneity testing.

8.3.1 Analytical techniques.

The analytical techniques used are described in Chapter 4, the procedures used are summarised as follows:

8.3.1.1 Aqua regia/ICP-MS.

In the aqua regia/ICP-MS method, duplicate 10 g aliquots were analysed. Each aliquot was stirred with 20 ml aqua regia for 1 hr at room temperature. The insoluble residue was filtered off and washed, the final solution being diluted to 100 ml. This solution in 20% aqua regia was analysed directly by ICP-MS. The instrument was calibrated with a standard solution containing the elements of interest prepared in 20% aqua regia.

From the results presented in Chapter 4, near quantitative extraction is expected for Au and Pd, but only partial extraction will occur for Pt and Rh (typically 18%), Ir (1%) and Ru and Os (low but uncertain due to lack of available RMs). Because some PGMs, known to be present in chromitite samples from the Shetland ophiolite, are insoluble in aqua regia (Section 7.3), this method will test the distribution of aqua regia soluble PGE, rather than that of total PGE. As results reflect not only the distribution of PGE and Au, but also the distribution of PGMs, this test may consequently be a more rigorous test of sample homogeneity.

8.3.1.2 Energy dispersive-x-ray fluorescence.

For XRF, powder pellets were prepared from single 7-8 g aliquots and analysed following procedures of Potts et al. (1984) and Webb et al. (1990). Both faces of the pellet were analysed such that duplicate determinations were made on independently analysed volumes though not on individually prepared samples. The approximate effective mass analysed has been estimated from the critical penetration depth in powder pellets of characteristic x-rays from the different analyte elements, these masses are reported in the results tables. Calibration was undertaken using a silicate analysis programme, designed for samples with <1% Cr; this calibration may not, therefore, fully account for the 10-15% Cr present in these chromitite samples, but should provide suitable comparative data from which conclusions about sample homogeneity may be drawn.

8.3.1.3 Instrumental neutron activation analysis.

Single 300 mg aliquots were analysed by INAA following procedures described by Potts et al. (1981; 1985). Calibration was undertaken against a microgranite spiked with Au, Ir, As and Sb. As with the XRF method, the calibration programme used had been prepared for silicate samples, but the chromitite matrices were not thought likely to influence unduly the accuracy of results other than gamma-ray interferences caused by the presence of high Cr activity at 320 keV. However, some instrumental problems were encountered during the analysis. One batch of irradiated samples could not be counted before substantial decay had rendered Au and As data unusable due to excessive decay of the relevant isotopes. In addition, an activity peak was occasionally missed by the spectrum analysis software. Consequently, the total number of determinations of some elements at the following characteristic gamma energy activity peaks was less than 24: CHR-Pt+: Au (411 keV): 15, As (559 keV): 6, As (657 keV): 4, Sb (564 keV): 16; CHR-Bkg: Ir (468 keV): 13, Fe (1291 keV): 23, Co (1332 keV): 23, Zn (1115 keV): 16. This is of relevance as the critical values of calculated statistics (Table 8.1) are dependent upon the number of analyses reported in the particular data set.

8.3.2 Statistical analysis of the results.

Statistical parameters were calculated and a suite of statistical tests were executed on the three data sets generated by the ICP-MS, INAA and XRF analyses, to test whether the differences within and between duplicate determinations were significant according to specific statistical criteria.

Analysis of variance.

The between-packet variance and the within-packet variance are compared by the statistical procedure, analysis of variance (ANOVA). This procedure compares directly the two variances by application of the F-test (Equ. 8.1) to see whether the difference is significant at the chosen confidence level. The ratio generated by the F-test is compared to values from statistical tables to determine the significance of the difference at the appropriate confidence level.

$$F_{(n1,\,n2)} = \frac{VAR_1}{VAR_2} = \frac{\text{(between-packet variance)}}{\text{(within-packet variance)}} \qquad \text{(Equ. 8.1)}$$

$n1$ = number of between-packet degrees of freedom

$n2$ = number of within-packet degrees of freedom.

The overall variability[2] could be estimated in two ways from either the between-packet variability or the within-packet variability. It was simple to calculate the overall variance and the between-packet variance. The pooled within-packet variance, however, required a combination of each of the 24 individual within-packet variances. To simplify the calculation of within-packet variance, use was made of the mathematical relationship between the sums of squares of the deviations (Equ. 8.2), such that the within-packet variance could be calculated from the between-packet and the total variances (Equ. 8.4).

within-packet sum of squares = total sum of squares - between-packet sum of

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[2] Because the term "variance" has a specific statistical definition, the term "variability" is used to refer in a non-quantitative way to compositional differences within the sample.

squares

$$= \sum_{i=1}^{n} (x_i - \bar{x})^2 - 2 \sum_{j=1}^{k} (\bar{x}_j - \bar{x})^2 \qquad \text{(Equ. 8.2)}$$

n = total number of data in set

x_i = an individual result in the data set= $x_1, x_2, x_3, \ldots, x_n$

$$\bar{x} = \text{mean of the data set} = \frac{\sum_{i=1}^{n} x_i}{n} \qquad \text{(Equ. 8.3)}$$

$\bar{x}_j$ = mean of the j^th^ duplicate analysis

k = number of duplicate analyses

$$\text{within-packet variance} = \frac{\text{within-packet sum of squares}}{\text{within-packet degrees of freedom}} \qquad \text{(Equ. 8.4)}$$

Computer software packages were used to generate ANOVA tables and F-ratios. Analysis of variance and its suitability in this study are considered further below.

Normality.

The most simple test for normality is to fit a normal curve to the sample data and to apply the chi square (χ^2) test for goodness of fit to the grouped frequencies. In this test, data is split into a number of categories, each containing the same proportion of data (i.e. narrow categories near the mean and broader categories towards the tails of the distribution). A comparison is made between the expected number of data in a category (expected frequency) and the actual number in that category (observed frequency) (Equ. 8.8). The χ^2 value generated is then compared with tabulated confidence limits. The chi square test was applied with 8 categories (n=48, except Ga: 6 categories)[3] or 4 categories ($12<n\leq24$) in order to have an expected frequency

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[3] Ga data was output with a precision such that dividing the normal distribution into 8 categories would leave two of the categories empty. The data was reported to the nearest µg g^{-1}. The range of some of the 8 categories were <1 µg g^{-1} whereas all the widths of the 6 categories were >1 µg g^{-}

greater than 3. In interpreting results, account must be made that, the chi square test may prove insensitive to real departures from normality (Pearson and Hartley, 1966). To avoid mis-interpreting results, Geary's a-test for normality was also applied to determine the significance of non-normality of the data set. Geary's test relates the mean deviation of the data set to the standard deviation (Equ. 8.9), the ratio is then compared to tabulated confidence limits.

Outliers.

Grubb's T-test was used iteratively to identify outliers. Grubb's test relates the deviation of an extreme value to the mean and standard deviation of the whole data set (Equ. 8.10). The statistic (Grubb's T_n) thus calculated is then compared to tabulated confidence limits.

Skewness and kurtosis.

The coefficients of skewness (Equ. 8.11) and kurtosis[4] (Equ. 8.12) describe the symmetry and pointedness respectively of the data distribution. The closeness of their values to 0 and 3, respectively, can be used as an indicator of the normality of the data set and can also be used in identifying outlying data. These coefficients were also calculated to support the decisions made by normality and outlier tests, on the understanding that discordant data could be identified with more confidence if there was some agreement between several of these tests.

Use of the F-test, Geary's and Grubb's tests was recommended by Lister (1982). In

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[1]. It was, therefore, not appropriate to use 8 categories to test the goodness of fit of Ga data using the chi square test.

[4] The coefficient of kurtosis cannot, however be used with INAA data as there are no tabulated critical values for n<50. The critical values for ICP-MS and XRF data ($44 \leq n \leq 48$) have been estimated from those for n=50.

the certification programme for PTO-1 (later renamed SARM 7), Steele et al. (1975) used the coefficients of skewness and kurtosis for the elimination of outliers then Geary's test to check for normality. The critical values for all the statistical tests used here are shown at the 95% and 99% confidence levels in Table 8.1.

8.3.2.1 Definition of statistical tests.

See previous sub-section (8.3.2 *Analysis of variance*) for definition of n, x_i and $\overline{x}$.

VAR = variance of the data set = $\dfrac{\sum_{i=1}^{n}(x_i-\overline{x})^2}{n-1}$ (Equ. 8.5)

s = standard deviation of the data set = $\sqrt{VAR}$ (Equ. 8.6)

Coefficient of variation, CV = $\dfrac{s}{\overline{x}}$ (Equ. 8.7)

Chi square test for goodness of fit, $\chi^2 = \displaystyle\sum_{j=1}^{J}\frac{(o_j-e)^2}{e}$ (Equ.

8.8)

J = total number of regions (categories)

o_j = number of data points observed in region j

e = expected number of data points in each of J regions

Geary's statistic, a = $\dfrac{\sum_{i=1}^{n}|x_i-\overline{x}|}{\sqrt{n\sum_{i=1}^{n}(x_i-\overline{x})^2}}$ (Equ. 8.9)

Grubb's test, $T_n=\dfrac{x_n-\overline{x}}{s}$ or $T_1=\dfrac{\overline{x}-x_1}{s}$ (Equ. 8.10)

Skewness, $\sqrt{b_1}=\dfrac{n\sum_{i=1}^{n}(x_i-\overline{x})^3}{\sqrt{n\left\{\sum_{i=1}^{n}(x_i-\overline{x})^2\right\}^3}}$ (Equ. 8.11)

$$\text{Kurtosis, } b_2 = \frac{n \sum_{i=1}^{n} (x_i - \bar{x})^4}{\left\{ \sum_{i=1}^{n} (x_i - \bar{x})^2 \right\}^2} \qquad \text{(Equ. 8.12)}$$

Table 8.1. Critical values for the statistical tests (only the values relevant to this study are tabulated).

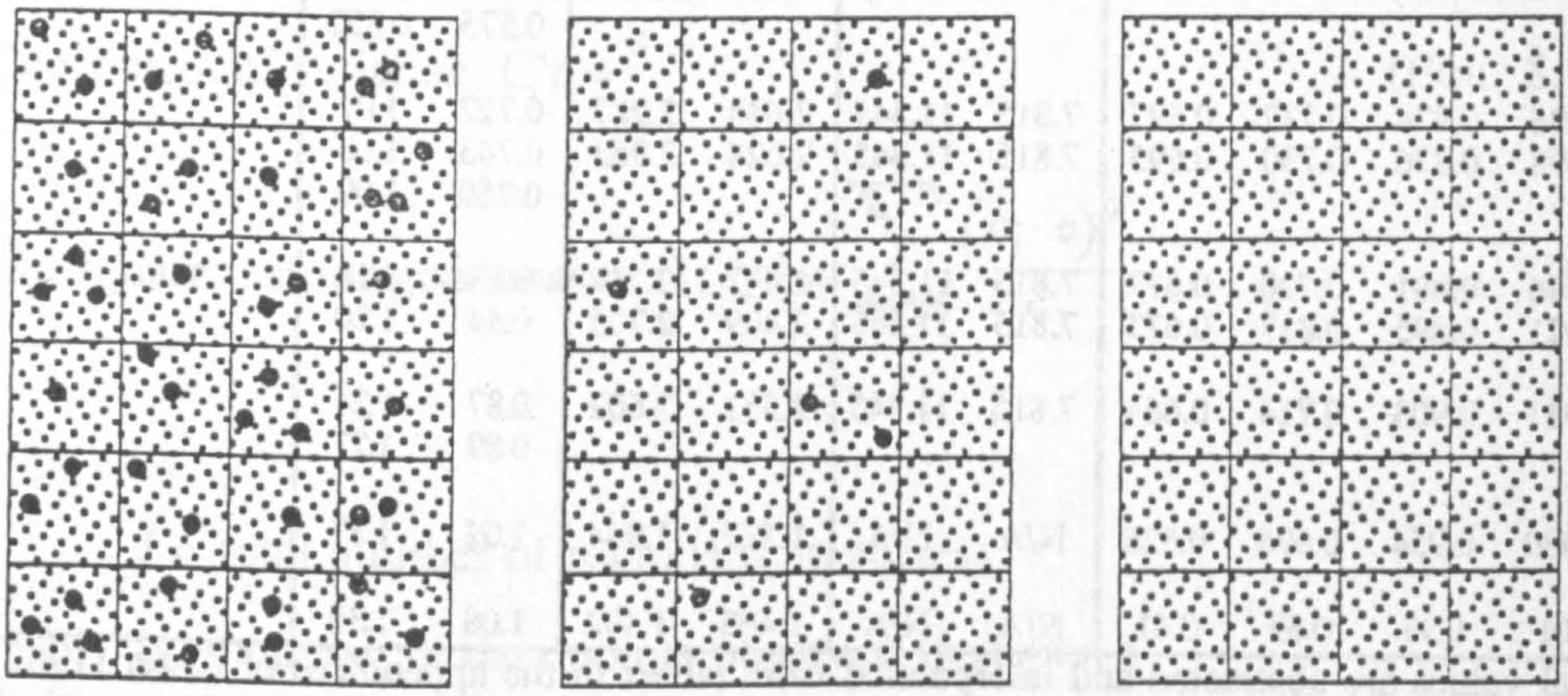
size	Geary's A-test				Chi-square test		Grubb's T-test		Skewness		Kurtosis			
n	upper 1%	upper 5%	lower 5%	lower 1%	95%	99%	95%	99%	95%	99%	upper 1%	upper 5%	lower 5%	lower 1%
48	0.867	0.850	0.750	0.726	14.067	18.475	2.939	3.318	0.544	0.802	4.89	3.99	2.15	1.95
47							2.931	3.310	0.548	0.810	4.89	3.99	2.15	1.95
46					Ga	Ga	2.922	3.301	0.553	0.817	4.90	3.99	2.15	1.95
45					11.070	15.086	2.914	3.292	0.558	0.825	4.90	3.99	2.15	1.95
44							2.904	3.228	0.564	0.834	4.91	3.99	2.15	1.95
43									0.570	0.843				
42									0.575	0.852				
24	0.896	0.874	0.732	0.697	7.815	11.345	2.644	2.987	0.727	1.07				
23	0.898	0.876	0.730	0.695	7.815	11.345	2.624	2.963	0.743	1.08				
22									0.759	1.09				
16	0.916	0.891	0.720	0.677	7.815	11.345	2.443	2.747	0.83	1.18				
15	0.921	0.895	0.817	0.673	7.815	11.345	2.409	2.705	0.84	1.20				
13	0.931	0.903	0.714	0.664	7.815	11.345	2.331	2.607	0.87	1.24				
12									0.89	1.27				
6	0.980	0.954	0.696	0.626	N/A	N/A	1.822	1.944	1.02	1.33				
4	1.01	0.98	0.69	0.61	N/A	N/A	1.463	1.492	1.08	1.35				

Critical values are abstracted and interpolated from tables in the appendices of Lister (1982).
Chi-square test: goodness of fit was tested with 8 categories (n=48, except Ga: 6 categories) or 4 categories ($12 \leq n \leq 24$) in order to have expected frequency, e>3; the tabulated values represent significant values for 7, 5 and 3 degrees of freedom, respectively.
No values are available for the significant levels for the coefficient of kurtosis with n<50; those values tabulated for kurtosis are approximate estimates from the tabulated values of n=50.

8.3.2.2 Analysis of variance and the nugget effect.

The F-test (Equ. 8.1) has been widely used in previous studies to test sample homogeneity (Steele et al., 1975; Lister, 1982), but has also come under criticism for being unsatisfactory for these requirements. Ellis et al. (1983) argued that the variation from sampling within the packet was usually much larger than that encountered in the selection of the powder for the packets, if each packet is a split taken from one large homogenised mass. However, the discrepancies between within- and between-packet sampling variability in the age of the chromitite reference material under study may be overshadowed by the mineralogical constraints imposed by the nature of chromitite samples used in this project. A significant proportion of PGE and Au are likely to occur in these samples both as small discrete PGMs (Prichard et al., 1989) and in solid solution in primary base metal sulphides (BMS) (Distler et al., 1978; Amossé et al., 1990). The distribution of the relatively abundant BMS phases is expected to contribute to sample inhomogeneity to a lesser extent than that of the individual PGMs and Au grains. In these circumstances, sample homogeneity may be significantly affected by the nugget effect, as discussed below.

Figure 8.2. Schematic representation of the random distribution of sub-microscopic (.) and particulate (•) PGM and/or Au grains in 24 splits of a sample. Represented are (a) the frequent occurrence, (b) the rare occurrence and (c) the absence of the larger grains. Adapted from Xie and Wang (1991).



(a) (b) (c)

Previously, the analytical consequences of the nugget effect have been concerned with a model in which Au grains have a uniform shape and size (Clifton et al., 1969). Xie and Wang (1991) showed that, in some circumstances, this model was too simple. From their studies results obtained a regional geochemical survey, they proposed the coexistence of relatively few particulate[5] Au grains (>5 µm) with a greater number of submicroscopic grains (<5 µm) forming a uniform matrix of dispersed Au. This model is illustrated in Figure 8.2, in which it can be seen that the greatest variation occurs for

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[5] The term "particulate" refers to the larger size range as proposed by Xie and Wang (1991) and, although being defined as >5 µm, often represents grains which are larger than this (20-250 µm and possibly even larger).

the sample with the middle range Au concentration. Samples that contain only submicroscopic Au, i.e grains <5 μm, (represented in Figure 8.2c) will have a homogeneous distribution of Au . Samples with many large Au grains (represented in Figure 8.2a) will have a homogeneous distribution of Au present in both grain size ranges. Samples with just a few particulate Au grains (represented in Figure 8.2b) will have a homogeneous distribution of Au present as submicroscopic grains but the sample may be rendered inhomogeneous by the presence of one or two particulate grains in a few of the sub-samples (packets).

Although these examples have been based on the distribution of Au grains, the arguments and model are equally applicable to the distribution of the PGE that also occur as discrete dense mineral grains. As mentioned in Chapter 4, samples from the same locality as CHR-Pt+ are known to contain individual grains of PGMs in the size range 5-25 μm and one as large as 250 μm (Prichard et al., 1989). The presence of submicroscopic grains not visible in thin section and below the resolution of ß-autoradiography (i.e. <1-2 μm) cannot be discounted. The presence of these submicroscopic grains, can be related to the model of Xie and Wang (1991) and, despite having small contribution to bulk precious metal concentration in the sample, they will contribute significantly to sample homogeneity.

If elemental distribution was totally homogeneous, the only variability would be subsample size-related, as described by Ellis et al. (1983). However, if the nugget effect is likely to cause significant variability in Au and PGE compositions, it is necessary to determine the significance of this variability at the sub-sample mass selected for analysing. If there is a chance that the nugget effect is so great as to invalidate the conditions for application of the F-test (see below), consideration must be given to application of a similar although less powerful statistical test to compare between- and within-packet variability. This test (the Kruscal-Wallis test) accommodates the wider spread of data that will be encountered in such samples.

8.3.2.3 Analysis of variance and the F-test.

Application of the F-test (Equ. 8.1) makes two assumptions, first that the data are normally distributed and second that the within-packet variances are equal. Normality has been tested as described above. Bartlett's test was applied to test the significance of the inequality of the within-packet variances. Bartlett's test basically compares the arithmetic and geometric means of the sample estimates of variance by referring the statistic μ (Equ. 8.13) to the χ^2 distribution.

$$\mu = \frac{N \ln\left(\frac{1}{N}\sum_{i=1}^{k} f_i \, \mathrm{VAR}_i\right) - \sum_{i=1}^{k} f_i \ln \mathrm{VAR}_i}{1 + \frac{1}{3(k-1)}\left(\sum_{i=1}^{k}\frac{1}{f_i} - \frac{1}{N}\right)} \qquad \text{(Equ. 8.13)}$$

k = number of packets analysed

VAR_i = estimate of the variance from the i^{th} packet

f_i = degrees of freedom in the analysis of the i^{th} packet = $n_i - 1$

n_i = number of data from analysis of the i^{th} packet (i.e. = 2)

$N = \sum_{i=1}^{k} f_i$

In this study $f_i = 1$ for all i and $N = k = 24$, so the calculation of μ is simplified to μ^* (Equ. 8.13*).

$$\mu^* = \frac{3}{4}\left\{24 \ln\left(\frac{1}{24}\sum_{i=1}^{24} \mathrm{VAR}_i\right) - \sum_{i=1}^{24} \ln \mathrm{VAR}_i\right\} \qquad \text{(Equ. 8.13*)}$$

When ANOVA followed by the F-test is not permitted, a non-parametric technique is applied to the data. This technique involves ranking the data from highest to lowest and calculating the Kruscal-Wallis statistic, H (Equ. 8.14).

$$\text{Kruscal-Wallis, } H = \frac{12}{n(n+1)} \sum_{i=1}^{k} \frac{R_i}{n_i} - 3(n+1) \qquad \text{(Equ. 8.14)}$$

R_i = sum of ranks of duplicate analyses.

Being non-parametric, this test statistic is independent of normality but does not account for the absolute values of the data, merely the relative ordinal size. Thus the test represents an extreme approximation of ANOVA F-test and will not be affected by gross or significant outliers. Although it does not offer as much information as the ANOVA, F-test, the Kruscal-Wallis non-parametric ANOVA presents a reasonable indication of the relationship of within-packet to between-packet variability for data that does not fit the normal model.

8.4 Evaluation of the results of homogeneity testing.

Statistical results of the homogeneity testing of CHR-Pt+ and CHR-Bkg are presented in Tables 8.2 (normality and outlier) and 8.3 (ANOVA and comparison of variances) and the spread of ICP-MS data is shown in the histograms of Figures 8.3 (CHR-Pt+) and 8.4 (CHR-Bkg). Statistical test data are reported at both the 95% and 99% confidence levels. The choice of confidence level is arbitrary for any statistical problem, however, these two levels are the two most often chosen for the examination of data and they provide suitable markers for this interpretation. In interpreting the significance of this data it should be borne in mind that for any normally distributed data set there is a statistical probability that 1 in 20 results will be significant at the 95% confidence level and 1 in 100 results will be significant at the 99% confidence level. It should not be unusual, therefore, to find 2 or 3 out of 48 results exceeding the 95% confidence limits, and it is not inconceivable that 1 in 48 results should exceed the 99% confidence limits.

Table 8.2 (results for tests for normality and outliers for homogeneity data from CHR-Pt+ and CHR-Bkg) and **Table 8.3** (results for tests for analysis of variance for homogeneity data for CHR-Pt+ and CHR-Bkg and comparison of between-bottle variance with overall variance of data from the cooperative analysis programme) are included in Appendix A at the end of the thesis.

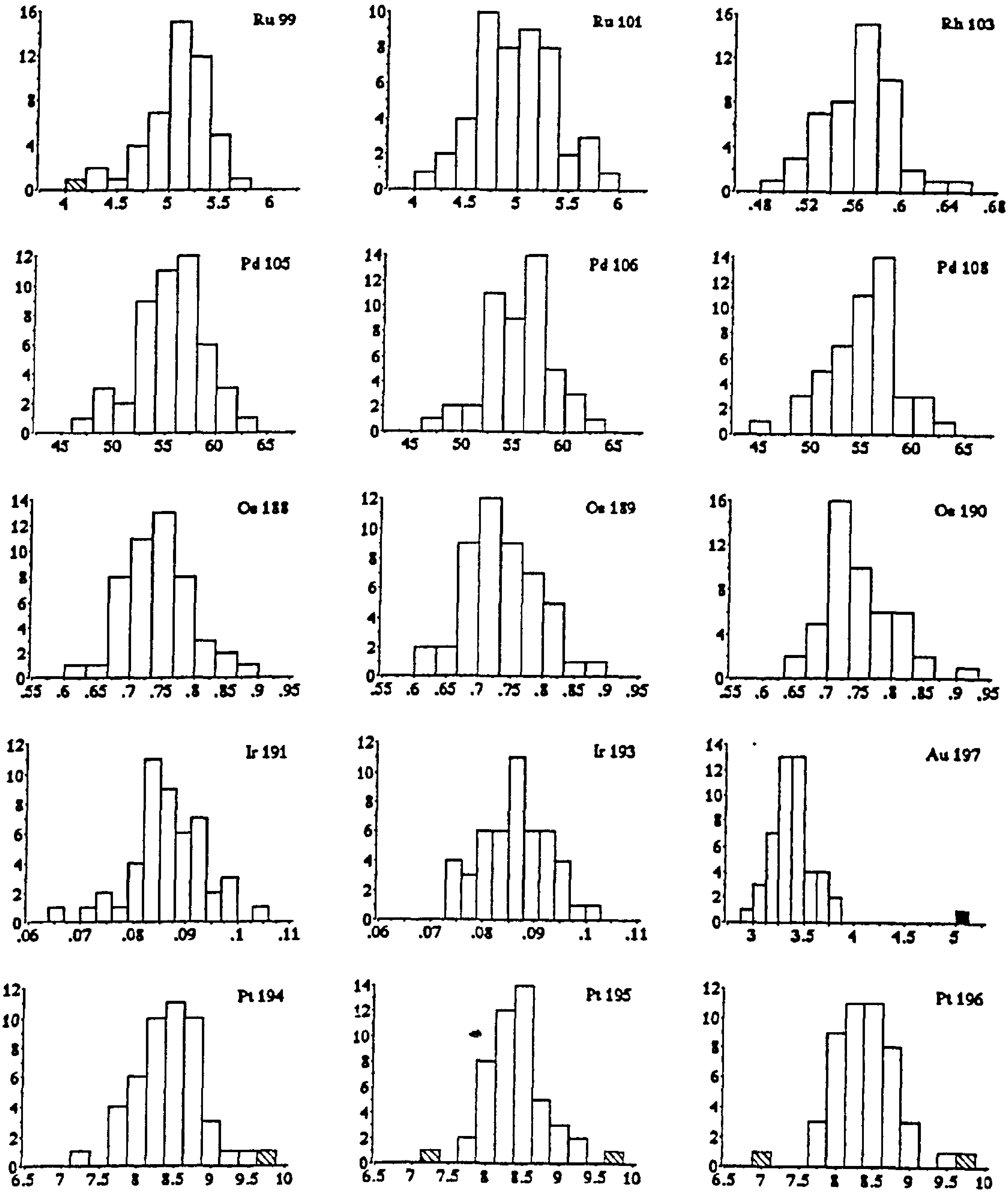
To account for any limitations in the interpretation of the F-test and to accommodate interpretation of the INAA data, for which there were no duplicates on which to calculate the F-ratio, particular emphasis is placed on tests for the presence of outliers and their relevance to the prediction of the level of sample homogeneity. Finally, a comparison is made of the significance of between-packet variation relative to the overall variation derived from data submitted to the cooperative analysis programme from a range of techniques by different participating laboratories. The overall variance from the cooperative analysis programme and the between-packet variance estimated from the ANOVA table (Equ. 8.3) have been normalised to their means to account for inadequacies in instrument calibration and varied preconcentration procedures, i.e. the comparison has been made between their coefficients of variation (Equ. 8.7). Without this normalisation, variance data derived from the partial leach here used would not be directly comparable with data representative of total element concentrations.

Conclusions regarding the mineralogical control over outlying data generally refer to a worst-case interpretation and necessarily assume the lack of gross analytical errors. This worst-case scenario is appropriate in this study as it is necessary to identify the greatest likelihood of generating an extreme result. In reality, it is suggested that the frequency of observation of the extreme value would be less than that predicted by these worst-case interpretations.

8.4.1 CHR-Pt+.

Application of the chi square test using 8 or 4 categories with expected frequencies between 3.75 and 6 shows that χ^2 is less than the critical value at the 95% confidence levels for 7 and 3 degrees of freedom for ICP-MS & XRF and INAA data, respectively, for all elements except Ir (308 keV) and ^{197}Au. Application of Geary's test identifies non-normality at the 95% confidence level for Ir (468 keV), Ir (308 keV), ^{195}Pt, Zn (1115 keV) and Ni and at the 99% confidence level for ^{197}Au. Bearing in mind the limitations in interpreting data in relation to confidence levels (mentioned above) and the characteristics of the analytical techniques {e.g. Cr (320 keV) interference on Ir (308 keV) peak}, the only significant departure from normality is considered to be that of the ^{197}Au data. This will be discussed further below.

Figure 8.3. Histograms showing the distribution of Au and PGE data from homogeneity studies of CHR-Pt+. Data identified as outliers by Grubb's test are indicated at the 95% confidence level (stippled shading) and at the 99% confidence level (solid shading).



Outliers were identified by Grubb's test at the 95% confidence level for ^{99}Ru, ^{194}Pt, ^{195}Pt (2 outliers), ^{196}Pt (2 outliers) and at the 99% confidence level for ^{197}Au and Zn. The outliers for the precious metals are highlighted in Figure 8.3. As with normality test, the only outlier that is considered to demand further consideration is that of ^{197}Au. Examination of the coefficients of skewness and kurtosis supports the conclusions of the normality and outlier tests.

In the absence of duplicate analyses, homogeneity of the elements determined by INAA is assessed by examination of normality and outliers test statistics. From examination of tests for normality and outliers, the only observation of significance to this study is the positive outlier causing non-normal distribution of Zn data. The relevance of this is discussed below in relation to the overall variance from the cooperative analysis programme.

As can be seen from Figure 8.3, the ^{197}Au outlier is responsible for the non-normality of the data, identified by the chi square and Geary's tests. The probability that this one extreme value is in fact part of the normally distributed cluster is very low and, assuming the absence of analytical irregularities, it must be assumed to indicate the presence of Au mineral(s) in that one analysed aliquot. The duplicate from this packet did not result in an extreme value. Assuming that duplicate determinations are totally independent aliquots of the bulk sample, there is a 1 in 48 chance that a randomly selected 10 g aliquot will contain an anomalously high concentration of Au.

8.4.1.1 ANOVA for CHR-Pt+ data.

Bartlett's test identifies significant inequality of variances at the 95% confidence level for ^{197}Au. The infinite values for As, Zn and Cu are artefacts of duplicate analyses of one or more packet having identical values within the precision of measurement. Recalculation of μ without these zero variances does not identify significant non-equality of variances.

Analysis of variance followed by the F-test is applicable to all data except ^{197}Au, which is invalidated due to its non-normality and non-equality of variances. Between-packet variance was found to be significantly greater than within-packet variance for ^{103}Rh, ^{189}Os, and Fe at the 95% confidence level and ^{99}Ru, ^{101}Ru, ^{105}Pd, ^{106}Pd, ^{108}Pd, Cr and Ni at the 99% confidence level. The differences in the Cr and Fe data can be explained by obvious analytical problems due to deficiencies in the analytical method.[6] Of the differences in the ICP-MS data, because the ^{189}Os difference is not corroborated by the other isotopes and there are no outliers for any of the Os isotopes, it can be concluded that the distribution of Os is not significantly inhomogeneous. The differences observed for Ru, Rh and Pd could be due to excessive instrumental drift during the analysis of strongly acidic solutions containing high levels of total dissolved solids. It can be seen from Table 8.3 that the between-packet variance is less than the overall variance from the cooperative analysis programme. The importance of this is that, despite being significantly greater than the within-packet variance and assuming the worst-case interpretation, the between-packet variances for Ru, Rh, Pd and Ni are overshadowed by the overall interlaboratory variation and is not likely to have a significant influence on the recommended values derived from the cooperative analysis programme.

The Kruscal-Wallis non-parametric ANOVA has to be used for ^{197}Au and it shows no significant difference between between-packet variance and within-packet variance, despite the presence of the outlier. It is also interesting to note that the elements for which the more crude non-parametric test identifies significant difference between between-packet variance and within-packet variance are those that give the highest

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[6] The 24 pellets were analysed in batches of 16 and 8, each analysed on both sides to obtain the duplicate analyses. There was considerable drift between both duplicate analytical runs, such that concentrations derived from one side of the pellet were systematically lower than those from the other side and the differences between the two sides of the smaller batch were less than those of the larger batch. This served to create an artificially large spread of data resulting in an artificially high within-packet variance and an even higher between-packet variance.

F-ratios (i.e. those normal distributions in which there is greatest difference between between-packet variance and within-packet variance). This correlation supports the premise that the Kruscal-Wallis test will identify the presence of significant between-packet variance in data that has a non-normal distribution.

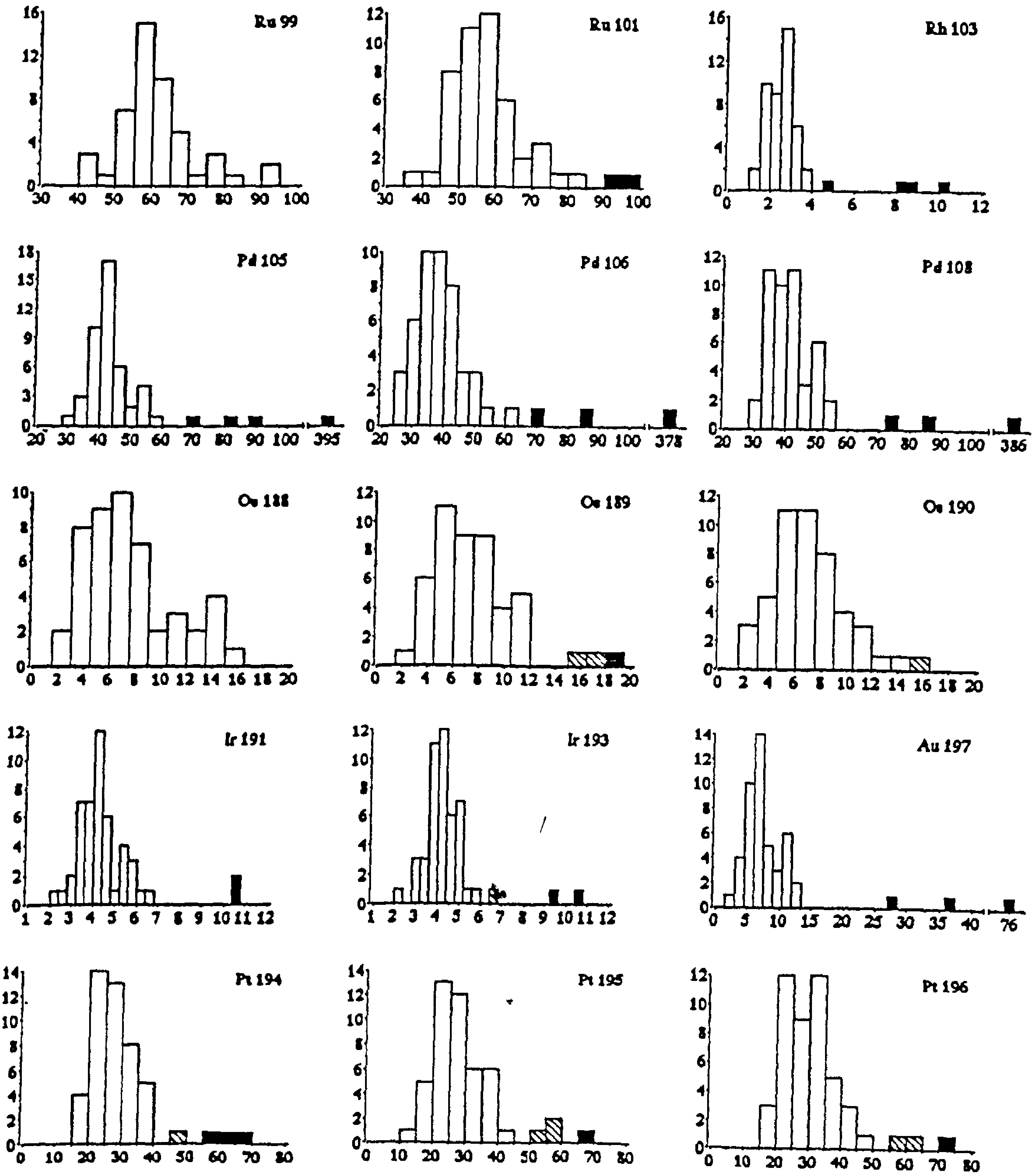
8.4.2 CHR-Bkg.

Application of the chi square test using 8, 6 or 4 categories with expected frequencies between 3.25 and 6 shows that, with 7, 5 or 3 degrees of freedom, χ^2 is less than the 95% confidence level for ^{188}Os, ^{189}Os, ^{190}Os, ^{194}Pt, ^{196}Pt and all elements analysed by XRF and INAA except Co (1332 keV), and additionally that χ^2 is less than the 99% confidence level for ^{101}Ru and ^{195}Pt. Application of Geary's test identifies non-normality at the 99% confidence level for all isotopes of Ru, Rh, Pd, Ir, Pt and Au by ICP-MS and Co (1332 keV), and additionally ^{189}Os at the 95% confidence level. Bearing in mind the limitations in interpreting data in relation to confidence levels, Ru, Rh, Pd, Ir, Pt and Au data by ICP-MS can be considered to be non-normal at the 99% confidence level, and Os data by ICP-MS and all XRF and INAA data except Co (1332 keV) can be considered normal at the 95% confidence level.

No outliers were identified by Grubb's test for ^{99}Ru, ^{188}Os, XRF and INAA data, but data for between 1 and 4 samples for all other isotopes were found to be significant at the 95% confidence level; most of these outliers were also significant at the 99% confidence level. Examination of the coefficients of skewness and kurtosis supports the conclusions of the normality and outlier tests. Additionally these coefficients identify two outliers for ^{99}Ru significant at the 99% confidence level, both of which hail from the same packets as the outliers identified for ^{101}Ru. The one miscorrelation is the identification by the coefficient of skewness of 6 outliers for ^{189}Os, significant at the 95% confidence level. Bearing in mind the other evidence of normality and outliers, these 'outliers' were not regarded as significant in this interpretation of the data.

In the absence of duplicate analyses, homogeneity of the elements analysed by INAA is assessed by examination of normality and outliers test statistics. For the reasons described above, the only observation of significance to this study is the non-normal distribution of Co data, which can be attributed to analytical problems encountered in the counting of the vials from one of the irradiation cannisters.

Figure 8.4. Histograms showing the distribution of Au and PGE data from homogeneity studies of CHR-Bkg. Data identified as outliers by Grubb's test are indicated at the 95% confidence level (stippled shading) and at the 99% confidence level (solid shading).



It can be seen graphically in Figure 8.4 that the distributions of data for the precious metals by ICP-MS represent normal distributions of the bulk of the data plus a few outliers. In particular the Pd and Au distributions show one gross outlier each, the outliers originated from different packets. Assuming the absence of analytical irregularities and the worst-case interpretation, no statistical anomaly was found for the duplicate aliquot from either of these packets. The presence of the gross outlier suggests that 1 out of 48 packets will contain a severely anomalously high concentration of Pd or Au. Although there is a probability (<5%) that the significant (non-gross) outliers could belong to the normal distribution of the bulk of the data, it is more realistic to relate these outliers to mineralogical effects and to say that 3 out of 48 packets will contain an anomalously high concentration of any one of these elements, in addition to the possibility of the severe Pd or Au anomalies.

It can also be seen from Figure 8.4 that all the outliers (highlighted) are present on the positive side of the bulk of the data, which suggests that between 0 and 4 aliquots have higher concentrations than a background level present in most of the aliquots. This distribution of Au and the PGE supports an assumption of the model hypothesised by Xie and Wang (1991), as illustrated in Figure 8.2b.

8.4.2.1 ANOVA for CHR-Bkg data.

Bartlett's test identifies significant inequality of variances for ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{193}Ir and ^{197}Au at the 99% confidence level and ^{195}Pt at the 95% confidence level (^{191}Ir is very close to being significant at the 95% confidence level). The infinite values for Zn, Cu and Ga are explained in the previous section. Bartlett's test, therefore, suggests that ANOVA followed by the F-test can be used in the interpretation of data for Ru, Os, Pt, Fe, Zn, Ni, Cr, Cu and Ga.

Considering the conclusions drawn from the above statistical tests, ANOVA followed by the F-test can be used for Os, Zn, Ni, Cu and Ga. Some information may be gleaned from the F-test for Ru, Pt, Fe and Cr, but the Kruscal-Wallis test should be used. The F-test is inapplicable for Rh, Pd, Ir and Au for which only the Kruscal-Wallis test can be applied.

From the limited information supplied by the Kruscal-Wallis test, it can be seen that only ^{101}Ru and Fe show differences between the between-packet variance and the within-packet variance significant at the 95% confidence level. Both these items are corroborated, along with Cr, by the high F-ratios, which are significant at the 99% confidence level. Within-packet variance is significantly greater than between-packet variance at the 95% confidence level for Zn. Between-packet variance is significantly greater than within-packet variance at the 95% confidence level for ^{190}Os, ^{194}Pt, ^{195}Pt and ^{196}Pt. Bearing in mind the limitations in interpreting data in relation to confidence levels and the non-agreement of other Os isotopes, the ^{190}Os F-ratio does not cause concern in this study. Analytical problems (see footnote 6, previous section) account for the Fe and Cr observations. It can be seen from Table 8.3 that for Pt and the XRF data, the between-packet variance is less than the overall variance from the cooperative analysis programme. The same could be said for the Ir data, but for the Ru, Rh, Os and Au, the between-packet variance is only slightly greater than the overall variance from the cooperative analysis programme. Moreover, for Pd the between-packet variance is in fact slightly less than the overall variance from the cooperative analysis programme.

8.5 Conclusions.

Conclusions and recommendations are made about the homogeneity of CHR-Bkg and CHR-Pt+. In recognition of the scope of this thesis, conclusions are also drawn concerning the suitability and applicability of the selective aqua regia extraction technique for homogeneity testing, as used in this study.

8.5.1 Homogeneity of CHR-Bkg and CHR-Pt+.

In the interpretation of data from the homogeneity tests, it must be recognised that the low concentrations of the precious metals in CHR-Bkg provide a challenge to the analytical capabilities of the selective aqua regia extraction technique and that the analytical contribution to the between-packet variance will be large. CHR-Bkg can be considered to be homogeneous in the minor elements determined by XRF and INAA. The precious metals seem to be distributed inhomogeneously, but the extent of inhomogeneity is no greater than the variability observed in the cooperative analysis programme.

It is appropriate to place the following restrictions on the use of CHR-Bkg as a reference material for Au and the PGE: when these elements are to be determined, two separate10 g samples should be analysed independently and agreement between the replicate analyses confirmed. If significant disagreement is found between the replicate analyses, the trial should be repeated on new 10 g aliquots. In this way and using the worst-case interpretation, the probability of gross error (i.e. both determinations being false) in either Pd or Au data will be 1 in 2304 (i.e. $\frac{1}{48} \times \frac{1}{48}$) and of additional significant errors in the data of any of the elements is 1 in 256 (i.e. $\frac{3}{48} \times \frac{3}{48}$). Similarly, when Au is to be determined in CHR-Pt+, agreement should be sought between analyses from two 10 g aliquots; the probability of both Au determinations being in error is 1 in 2304.

8.5.2 Applicability of the analytical technique.

The reason for using the aqua regia extraction method for this homogeneity testing programme was two-fold. The use of just one analytical technique eliminates the significance of inter-method bias. Because the technique is a selective extraction, only those minerals that are soluble in aqua regia will contribute to the homogeneity test data and, assuming a uniform distribution of aqua regia soluble species of Au and the PGE, an indication of mineral homogeneity can be gained as well as that of element homogeneity. The leachate, therefore, not only contains a lower proportion of total dissolved solids, but also offers a more rigorous test of sample homogeneity.

Table 8.4. Coefficients of variation of data from homogeneity studies of CHR-Pt+and CHR-Bkg, calculated without the specified number of outliers for each element.

	CHR-Pt+		CHR-Bkg	
Isotope	No. of outliers	CV ($n \leq 48$)	No. of outliers	CV ($n \leq 48$)
Ru 99	0	6.4%	2	14%
Ru 101	0	7.9%	2	16%
Rh 103	0	5.6%	4	24%
Pd 105	0	6.2%	3	16%
Pd 106	0	6.1%	3	20%
Pd 108	0	6.5%	3	16%
Os 188	0	7.1%	0	46%
Os 189	0	7.6%	0	47%
Os 190	0	7.4%	0	42%
Ir 191	0	8.3%	2	22%
Ir 193	0	7.6%	2	18%
Pt 194	0	5.4%	3	24%
Pt 195	0	5.2%	3	27%
Pt 196	0	5.4%	3	25%
Au 197	1	5.9%	3	37%

Examination of the distribution histograms of Figures 8.3 and 8.4 indicated that the extraction was well suited to the analysis of the mineralised sample CHR-Pt+ and, outlying data apart, CHR-Bkg. Analysis of the concentrated solutions directly by ICP-MS proved acceptable for solutions derived from CHR-Pt+ (coefficients of variation were in the range 5-8%, see Table 8.4). Total variance consists of components from sampling and analytical errors. That the analytical technique is sufficiently precise for the analysis of solutions derived from CHR-Pt+ suggests that the source of the variance can be regarded as coming from sampling errors, as described in the previous section.

Similar concentrations of matrix elements together with lower concentrations of precious metal elements gave rise to relatively larger matrix effects in the analysis of solutions derived from CHR-Bkg compared to analysis of solutions derived from CHR-Pt+. These increased levels of inteferences resulted in less precise analyses (e.g. coefficients of variation, calculated without outliers, were in the range 14-47%, see Table 8.4). The errors in the bulk of the data could, therefore, be largely of analytical origin such that any between-packet variability is masked by the relatively large analytical error. If this is the case, then it must be concluded that, as it stands, the aqua regia leach technique is not sufficiently precise for this application and the analyte solutions require further chemical separation to isolate the analytes. Although little information can be gleaned from this data as to the homogeneity of CHR-Bkg, it is encouraging that the sampling variance is not greater than that derived from data submitted to the cooperative analysis programme.

In summary, it can be said that the application of the selective aqua regia leach to this homogeneity study was satisfactory for CHR-Pt+, although a more sensitive technique such as flow injection analysis[7] (Zicheng Peng et al., 1991), would have been more appropriate for CHR-Bkg.

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[7] Flow injection analysis is a relatively recent development and was not available when these analyses were undertaken.

Chapter 9.
Summary.

The precious metals, some of their uses and their occurrence in the geological environment have been described at the start of this thesis. The different methods and techniques available for sample decomposition, preconcentration and separation of the precious metals and their subsequent determination have also been reviewed. The detailed study described in this thesis has involved the development of one method of analysis: an aqua regia leach followed by direct determination by ICP-MS or, alternatively, a subsidiary selective solvent extraction for subsequent determination by GFAAS. Detailed investigations have been undertaken to optimise extraction conditions and instrumental analysis procedures and the advantages and limitations of this method have been discussed. The developed method has been used as the principal method for characterising the homogeneity of Au and PGE in two candidate reference materials. These studies have largely involved an analysis of ultramafic rocks (with particular interest in chromitites) as well as relevent reference materials. This chapter will highlight the new areas of research carried out.

9.1 Aqua regia dissolution.

Aqua regia dissolution has previously been used as a standard method in the determination of Au. This work has shown that such a method can be extended to the determination of Pd and Pt (after inclusion of a roasting step in the sample preparation to convert insoluble Pt minerals such as sperrylite into an aqua regia soluble species). Although the extraction of Pd (and Pt) is only semi-quantitative, there are likely to be comparable degrees of extraction of these metals from similar geological samples. Thus, the technique will be ideally suited to projects where it is of interest to identify qualitatively few samples with anomalous concentrations from large sample batches rather than to produce quantitative analyses of such large batches (e.g. a geochemical exploration programme). Indeed, significant interest has been shown in this work by two commercial analytical laboratories - one in the USA and one in Australia with a view to offering Pd as a determinand as well as Au after aqua regia dissolution.

Previous application of aqua regia digestion usually involved leaving samples in the acid overnight, often with heating applied. It has been shown in this work that a large proportion of the precious metals are, in fact, extracted within the first fifteen minutes. It has also been demonstrated that Os and Ru can be extracted - albeit to variable extents - and retained in solution, contrary to popular belief that these elements would be largely lost by evaporation as volatile tetroxides which would be likely to form under the prevailing oxidising conditions.

9.2 Selective solvent extraction.

Four solvent extraction mechanisms have been studied in detail, using aqua regia matrices rather than chloride matrices, previously reported in studies of the extraction efficiency of triphenyl phosphine (TPP) and diphenyl thiourea (DPTU) into 1,2-dichloroethane (DCE) or chloroform. Data have been presented using all four methods in the extraction of the precious metals from matrix-free (single element) solutions. Further studies have been undertaken to evaluate one method - complexation with DPTU and extraction into DCE - using complex solutions made up with artificially prepared matrices and from digests of representative geological samples.

9.3 Atomic absorption spectrometry.

Although atomic absorption spectrometry is in principle a simple technique, determination of individual precious metals in solution of a complex matrix can be subject to complicated and diverse interference effects. The magnitudes of such interference effects for a large number of interfering elements (precious metals and concomitant matrix elements) are shown in Table 6.1. These data indicate that the magnitude and range of interferences previously published for earlier generations of GFAAS instrumentation are not representative of the performance of a modern instrument fitted with a state-of-the-art background correction system, which permits analyses with greater sensitivity.

9.4 Reference materials.

The use of reference materials is integral in the development of any analytical technique. The development of this technique has highlighted the need for reference materials with well characterised concentrations of the precious metals, particularly at low levels. During the course of this work an opportunity arose to contribute to the characterisation of homogeneity of two specialised candidate reference materials comprising a PGE-enriched and a barren chromitite from the Unst ophiolite, Shetland. Indeed, aqua regia extraction, followed by direct determination of Au and the PGE by ICP-MS was used as the principle method of homogeneity testing based on duplicate determinations of 24 splits of each of the 2 reference materials .

Thorough application of statistical tests on the data showed that discrepancies existed for selected elements in 3 splits of the barren chromitite which were correlated with mineralogical inhomogeneity effects (the nugget effect). These results led directly to specific recommendations on the use of these reference materials in validating analytical results - specifically that representative samples of the reference materials should be analysed in duplicate.

9.5 Future work.

The work presented in this thesis has opened a number of avenues for future work, largely centred on the mineralogical control over the success of the analytical technique. In particular, work presented in Chapter 7 on the solubility in aqua regia of sperrylite indicated that the major control over extraction efficiency was not the expected problem of PGE minerals being occluded within refractory matrix grains, thus protected from aqua regia attack, but rather the inherent solubility of individual PGE minerals. Some success was encountered when roasting samples prior to aqua regia attack to convert insoluble minerals into more soluble forms. However, only a limited amount of information was found in the literature and a clear opportunity exists in further studies of the solubilities of individual minerals in aqua regia. Such work would permit a greater understanding of the limitations to quantitative extraction of the PGE imposed by the insolubility of selected PGM.

As part of these further developments it would be appropriate to extend the beta-autoradiography work with microprobe studies to obtain direct evidence of mineral solubility from specific sites in representative samples. This would increase appreciation the limiting effects of insoluble minerals and could lead to a method for the rapid characterisation of PGE in bulk samples.

Further experiments are required to develop a more effective solvent extraction procedure, possibly exploring the application of other PGE-specific complexing or chelating agents. Although the systems studied gave good recoveries for Au, Rh and, sometimes, Pt and satisfied criteria for a rapid technique, the extraction efficiency for Pd and Ru was disappointingly lower than quantitative and was apparently influenced by matrix composition. To be fully effective when used in conjunction with the aqua regia leach, a system is required that will, at least, offer more favourable extraction of Pd, and ideally, quantitative extraction of all the elements of interest.

References.

Adeloju S.B., Bond A.M., Tan S.M., Wei G., (1990). Voltametric determination of platinum in inorganic complexes and in water, geological and biological matrices using laboratory- and field-based instrumentation, *Analyst*, 115(12), 1569-1576.

Adriaenssens E., Knoop P.(1973). A study of the optimal conditions for flameless AAS of Ir, Pt and Rh., *Analytica Chimica Acta*, 68, 37-48.

Adriaenssens E., Verbeek F., (1974). The determination of silver, gold, palladium and platinum by a combined fire-assay atomic absorption procedure, *Atomic Absorption Newsletter*, 13(2), 41-44.

Aggett J., Sprott A.J., (1974). Non-flame atomisation in AAS, *Analytica Chimica Acta*, 72, 49-56.

Aggett J., West T.S., (1971). Atomic absorption and fluorescence spectroscopy with a carbon filament atom reservoir. Part IV, the determination of gold by atomic fluorescence and atomic absorption spectroscopy with an enclosed atom reservoir, *Analytica Chimica Acta*, 55, 349-357.

Agiorgitis G., Wolf R., (1984). Variations of the Os/Ir ratio in terrestial rocks and minerals, *Chemical Geology*, 42, 277-286.

Agrinier H., (1962). Semiquantitative determination of gold in minerals, soils and rocks by ascending paper chromatography, *Comptes Rendue*, 255, 2801-2803.

Ajayi O.O., Littlejohn D., Boss C.B., (1989). Influence of graphite furnace tube design on vapour temps and chemicl interferences in ETA-AAS, *Talanta*, 36(8), 805-810.

Akman S., Genç Ö., Bektas S., (1991). Investigation of the atomisation mechanisms of copper, platinum, iridium and manganese in graphite furnace atomic-absorption spectrometry, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 46B(14), 1829-1839.

Al-Bazi S.J., Chow A., (1984). Pt metals-solution chemistry and separation methods (ion exchange and solvent extraction), *Talanta*, 31(10A), 815-836.

Alimarin I.P.Basova E.M., Malykhin A.Yu., Bol'shova T.A., (1990). Separation of some platinum metal 8-hydroxyquinolinates by normal phase high performance liquid chromatography, *Talanta*, 37(5), 485-489.

Alkemade C.T.J., Milatz J.M.W., (1955). A double beam method of spectral selection from flames, *Applied Science Research*, B4, 289-299.

Alvarado J., Petrola A., (1989). Determination of Cd, Cr, Pb, Ag and Au in Venezuelan red mud by AAS, *Journal of Analytical Atomic Spectrometry*, 4(5), 411-414.

Amossé J., Fischer W., Allibert M., Piboule M., (1986). Méthode de dosage d' ultra-traces de platine, palladium, rhodium et or dans les roches silicatées par spectrophotométrie d' absorption atomique électrothermique (French), *Analusis*, 14(1), 26-31.

Amossé J., AllibertM., Fischer W., Piboule M., (1990). Experimental study of the solubility of platinum and iridium in basic silicate melts – Implications for the differentiation of platinum-group elements during magmatic processes, *Chemical Geology*, 81(1/2), 45-53.

Aneva Z., Arpadjan S., Kalaidsieva I., (1990). Graphite furnace atomic absorption spectrometric determination of iridium, rhodium and ruthenium in high-purity platinum after matrix extraction, *Analytica Chimica Acta*, 236, 385-389.

Angino E.E., Billings G.K., (1972). Atomic absorption spectrometry in Geology-2nd edition, Elsevier, Amsterdam.

Arpadjan S., Karadjova I., Tserovsky E., Aneva Z., (1990). Electrothermal atomic absorption spectrometric determination of metallic impurities in platinum and palladium, *Journal of Analytical Atomic Spectrometry*, 5(3), 195-198.

Artem'ev O.I., Stepanov V.M., (1982). Assay concentration of platinum metals in neutron activation analysis, *Industrial Laboratory*, 48(8), 745-750.

Asif M., Parry S.J., (1989). Elimination of reagent blank problems in the fire assay pre-concentration of the PGE and Au with a NiS bead of <1g mass, *Analyst*, 114(9), 1057-1059.

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 and Petrology*, 42, 321-326.

Austen C.E., (1977). The determination, by x-ray fluorescence spectrometry, of noble and base metals in matte-leach residues, *National Institute for Metallurgy, Johannesburg*, 1912, 6 pp.

Balcerzak M., (1988). Senstive spectrophotometric determination of osmium with tin (II) chloride and rhodamine B after floatation using cyclohexane, *Analyst*, 113, 129-132.

Barnes J.E., Edwards J.P.(1982). Solvent extraction at Inco's Acton precious metal refinery, *Chemistry and Industry*, March 6, 151-155.

Barnes S-J., Naldrett A.J., Gorton M.P.(1985). The origin of the fractionation of PGE in terrestrial magmas, *Chemical Geology*, 53, 303-323.

Basova E.M., Bol'shova T.A., Ivanov V.M., Morozova N.B., (1989). Determination of palladium, platinum and rhodium by high performance liquid chromatography following extractive concentration, *Journal of Analytical Chemistry of the USSR*, 44(4ii), 553-561.

Basova E.M., Ivanov V.M., Bol'shova T.A., Babkova N.A., (1990). Preconcentration of palladium, platinum and rhodium by extraction chromatography, *Journal of Analytical Chemistry of the USSR*, 45(4i), 477-482.

Beamish F.E., (1966). The analytical chemistry of the noble metals, Pergamon, London, 609 pp.

Beamish F.E., Van Loon J.C., (1972). Recent advances in the analytical chemistry of the noble metals, Pergamon, Oxford, 511 pp.

Beevers J.R., (1967). A method for the determination of the gold content of samples by solvent extraction and AA spectrophotometry, *Economic Geology*, 62, 426-428.

Bekov G.I., Kurskii A.N., Letokhov V.S., Pakhomov D.Yu., Radaev V.N., (1989). Determination of rhodium in rocks, ores and natural waters by laser photoionisation spectroscopy, *Journal of Analytical Chemistry of the USSR*, 44(4ii), 561-566.

Belyaev V.N., Vladimirskaya I.N., Kolonina L.N., Kovalev G.G., Kuznetsov L.B., Shiryaeva O.A., (1985). Decomposition of platinum-containing materials by chlorination in closed systems, *Journal of Analytical Chemistry of the USSR*, 40(1), 116-121.

Bem H., Ryan D.E., (1985). Determination of palladium in different samples by neutron activation after selective preconcentration with alpha-benzildioxime, *Analytica Chimica Acta*, 169, 79-85.

Benedetti M.F., De Kersabiec A.M., Boulegue J., (1987). Determination of Au in 20 geochemical reference samples by flameless AAS, *Geostandards Newsletter*, 11(1), 127-129.

Bergeron M., (1990). Determination of platinum group elements in rock: Review of analytical techniques based on lead and nickel sulphide fire assays (French), *CIM Bulletin (French)*, 83(936), 108-113.

Berglund M., Frech W., Baxter D.C., (1991). Achieving efficient multielement atomisation conditions for atomic absorption spectrometry using a platform-equipped, integrated-contact furnace and a palladium modifier, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 46B(13), 1767-1777.

Bettinelli M., (1983). Determination of trace metals in siliceous standard reference materials by electrothermal atomic absorption spectrometry after lithium tetraborate fusion, *Analytica Chimica Acta*, 148, 193-201.

Boisvert R., Bergeron M., Turcotte J., (1991). Re-examination of the determination of palladium, platinum and rhodium in rocks by nickel sulphide fire assay followed by graphite furnace atomic absorption spectrometry, *Analytica Chimica Acta*, 246(2), 365-373.

Bonilla C.F., (1932). Aqua regia and base metals, *Industrial and Engineering Chemistry (Analytical Edition)*, 4(1), 128-130.

Bowditch D.C., (1973). A comparative study of 3 analytical processes for the collection and determination of Au and the platinoids in precious metal bearing ores, *Bulletin of the Australian Mineral Development Laboratories (AMDEL)*, No. 15, 71-87.

Bozic J., Maskery D., Maggs S., Susil H., Smith F.E., (1989). Rapid procedure for the dissolution of a wide variety of ore and smelter samples prior to analysis by inductively coupled plasma atomic emission spectrometry, *Analyst*, 114(11), 1401-1403.

Brajter K., Slonawska K., (1987). Determination of gold in the presence of platinum and palladium by electrothermal atomisation atomic absorption spectrometry, *Journal of Analytical Atomic Spectrometry*, 2(2), 167-170.

Brenner I.B., Lang Y., Le Marchand A., Grosdaillon P.(1987). A versatile technique for multielement ICP-AES analysis of geological samples, *International Lababoratory*, Dec, 18.

Briner M.E., (1916). Sur le mécanisme des réactions dans l' eau régale (French), *Comptes Rendue*, 162, 387-389.

Briner M.E., Durand E.L.,, (1912). Conditions of the formation of nitic and nitrous acids from nitrogen oxides and water; application of the law of mass action, *Comptes Rendue*, 155, 582-585.

Brooks R.R., Bee-Saik Lee, (1988). The determination of platinum and palladium in rocks and soils by electrothermal atomic absorption spectrometry of their iodo complexes, *Analytica Chimica Acta*, 204, 333-337.

Bruening R.L., Tarbet B.J., Krakowiak K.E., Bruening M.L., Izatt R.M., Bradshaw J.S., (1991). Quantitation of cation binding by silica gel bound thiamacrocycles and the design of highly selective concentration and purification columns for palladium (II), gold (III), silver (I) and mercury (II), *Analytical Chemistry*, 63(10), 1014-1017.

Brügmann G.E., Gorton M.P.Hancock R.G.V., (1990). Simultaneous determination of noble metals, Re, Se, As, and Sb by radiochemical neutron activation analysis, *Journal of Geochemical Exploration*, 37(1), 25-36.

Brynard H.J., De Villiers J.P.R., Viljoen E.A., (1976). A mineralogical investigation of the Merensky Reef at the Western Platinum Mine, near Marikana, South Africa, *Economic Geology*, 71(7), 1299-1307.

Bumstead E.D., (1984). Some comments on the precision and accuracy of gold analysis in exploration, *Procedings of the Australasian Institute of Mining and Metallurgy*, 289, 71-78.

Cabri L.J., Chryssoulis S.L., DeVilliers J.P.R., Laflamme J.H.G., Buseck P.R., (1989). the nature of "invisible" gold in arsenopyrite, *Canadian Mineralogist*, 27(3), 353-362.

Cabri L.J., Laflamme J.H.G., (1976). The mineralogy of some platinum-group elements from some copper-nickel deposits of the Sudbury area, Ontario, *Economic Geology*, 71(7), 1159-1195.

Campbell W.C., Ottaway J.M., (1974). Atom-formation processes in carbon furnace atomisers used in AAS, *Talanta*, **21**, 837-844.

Cathelineau M., Boirin M.C., Holliger Ph., Marion Ph., (1988). Gold-rich arsenopyrites: Crystal chemistry, gold location and state, physical and chemical conditions of crystallisation, *Bicentenial Gold 88, Melbourne, Geological Society of Australia*, **22**, 235-240.

Caughlin B.L., (1989). Analysis of geological materials for precious metals using plasma atomic fluorescence spectroscopy, *Journal of Geochemical Exploration*, 34(3), 245-254.

Chakrabarti C.L., Wan C.C., Teskey R.J., Chang S.B., Hamed H.A., Bertels P.C., (1981). Mechanism of atomisation at constant temperature in capicitative discharge GFAAS, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 36B(5), 427-438.

Chao T.T., (1984). Use of partial dissolution techniques in geochemical exploration, *Journal of Geochemical Exploration*, **20**, 101-135.

Chuburkov Yu.T., Zhuikov B.L., Gerbis S., Al'pert L.K., Chan Zui Ty, (1990). Noble-metal accumulation by distillation in large-specimen analysis, *Journal of Analytical Chemistry of the USSR*, 45(1i), 23-29.

Church S.E., Mosier E.L., Motooka J.M., (1987). Mineralogical basis for the interpretation of multielement (ICP-AES), oxalic acid, and aqua regia partial digestions of stream sediments for reconnaissance exploration geochemistry, *Journal of Geochemical Exploration*, **29**, 207-233.

Chyi L.L., Crocket J.H., (1976). Partition of Pt, Pd, Ir and Au among coexisting minerals from the deep ore zone, Strathcona Mine, Sudbury, Ontario, *Economic Geology*, 71(7), 1196-1205.

Clark J.R., Viets J.G., (1981). Multielement extraction system for the determination of 18 trace elements in geochemical samples, *Analytical Chemistry*, 53(1), 61-65.

Cleare M.J., Charlesworth P.Bryson D.J., (1979). Solvent extraction in platinum group metal refining, *Journal of Chemical Technology and Biotechnology*, **29**, 210-224.

Clifton H.E.,Hunter R.E., Swanson F.J., Phillips R.L., (1969). Sample size and meaningful gold analysis; shorter contributions to economic geology, *US Geological Survey professional paper*, **625-C**.

Constantinides C.C., Kingston G.A., Fisher P.C., (1980). The occurrence of platinum-group minerals in the chromitite of the Kokkinorotsos chrome mine, Cyprus, in: Panagiotou A. (editor). Proceedings of the international ophiolite symposium, Cyprus,1979, Ministry of Agriculture and Natural Resources, Geological Survey Department, Nicosa, Cyprus, 93-101.

Coombes R.J., Chow A., (1979). A comparison of methods for the determination of platinum in ores, *Talanta*, **26**, 991-998.

Crocket J.H., (1979). Platinum-group elements in mafic and ultramafic rocks: A survey, *Canadian Mineralogist*, **17**, 391-402.

Crocket J.H., Teruta Y., Garth J., (1976). The relative importance of sulphides, spinels and platinoid minerals as carriers of Pt, Pd, Ir and Au in the Merensky Reef at Western Platinum Limited, near Marikana, South Africa, *Economic Geology*, 71(7), 1308-1323.

Danilova F.I., Fedotova I.A., Nazarenko R.M., (1982). Chemical spectral assay of platinum metals and gold in copper-nickel sulphide ores and products of ore processing, *Industrial Laboratory*, 48(8), 754-757.

Date A.R., Davis A.E., Cheung Y.Y., (1987). The potential of fire assay and ICP source MS for the detn of PGE in geological materials, *Analyst*, 112(9), 1217-1222.

De Castro M.A., Bugagao R., Ebarvia B., Roque N., (1988). Application of an iodide extraction system for the determination of Ag, Cd, Mo and Tl in rocks by GFAAS, *Geostandards Newsletter*, 12(1), 47-51.

Denoyer E., Ediger R., Hager J., (1989). The determination of the precious metals in geological samples by ICP-mass spectrometry, *Atomic Spectroscopy*, 10(4), 97-102.

Dhara S.C., (1984). Solvent extraction of precious metals with organic amines, *TMS-AIME*, 199-226.

Diamantatos A., (1977). Recovery of platinum, palladium, rhodium, iridium and gold after lead fusion and perchloric acid parting, *Analytica Chimica Acta*, 92, 171-181.

Diamantatos A., (1981). A solvent-extraction scheme for the determination of platinum, palladium, rhodium, iridium and gold in platiniferous materials, *Analytica Chimica Acta*, 131, 53-62.

Diamantatos A., (1986). Accurate determination of platinum, palladium, gold and silver in ores and concentrates by wet chemical analysis of the lead fire assay button, *Analyst*, 111, 213-215.

Dickin A.P.McNutt R.H., McAndrew J.I., (1988). Osmium isotope analysis by ICP-MS, *Journal of Analytical Atomic Spectrometry*, 3(2), 337-342.

Dillon-Leitch H.C.H., Watkinson D.H., Coats C.J.A., (1986). Distribution of the platinum-group elements in the Donaldson West deposit, Cape Smith Belt, Quebec, *Economic Geology*, 81(5), 1147-1158.

Distler V.V., Malevskiy A.Yu., Laputina I.P.(1977). Distribution of platinoids between pyrrhotite and pentlandite in crystallisation of a sulphide melt, *Geokhimiya*, 61, 330-340.

Dmitriev S.N., Shishkina T.V. Zhuravleva E.L., Chimeg A., (1991). Determination of gold in geological samples by X-ray fluorescence spectrometry after extraction with tributylphosphate, *Analytica Chimica Acta*, 243, 81-87.

Dolan R., Van Loon J., Templeton D., Paudyn A., (1990). Assessment of ICP-MS for routine multielement analysis of soil samples in environmental trace element studies, *Fresenius' Journal of Analytical Chemistry*, 336, 99-105.

Durrant P.J., Durrant B., (1970). Introduction to advanced inorganic chemistry-2nd edition, Longman, London, 1250 pp.

Ebdon L.C., (1972). Analytical atomic spectroscopy in flame and non-flame cells, unpublished PhD Thesis, Imperial College, London University.

Eller R., AltF., Tölg G., Tobschall H.J., (1989). An efficient combined procedure for the extreme trace analysis of gold, platinum, palladium and rhodium with the aid of graphite furnace atomic absorption spectrometry and total-reflection X-ray fluorescence analysis, *Fresenius' Zeitschrift für Analytische Chemie*, 334, 723-739.

Ellis P.J., Venter J.H., Steele T.W., (1983). Estimation of material variation in powdered materials, *Geostandards Newsletter*, 7, 261-272.

Elson C.M., Chatt A., (1983). Determination of gold in silicate rocks and ores by coprecipitation with tellurium and neutron activation—gamma-spectrometry, *Analytica Chimica Acta*, 115, 305-310.

Evans E.H., Ebdon L., (1990). Effect of organic solvents and molecular gases on polyatomic ion interferences in inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry*, 5(6), 425-430.

Everett G.L., (1976). The determination of the precious metals by flameless AA spectrophotometry, *Analyst*, 101, 348-355.

Everett G.L., (1982). Use of plasma emission for noble metal analysis, *Analytical Proceedings*, **19**, 88-90.

Ezerskaya N.A., (1991). Voltammetric determination of platinum metals, *Journal of Analytical Chemistry of the USSR*, **46**(4i), 480-486.

Ezerskaya N.A., Kisleva I.N., Solovykh T.P.Bel'skii N.K., Shubochkin L.K., (1989). Determination of rhodium iun concentrates by controlled-potential coulometry, *Industrial Laboratory*, **55**(10), 1114-1115.

Fal'kova O.B., Zdorova É.P.Markova N.V., Popova N.N., Rakovskii É.E., Fishkova N.L., Shvartsman S.I., (1981). Comparison of results of determination of noble metals in ores by different methods, *Journal of Analytical Chemistry of the USSR*, **36**(2), 203-209.

Farago M.E., Parsons P.J., (1982). Determination of Pt, Pd and Rh by AA spectroscopy with electrothermal atomisation, *Analyst*, **107**, 1218-1228.

Faye G.H., Inman W.R., (1961). The determination of platinum and palladium in copper-nickel matte and ore concentrates: a fire assay method using tin as a collector, *Analytical Chemistry*, **33**(2), 278-283.

Feather C.E., (1976). Mineralogy of platinum-group minerals in the Witwatersrand, South Africa, *Economic Geology*, **71**(7), 1399-1428.

Firsova I.N., Ryseva G.V., Savchukova M.G., Potylitsyna N.G., (1965). Analysis of an Ural platinum slick ore, *Analiz Blagorod Metal, Moscow*, 199-206.

Fishkova N.L., Vilenkin V.A., (1978). Use of an HGA-74 graphite atomiser for the atomic-absorption determination of gold, silver, platinum and palladium in solutions of complex composition, *Journal of Analytical Chemistry of the USSR*, **33**(5), 695-699.

Fletcher W.K., (1981). Handbook of exploration geochemistry. Volume 1: Analytical methods in geochemical prospecting, Elsevier Scientific Publishing Company, Amsterdam, 256 pp.

Flett D.S., (1982). Solvent extraction in precious metals refining, *IPMI, International Seminar, sampling, assaying & refining of precious metals*, **Oct**, 145-168.

Frech W., Baxter D.C., Hütsch B., (1986). Spatially isothermal graphite furnace for atomic absorption spectrometry using side heated cuvettes with integrated contacts, *Analytical Chemistry*, **58**(9), 1973-1977.

Freiser H., (1984). Kinetics and mechanism of metal chelation processes via solvent extraction techniques, *Accounts of Chemical Research*, **17**(4), 126-131.

Fryer B.J., Kerrich R., (1978). Determination of precious metals at ppb levels in rocks by combined wet chemical and flameless AA method, *Atomic Absorption Newsletter*, **17**, 4-6.

Fuwa A., (1987). Solvent extraction technology in recovery and refining of platinum group metals, *Metallurgical review of the Mining and Metallurgical Institute of Japan*, **4**(1), 98-115.

Gedye R.N., Bozic J., Durbano P.M., Williamson B., (1989). The preparation of n-octylaniline and its application in the extraction of noble metals, *Talanta*, **36**(10), 1055-1089.

Genkin A.D., Evstigneeva T.L., (1986). Associations of the platinum-group minerals of the Noril'sk copper-nickel sulphide ores, *Economic Geology*, **81**(5), 1203-1212.

Gijbels R.H., Millard H.T.Jr., Desborough D.A., Bartel A.J., (1974). Osmium, ruthenium, iridium and uranium in silicates and chromite from the eastern Bushveld Complex, South Africa, *Geochimica et Cosmochimica Acta*, **38**, 319-337.

Gil'bert É. N., Shabonova L.N., (1990). Analytical control of the production of noble metals in non-ferrous metallurgy, *Industrial Laboratory*, 56(10), 1156-1160.

Gladney E.S., Roelandts I., (1990). 1988 compilation of elemental concentration data for USGS geochemical exploration reference materials GXR-1 to GXR-6, *Geostandards Newsletter*, 14(1), 21-118.

Gowing C.J.B., Potts P.J., (1991). Evaluation of a rapid technique for the determination of precious metals in geological samples based on a selective aqua regia leach, *Analyst*, 116(8), 73-779.

Gray A.L., Williams J.G., (1987). System optimisation and the effect of polyatomic, oxide and doubly charged ion response of a commercial inductively coupled plasma mass spectrometry instrument, *Journal of Analytical Atomic Spectrometry*, 2(7), 599-606.

Greenwood N.N., Earnshaw A., (1984). Chemistry of the elements, Pergamon, Oxford, 1544 pp.

Gregoire D.C., (1988). Determination of Pt, Pd, Ru and Ir in geological material by ICP-MS with sample introduction by electrothermal vaporisation, *Journal of Analytical Atomic Spectrometry*, 3(2), 309-314.

Griffith W.P.(1967). The chemistry of the rarer platinum metals, Wiley Interscience, New York, 491pp.

Grimaldi F.S., Schnepfe M.M., (1967). Determination of Pd in the ppb range in rocks, *US Geological Survey professional paper*, 575-C, C141-C144.

Grimaldi F.S., Schnepfe M.M., (1968). Determination of Pd and Pt in rocks, *US Geological Survey professional paper*, 600-B, B99-B103.

Grimaldi F.S., Schnepfe M.M., (1969). Mode of occurence of Pt, Pd and Rh in chromite, *US Geological Survey professional paper*, 650-C, C149-C151.

Grote M., Kettrup A., (1987). Ion-exchange resins containing S-bonded dithizone and dehydrodithizone as functional groups. Part 3. Determination of gold, platinum and palladium in geological samples by means of a dehydrodithizone resin and plasma emission spectrometry, *Analytica Chimica Acta*, 201, 95-107.

Guerin B.D., (1972). The determination of the noble metals by AA spectrophotometry with the carbon rod furnace, *Journal of the South African Chemical Institute*, 25, 230-243.

Haffty J., Riley L.B., Goss W.D., (1977). A manual on fire assaying and determination of the noble metals in geological materials, *US Geological Survey bulletin*, 1445, 58 pp. ,

Haines J., Robért R.V.D., (1984). Measurement of paltinum, palladium, rhodium, ruthenium and iridium by atomic-absorption spectrometry using electrothermal atomisation, *South African Journal of Chemistry*, 37(3), 121-123.

Hall G.E.M., Bonham-Carter G.F., (1988). Review of methods to determine Au, Pt and Pd in production oriented geochemical laboratories, with application of a statistical procedure to test for bias, *Journal of Geochemical Exploration*, 30, 255-286.

Hall G.E.M., Coope J.A., Weiland E.F., (1989a). Bias in analysis for gold, *Explore*, 65, 17-18.

Hall G.E.M., Vaive J.E., Coope J.A., Weiland E.F., (1989b). Bias in the analysis of geological materials for gold using current methods, *Journal of Geochemical Exploration*, 34(2), 157-171.

Halls D.J., (1984). Speeding up determinations by electrothermal AAS, *Analyst*, 109, 1081-1084.

Hamid H.A., (1989). Determination of ruthenium by graphiter furnace AAS, *Atomic Spectroscopy*, 10(1), 16-18.

Hannaker P.Hou Qing-Lie, (1984). Dissolution of geological material with orthophosphoric acid for major element determination by flame atomic absorption spectroscopy and inductively-coupled plasma atomic-emission spectroscopy, *Talanta,* 31(12), 1153-1157.

Harris D.C., (1990). The mineralogy of gold and its relevence to gold recoveries, *Mineralium Deposita,* 25(supplement), S3-S7.

He Xing-Cun, (1991). Ion flotation of rhodium (III) and palladium (II) with anionic surfactants, *Talanta,* 38(3), 319-323.

Herring D.P.Price B.D., Staunton W.P.(1987). Platinum group metal analysis - an overview, *Australian Institute of Mining and Metalurgy. Equipment in the minerals industry: Exploration, mining and processing conference,* 123-126.

Hidalgo M., Masana A., Salvado V., Muñoz M., Valiente M., (1991). Extraction of palladium with tri-isobutyl phosphine sulphide (cyanex 471) in toluene from chloride solutions containing thiocyanate, *Talanta,* 38(5), 483-488.

Hill S.J., Hartley J., Ebdon L., (1992). Determination of trace metals in volatile organic solvents using inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry,* 7(1), 23-28.

Hoffman E.L., Naldrett A.J., Van Loon J.C., Hancock R.G.V., Manson A., (1978). The determination of all the PGE and Au in rocks and ore by NAA after preconcentration by a NiS-FA technique on large samples, *Analytica Chimica Acta,* 102, 157-166.

Hoffman I., Westland A.D., Lewis C.L., Beamish F.E., (1956). Assay for platinum metals in ores and concentrates, *Analytical Chemistry,* 28(7), 174-1177.

Hoke C.M., Moore R.J., (1916). Solution of platinum in aqua regia, *Metal Industry,* 14(7), 296-298.

Hubert A.E., Chao T.T., (1985). Determination of gold, indium tellurium and thallium in the same sample digest of geological materials by atomic-absorption spectroscopy and two-step solvent extraction, *Talanta,* 32(7), 568-570.

Jackson L.L., Fries T.L., Grossman J.N., King B-S.W., Lamothe P.J., (1991). Geological and inorganic materials, *Analytical Chemistry,* 63(12), 33R-48R.

Jackson S.E., Fryer B.J., Gosse W., Healey D.C., Longerich H.P.Strong D.F., (1990). Determination of the precious metals in geological materials by inductively coupled plasma-mass spectrometry (ICP-MS) with nickel sulphide fire-assay collection and tellurium coprecipitation, *Chemical Geology,* 83(1-2), 119-132.

Jain V.K., Lall P.M., Tiwari J.S., (1987). Determination of ultratrace levels of gold in geochemical soil samples by atomic absorption spectrophotometry, *Atomic Spectroscopy,* 8(2), 77-78.

Jarvis I., Jarvis K.E., (1992). Plasma spectrometry in the earth sciences: techniques, applications and future trends, *Chemical Geology,* 95(1/2), 1–33.

Jiucheng Li, Xiaohong Li, Xiangan Li, (1989). Extraction of absorption-type precious metals from decayed rocks (Chinese), *Faming Zhuanli Shenqing Gongkai Shuomingshu,* CN 1,037,127.

Jones E.A., Kruger M.M., Wilson A., (1971). The determination of osmium, *National Institute for Metallurgy, Johannesburg,* 1232, 11 pp.

Kachin S.V., Poddubnykh L.P.Runov V.K., (1991). Extraction-fluorometric determination of gold with unsubstituted rhodamine, *Industrial Laboratory,* 57(9), 881-882.

Kalinin S.K., Vinnitskaya E.G., (1980). Methods for determining the platinum metals in lean products, *Journal of Analytical Chemistry of the USSR,* 35(11), 1452-1466.

Kallmann S., (1984). Analytical chemistry of the precious metals: Interdependance of classical and instrumental methods, *Analytical Chemistry, 56(9)*, 1020A-28A.

Kallmann S., (1986). Analysis of sweeps: The cuprous sulphide collecting system, *Talanta,* 33(1), 75-83.

Kallmann S., (1987). A survey of the determination of the platinum group elements, *Talanta,* 34(8), 677-698.

Kallmann S., Maul C., (1983). Referee analysis of precious metal sweeps and related materials, *Talanta,* 30(1), 21-39.

Kane J.S., Arbogast B., Leventhal J., (1990). Characterisation of Devonian Ohio Shale SDO-1 as a USGS geochemical reference sample, *Geostandards Newsletter,* 14(1), 169-196.

Kasper H.U., Aslanidis P.Schuster M., (1989). Determination of platinum-group metals in ultra basic rocks and chromite ores after extraction and preconcentration (German), *Colloquium für Atomspektrometrie und Spurenanalyse,* 5, 449-456.

Kasrai M., Fozoonmayeh L., Payrovan H., (1988). Quantitative determination of gold in ore using energy-dispersive XRF spectrometry, *X-ray Spectrometry,* 17, 219-222.

Kavanagh J.M., Beamish F.E., (1960). New fire assay for osmium and ruthenium, *Analytical Chemistry,* 32, 490-491.

Khosla M.M.L., (1983). Selective extraction of palladium with N-butyl aniline in chloroform, *Trace Analysis and Technological Development, Special Contribution Paper, 1st International Symposium,1981,* Special contribution, 251-256.

Khvostova V.P.Baryshev V.B., Zolotarev K.V., (1991). Determining Pd, Rh and Ru by the use of dispersive filters in synchotron radiation beams, *Journal of Analytical Chemistry of the USSR,* 46(8ii), 1167-1171.

Kingston G.A., El-Dosuky B.T., (1982). The platinum-group mineralogy of the Merensky Reef at the Impala platinum mines, Bophuthatswana, *Economic Geology,* 77(6), 1385-1394.

Kirkbright G.F., Tinsley H.M., (1979). Determination of platinum metals and gold by optical emission spectrometry with a radio frequency inductively coupled argon plasma, *Talanta,* 26(1), 41-45.

Kolmogorov Yu.P.Lapukhov A.S., Melnikova R.D., Khvostova V.P.(1989). X-ray fluorescence technique in geochemical studies of noble metals, *Nucular Instruments and Methods in Physics Research,* A282, 692-694.

Kolosova L.P.Aladyshkina A.E., Novatskaya N.V., (1984). Determination of platinum, palladium, rhodium, iridium, ruthenium and gold in natural and industrial materials by chemical spectroscopy with concentration by lead and partial cupellation, *Journal of Analytical Chemistry of the USSR,* 39(8), 1168-1172.

Kontas E., Niskavaara H., Virtasalo J., (1986). Flameless AA determination of Au and Pd in geological reference samples, *Geostandards Newsletter,* 10(2), 169-171.

Kontas E., Niskavaara H., Virtasalo J., (1990). Gold, palladium and tellurium in South African, Chinese and Japanese geological reference samples, *Geostandards Newsletter,* 14(3), 477-478.

Kuldvere A., (1989). Extraction of geological materials with mineral acids for the determination of As, Sb, Bi and Se by hydride generation AAS, *Analyst,* 114(2), 125-131.

Kus S., Marczenko Z., (1989). Determination of µg amounts of Pt as dithizonate in the presence of Pd by second derivative spectrophotometry, *Analyst,* 114(2), 207-210.

L'vov B.V., (1961). The analytical use of atomic absorption spectra, *Spectrochimica Acta, part B. Atomic Spectroscopy*, **17B**, 761-770.

L'vov B.V., (1987). Recent advances in the theory of atomisation in GFAAS: the oxygen-carbon alternative, *Analyst*, **112**, 355-364.

L'vov B.V., (1990). Recent advances in absolute analysis by graphite furnace atomic absorption spectrometry, *Spectrochimica Acta, part B. Atomic Spectroscopy*, **45B(6)**, 633-655.

L'vov B.V., Pelieva L.A., Mandrazhi E.K., Kalinin S.K., (1979). AA determination of PGE in an HGA graphite furnace, *Industrial Laboratory*, **45(12)**, 1348-1351.

Lakin H.W., Nakagawa H.M., (1965). A spectrophotometric method for the determination of traces of gold in geologic materials, *US Geological Survey professional paper*, **525-C**, C168-C171.

Latimer W.M., Hildebrand J.H., (1940). Reference book of inorganic chemistry-Revised edition, The Macmillan Company, New York, 563 pp.

Lechotycki A., (1990). Factors affecting the determination of molybdenum and vanadium in aqua regia digests of soil by graphite furnace atomuc absorption spectrometry, *Journal of Analytical Atomic Spectrometry*, **5(1)**, 25-28.

Lister B., (1982). Evaluation of analytical data: A practical guide for geoanalysts, *Geostandards Newsletter*, **6(2)**, 175-205.

Littlejohn D., Egila J.N., Gosland R.M., Kunwar U.K., Smith C., Xiao-Quan Shan, (1991). Graphite furnace analysis - getting easier and achieving more?, *Analytica Chimica Acta*, **250**, 71-84.

Liu K., Kovaic N., Barnes R.M., (1990). High-power oxygen ICP discharge for spectrochemical analysis, *Spectrochimica Acta, part B. Atomic Spectroscopy*, **45B(1/2)**, 145-156.

Longerich H.P.Jenner G.A., Fryer B.J., Jackson S.E., (1990). Inductively coupled plasma- mass spectrometic analysis of geological samples: a critical evaluation based on case studies, *Chemical Geology*, **83(1/2)**, 105-118.

Macalalad E., Bayoran R., Ebarvia B., Rubeska I., (1988). A concise analytical scheme for 16 trace elements in geochemical exploration samples using exclusively AAS, *Journal of Geochemical Exploration*, **30**, 167-177.

Malhotra P.D., Venkaji K., Das H.B., (1983). Determination of palladium in association with precious metal mineralisation by a chemical enrichment spectrographic method, in: Sankar Das M., (editor). Trace analysis and technological developement, Wiley Eastern Ltd., New Delhi, 248-250.

Mallett R.C., Pearton D.C.G., Ring E.J., Steele T.W., (1972). Interferences and their elimination in the determination of the noble metals by atomic absorption spectrophotometry, *Talanta*, **19**, 181-195.

Manning D.C., Slavin W., Myers S., (1979). Sampling at a constant temperature in GFAAS, *Analytical Chemistry*, **51(14)**, 2375-2378.

Marczenko Z., Kus S., Mojski M., (1984). Extractive separation and spectrophotometric determination of Pd and Pt with dithizone in the presence of SnCl2, *Talanta*, **31(11)**, 959-962.

McAdam R.C., Sutarno, Moloughney P.E., (1971). Platiniferous black sand PTA: Its characterisation and preparation for use as a standard reference material, Deptartment of Energy, Mines and Resources, Mines Branch, Ottawa, Technical Bulletin, Number TB138.

McAdam R.C., Sutarno, Moloughney P.E., (1973a). Noble metals-bearing sulphide concentrate PTC: Its characterisation and preparation for use as a standard reference material, Deptartment of Energy, Mines and Resources, Mines Branch, Ottawa, Technical Bulletin, Number TB176.

McAdam R.C., Sutarno, Moloughney P.E., (1973b). Noble metals-bearing nickel-copper matte PTM: Its characterisation and preparation for use as a standard reference material, Deptartment of Energy, Mines and Resources, Mines Branch, Ottawa, Technical Bulletin, Number TB182.

McHugh J.B., (1983). Determination of gold in water in the nanogram range by electrothermal atomisation after coprecipitation with tellurium, *Atomic Spectroscopy*, **4**, 66-68.

McHugh J.B., (1986). Determining gold in water by anion-exchange batch extraction, *Talanta*, 33(4), 349-351.

Medyantseva É.P.Ulakhovich N.A., Romanova O.N., Budnikov G.K., (1989). Extraction alternating current polarography of Ru, Os and ir 8-mercaptoquinolinates, *Journal of Analytical Chemistry of the USSR*, **44**(4ii), 566-568.

Mertie J.B., (1969). Economic geology of the platinum metals, *US Geological Survey professional paper*, **630**, 120 pp.

Mironov A.G., Geletiy V.F., (1979). Experimental study of gold distribution in sulphides, *Dokl. Academy of Science, USSR, Earth Science Section*, **247**, 194-197.

Misra A.K., Rajput R.P.S., (1990). Electrochromatography of metal ions on zirconium (IV) phosphoantimonate papers: quantitative separation of platinum (IV) from platinum group and other metal ions, *Journal of Liquid Chromatography*, 13(7), 1435-1445.

Mitchell R.H., Keays R.R., (1981). Abundance and distribution of gold, palladium and iridium in some spinel and garnet lherzolites: implication for the nature and origin of precious metal-rich intergranular components in the upper mantle, *Geochimica et Cosmochimica Acta*, **45**, 2425-2442.

Mo Shengjun, Holcombe J.A., (1990). Preconcentration of nickel and cobalt on algae and determination by graphite-furnace atomic absorption spectrometry, *Talanta*, 38(5), 503-510.

Mo Shengjun, Holcombe J.A., (1990). Preconcentration of copper on algae and determination by slurry graphite-furnace atomic-absorption spectrometry, *Analytical Chemistry*, **62**(18), 1994-1997.

Mojski M., (1980). Extraction of Platinum metals from HCl medium with triphenyl phosphine in 1,2-dichloroethane, *Talanta*, **27**, 7-10.

Moloughney P.E., (1980). A fire-assay and wet chemical method for the determination of palladium, platinum, gold and silver in ores and concentrates, *Talanta*, **27**, 365-367.

Moloughney P.E., (1986). Assay methods used in CANMET for the determination of precious metals, *Mineral Science Laboratories, CANMET*, **SP86-1E.**

Moloughney P.E., Faye G.H., (1976). A rapid fire assay/atomic absorption method for the determination of platinum, palladium and gold in ores and concentrates: a modification of the tin-collection scheme, *Talanta*, **23**, 377-381.

Mostert A.B., Hofmeyr P.K., Potgieter G.A., (1982). The influence of the Driekop dunite pipe on the platinum-group mineralogy of the UG-2 chromitite in its vicinity, *Economic Geology*, **77**(6), 1432-1438.

Mueller B.J., Lovett R.J., (1985). Determination of low levels of rhodium and palladium as their solvent extracted dithiocarbamate complexes by liquid chromatography, *Analytical Chemistry*, **57**(13), 2693-2699.

Myasoedova G.V., Antokol'skaya I.I., Dmitrieva G.A., Kubarev S.V., Moiseeva G.A., Danilova F.I., Grishna O.N., Zhukova N.G., Savvin S.B., (1988). Pt, Pd and Rh sorption on poliorgs XI chelating sorbent followed by X-ray fluorescence determination, *Journal of Analytical Chemistry of the USSR*, 43(4ii), 531-533.

Nadkarni R.A., Morrison G.H., (1974). Determination of the noble metals in geological materials by neutron activation analysis, *Analytical Chemistry*, 46(2), 232-236.

Naldrett A.J., Duke J.M., (1980). Platinum metals in magmatic sulphide ores, *Science*, **208**, 1417-1424.

Němcová I., Rychlovsky P.Kleszczewska E., (1990). A spectrometric study of the determination of gold with phenothiazine, *Talanta*, 37(8), 855-858.

Niskavaara H., Kontas E., (1990). Reductive coprecipitation as a separation method for the determination of gold, palladium, platinum, rhodium, silver selenium and tellurium in geological samples by graphite furnace furnace atomic absorption spectrometry, *Analytica Chimica Acta*, 231(2), 273-282.

O'Leary R.M., Meier A.L., (1986). Analytical methods used in geochemical exploration, 1984, *US Geological Survey circular* , circ948, 48 pp.

Ohnenstetter D., Watkinson D.H., Jones P.C., Talkington R., (1986). Cryptic compositional variation in laurite and enclosing chromite from the Bird River Sill, Manitoba, *Economic Geology*, **81**(5), 1159-1168.

Oshin I.O., Crocket J.H., (1982). Noble metals in Thetford mine ophiolites, Quebec, Canada. Part 1: Distribution of Au, Ir, Pt and Pd in the ultramafic and gabbroic rocks, *Economic Geology*, **77**, 1556-1570.

Palaniappan R., (1989). Indirect differential-pulse polarographic detn of Pt(II): An efficient micro-analytical method, *Analyst*, 114(9), 1043-1045.

Palmer I., Streichert G., Wilson A., (1971). The acid extraction of noble metals from low grade concentrates and ores, and the subsequent determination of Pt, Pd, Rh and Au, *National Institute for Metallurgy, Johannesburg*, **1218**.

Palmer I., Palmer R., Steele T.W., (1972). The separation of Pt, Pd, Rh and Au from ores and concentrates by aqua regia extraction and by high-temperature chlorination followed by acid leaching, *Journal of the South African Chemical Institute*, **25**, 190-197.

Palmer R., Watterson J.I.W., (1971). The recovery of noble metals for analysis. A radiotracer investigation of losses, *National Institute for Metallurgy, Johannesburg*, **1185**, 11 pp.

Parkes A., Murray-Smith R., (1979). A rapid method for the determination of gold and palladium in soils and rocks, *Atomic Absorption Newsletter*, 18(2), 57-59.

Parry S.J., (1982). Neutron-activation analysis for the noble metals in geological samples, *Analytical Proceedings*, **19**, 90.

Pavlenko L.I., Popova I.A., Marcheva E.V., Myasoedova G.V., Maloofeeva G.I., (1980). Chemical-spectrographic determination of platinum metals, *Journal of Analytical Chemistry of the USSR*, 35(4), 485-491.

Payne S.T., (1960). The separation and determination of the platinum metals, *Analyst*, **85**, 698-714.

Pearson E.S., Hartley H.D., (1966). Biometrika tables for statisticians, Volume 1 - 3rd edition, Cambridge University Press, Cambridge.

Pearson R.G., (1966). Acids and bases, *Science*, **151**, 172-177.

Pechenyuk S.I., Kuz'mich L.F., (1988). Interaction of chloride complexes during separation and precipitation of platinum metals, *Journal of Analytical Chemistry of the USSR*, 43(11), 1624-1628.

Peräniemi S., Parkkinen J., Smolander K., Mustalahti P., Ahlgrén M., (1992). Determination of gold in ore samples by EDXRF after thiourea leaching and adsorption on activated charcoal, *Fresenius' Journal of Analytical Chemistry*, 343(3), 292-296.

Pilipenko A.T., Karentnikova E.A., D'yachenko N.A., (1990). 4-methyl-2-(2'-hydroxynaphthylazo-1')-thiazole and 4-adamantyl-2-(2'-hydroxynaphthylazo-1')-thiazole as reagents for photometric determination of palladium, *Journal of Analytical Chemistry of the USSR*, 45(4i), 490-493.

Pilipenko A.T., Shevchenko T.L., (1989). Fluorometric determination of small amounts of palladium (II) using carbamic acid, *Journal of Analytical Chemistry of the USSR*, 44(7ii), 1030-1033.

Potts P.J., (1984). Neutron activation induced ßautoradiography as a technique for locating minor phases in thin section: application to REE and PGE mineral analysis, *Economic Geology*, 79, 738-747.

Potts P.J., (1987). A handbook of silicate rock analysis, Blackie, Glasgow, 622 pp.

Potts P.J., Prichard H.M., (1986). Mineralogical applications of neutron activation induced ß-autoradiography: the search for gold mineralisation in thin section, Metallogeny of basic and ultrabasic rocks, 455-465.

Potts P.J., Thorpe O.W., Watson J.S., (1981). Determination of the rare earth element abundances in 29 international rock standards by instrumental neutron activation analysis: a critical appraisal of calibration errors, *Chemical Geology*, 34, 331-352.

Potts P.J., Webb P.C., Watson J.S., (1984). Energy dispersive X-ray fluorescence analysis of silicate rocks for the major and trace elements, *X-ray Spectrometry*, 13(1), 2-15.

Potts P.J., Williams-Thorpe O., Isaacs M.C., Wright D.W., (1985). High precision instrumental neutron activation analysis of geological samples employing simultaneous counting with both planar and coaxial detectors, *Chemical Geology*, 48, 145-155.

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 Newsletter*, 16(1), 81-108.

Powell A.R., (1962). The platinum metals, in: Wilson C.L. and Wilson D.W. (1962). Comprehensive analytical chemistry vol.1c. Classical analysis: gravimetric and titrimetric determination of the elements, Elsevier publishing company, Amsterdam.

Prichard H.M., (1985). The Shetland ophiolite, in: Gee D.G. and Sturt B.A. (editors). The Caledonide orogen-Scandanavia and related areas, Wiley, New York, 1173-1184.

Prichard H.M., Lord R.A., (1990). Platinum and palladium in the Troodos complex, Cyprus, *Canadian Mineralogist*, 28, 607-617.

Prichard H.M., Potts P.J., Neary C.R., Lord R.A., Ward G.R., (1989). Development of techniques for the determination of the PGE in ultramafic rock complexes of potential economic significance: mineralogical studies, *Report CD-NA-11631-EN-C (1989), European Communities Commision (Luxembourg)*, CD-NA-11631-EN-C, 163 pp.

Rakovskii É.E., Starozhitskaya M.I., (1974). Extraction of the noble metals with organic sulphides, *Journal of Analytical Chemistry of the USSR*, 29(11), 1799-1801.

Rakovskii É.E., Shvedova D.A., Berliner L.D., (1974). Extraction of the platinum metals in the presence of tin (II) chloride and Di-o-tolylthiourea, *Journal of Analytical Chemistry of the USSR*, 29(11), 1933-1935.

RakovskiiÉ.E., Zdorova É.P.Kuligin V.I., Popova N.N., Fishkova N.L., Shvedova N.V., (1982). Combination methods of determination of noble metals based on assay concentration in the lead button, *Industrial Laboratory*, 48(8), 757-760.

Rakovskii É.E., Shvedova N.V., Shkil' A.N., (1984). Spectrophotometric determination of palladium, platinum and iridium with solvent extraction, *Journal of Analytical Chemistry of the USSR*, 39(8), 1163-1168.

Razina I.S., Viktorova M.E., (1970). Concentration and separation of platinum group elements and gold by ion exchange and paper partition chromatography, *Journal of Analytical Chemistry of the USSR*, 25(6), 1003-1007.

Rivoldini A., Haile T., (1989). Gold determination in ore and concentrated samples by flame atomic absorption spectrometry after chromatographic separation with amberlite XAD-7 resin, *Atomic Spectroscopy*, 10(3), 89-91.

Robért R.V.D., Van Wyk E., (1975). The effects of various matrix elements on the efficiency of the fire-assay procedure using nickel sulphide as the collector, *National Institute for Metallurgy, Johannesburg*, 1705, 9 pp.

Robért R.V.D., Van Wyk E., Palmer R., (1971). Concentration of the noble metals by a fire-assay technique using nickel sulphide as the collector, *National Institute for Metallurgy, Johannesburg*, 1371, 14 pp.

Rowbottom W.H., (1991). Determination of ammonium acetate extractable molybdenum in soil, and aqua regia (hydrochloric acid + nitric acid, 3+1) soluble molybdenum in soil and sewage sludge by electrothermal atomic absorption spectrometry, *Journal of Analytical Atomic Spectrometry*, 6(2), 123-127.

Rowston W.B., Ottaway J.M., (1979). Determination of noble metals by carbon furnace AAS. Part1- Atom formation process, *Analyst*, 104, 645-659.

Samchuk A.I., Latysh I.K., (1982). Assay- atomic absorption determination of platinum and palladium in rocks, *Soviet Progress in Chemistry*, 48, 83-84.

Samchuk A.I., Kazakevich Yu.E., Danilova E.Ya., Khabazova T.A., Emets L.V., Kokot T.K., (1988). AA determinarion of heavy metals in natural waters, *Journal of Analytical Chemistry of the USSR*, 43(4i), 490-492.

Sandell E.B., (1959). Colorimetric determination of traces of metals - 3rd edition, Interscience Publishers Inc., New York, 1054 pp.

Savel'eva A.N., Agapova T.E., (1979). Effects of sample composition on gold determination by nonflame atomic absorption, *Journal of Analytical Chemistry of the USSR*, 34(9), 1344-1348.

Schlemmer G., Welz B., (1986). Palladium and magnesium nitrates, a more universal matrix modifier for GFAAS, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 41B(11), 1157-1165.

Schoeller W.R., Powell A.R., (1955). The analysis of minerals and ores of the rarer elements - 3rd edition, Charles Griffin & co. Ltd., London, 408 pp.

Scoates R.F.J., Eckstrand O.R., (1986). Platinum-group elements in the upper central layered zone of the Fox River Sill, Northeastern Manitoba, *Economic Geology*, 81(5), 1137-1146.

Seeverens P.J.H., Klaassen E.J.M., Maessen F.J.M.J., (1983). A critical evaluation of the performance of TPP and N,N'-DPTU in solvent extraction concentration of precious metals for ICAP-AES analysis, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 38B(5/6), 727-737.

Sen Gupta J.G., (1972). The determination of noble and base metals in osmiridium, native platinum and sperrylite by atomic absorption spectrophotometry, *Analytica Chimica Acta*, 58, 23-37.

Sen Gupta J.G., (1973). A review of the methods for the determination of the platinum-group metals, silver and gold by atomic absorption spectroscopy, *Mineral Sciences Engineering*, 5(3), 207-218.

Sen Gupta J.G., (1989). Determination of trace and ultra-trace amounts of noble metals in geological and related materials by GFAAS after separation by ion exchange or coprecipitation with tellurium, *Talanta*, 36(6), 651-656.

Sen Gupta J.G., Gregoire D.C., (1989). Determination of Ru, Pd and Ir in 27 international reference silcate and iron-formationn rocks, ores and related materials by isotope dilution ICP-MS, *Geostandards Newsletter*, 13(2), 197-204.

Senise P.Levi F., (1964). Solvent extraction studies of addition compounds of metal halides and triphenylphosphine, -arsine and -stibine: Part1. detection of palladium, *Analytica Chimica Acta*, 30, 422-426.

Shazali I., Van't Dack L., Gijbels R., (1987). Determination of precious metals in ores and rocks by thermal neutron activation/ Y-spectrometry after pre-concentration by nickel sulphide fire assay and coprecipitation with tellurium, *Analytica Chimica Acta*, 196, 49-58.

Shazali I., Van't Dack L., Gijbels R., (1988). Preconcentration of precious metals by tellurium sulphide fire assay followed by instrumental neutron activation analysis, in: Prichard H.M., Potts P.J., Bowles J.F.W., Cribb S.J. (Editors). Geo-Platinum 87, Elsevier, London, 29-42.

Shkil' A.N., Rukhadze E.G., (1989). Extraction of silver, gold, palladium, platinum and iridium by thiobenzanilide and N-substituted derivatives of a-thiopicolinamide in the presence of oxidants and complexing agents, *Journal of Analytical Chemistry of the USSR*, 44(7i), 981-984.

Shkil' A.N., Zolotov Yu.A., (1988). Solvent extraction of platinum with thiobenzanilide. Separation of platinum from copper, *Journal of Analytical Chemistry of the USSR*, 43(8ii), 1188-1193.

Shukun Xu, Lijing Sun, Zhaolun Fang, (1991). Determination of gold in ore by flame atomic absorption spectrometry with flow-injection on-line sorbent extraction preconcentration, *Analytica Chimica Acta*, 245(1), 7-11.

Sighinolfi G.P.Gorgoni C., Mohamed A.H., (1984). Comprehensive analysis of precious metals in some geological standards by flameless AA spectroscopy, *Geostandards Newsletter*, 8(1), 25-29.

Slavin W., (1987). The present and future of graphite furnace atomic absorption spectrometry, *Trends in Analytical Chemistry*, 6(8), 194-201.

Smith E.A., (1987). The sampling and assay of the precious metals - 2nd revised edition, Met-Chem Research, Inc., Boulder, Colorado.

Smolander K., Kauppinen M., (1991). Direct determination of gold by d.c. argon plasma emission spectrometry, *Analytica Chimica Acta*, 248, 569-574.

Srivastava S., Rao G.N., (1990). Separation of palladium from transition elements using an ion exchange salicylaldoxime-formaldehyde resin, *Analyst*, 115(12), 1607-1609.

St. Louis R.M., (1987). Gold in BHVO-1,BIR-1,DNC-1,BCR-1 by fire assay preconcentration neutron activation analysis: sample size vs accuracy, *Geostandards Newsletter*, 11(2), 151-157.

Stafilov T., Todorovski T, (1987). Determination of gold in arsenic-antimony ore by flameless atomic absorption spectrometry, *Atomic Spectroscopy*, 8(1), 12-14.

Steele T.W., Levin J., Copelowitz I., (1975). The preparation and certification of a reference sample of a precious metal ore, *National Institute for Metallurgy, Johannesburg*, 1696.

Steger H.F., Bowman W.S., (1980). SU-1a: A certified nickel-copper-cobalt reference ore, *CANMET report*, 80-9E.

Stockman H.W., (1983). Neutron activation determination of noble metals in rocks; a rapid radiochemical separation based on tellurium coprecipitation, *Journal of Radioanalytical Chemistry*, 78(2), 307-317.

Strong M.B., Murray-Smith R., (1974). Determination of gold in copper-bearing sulphide ores and metallurgical flotation products by AAS, *Talanta*, 21, 1253-1258.

Sturgeon R.E., Chakrabarti C.L., Langford C.H., (1976). Studies on the mechanism of atom formation in GFAAS, *Analytical Chemistry*, 49(8), 1792-1807.

Sturgeon R.E., Falk H., (1988). Sample atomisation and oxident release in GFAAS, *Journal of Analytical Atomic Spectrometry*, 3(1), 27-34.

Sutano R., Steger H.F., (1985). The use of certified reference materials in the verification of analytical data and methods, *Talanta*, 32(6), 439-445.

Tarkian M., Prichard H.M., (1987). Irarsite-hollingworthite solid solution series and other associated Ru-, Os-, Ir- and Rh-bearing PGMs from the Shetland ophiolite complex, *Mineralium Deposita*, 22, 178-184.

Taskaev E., Penev I., Schelhorn H., Geisler M., (1987). Radiochemical determination of gold in rocks, *Geostandards Newsletter*, 11(1), 103-106.

Terashima S., (1988). Determination of Au in 60 geochemical reference samples by flameless AAS, *Geostandards Newsletter*, 12(1), 57-60.

Terashima S., (1991). Determination of platinum and palladium in sixty eight geochemical reference samples by flameless atomic absorption spectrometry, *Geostandards Newsletter*, 15(1), 125-128.

Thompson C.E., Nakagawa H.M., VanSickle G.H., (1968). Rapid analysis for gold in geologic materials, *US Geological Survey professional paper*, 600-B, B130-B132.

Tikhomirova T.I., Fadeeva V.I., Kudryavtsev G.V., Nesterenko P.M., Ivanov V.M., Savitchev A.T., Smirnova N.S., (1991). Sorption of noble-metal ions on silica with chemically bonded nitrogen-containing ligands, *Talanta*, 38(3), 267-274.

Timberbaev A.R., Petrukhin O.M., Alimarin I.P.Bol'shova T.A., (1991). High-performance liquid chromatography of metal chelates; environmental and industrial trace metal control, *Talanta*, 38(5), 467-476.

Totland M., Jarvis I, Jarvis K.E., (1993). Determination of the platinum-group elements and gold in solid samples by slurry nebulisation ICP-MS, *Chemical Geology*, 104, 175-188.

Trancoso M.A., Barros J.A., (1989). Determination of gold in complex sulphide-minerals by differential-pulse anodic stripping voltametery after anion exchange separation, *Analyst*, 114(9), 1053-1056.

Trotman-Dickenson A.F. (Executive Editor), (1973). Comprehensive inorganic chemistry - volume 3, Pergamon, Oxford, 1387 pp.

Van Loon J.C., (1977). Analytical chemistry of the noble metals, *Pure and Applied Chemistry*, 49, 1495-1505.

Van Loon J.C., (1984). Accurate determination of the noble metals: sample decomposition and methods of separation, *Trends in Analytical Chemistry*, 3(10), 272.

Van Loon J.C., (1985). Accurate determination of the noble metals: determination methods, *Trends in Analytical Chemistry*, 4(1), 24-29.

Van Loon J.C., Barefoot R.R., (1991). Determination of the precious metals - selected instrumental methods, John Wiley and Sons, Chichester, 276 pp.

VanSickle G.H., Lakin H.W., (1968). An atomic-absorption method for the determination of gold in larger samples of geologic materials, *US Geological Survey circular* , circ561, 4 pp.

Vermaak C.F., Hendriks L.P.(1976). A review of the mineralogy of the Merensky Reef, with special reference to new data on the precious metal mineralogy, *Economic Geology*, 71(7), 1244-1269.

Vermeulen J.M., (1989). Rapid determination of Au in geological materials by amyl acetate extraction, ascorbic acid reduction and ETA-AAS, *Journal of Analytical Atomic Spectrometry*, 4(1), 77-82.

Vest P.Schuster M., König K.-H, (1991). Solvent extraction of gold with N-substituted benzoythioureas, *Fresenius' Journal of Analytical Chemistry*, 341(9), 566-568.

Vines R.F., (1941). The platinum metals and their alloys, The International Nickel Company Inc., New York, 141 pp.

Volfinger M., (1989). A new quantitative radiochemical separation procedure to determine Ir at 10-12 g/g level in geological samples by a long chain primary amine extraction, *Journal of Radioanalytical and Nuclear Chemistry*, 130(2), 321-331.

Vorob'eva G.A., Zolotov Yu.A., Izosenkova L.A., Karyakin A.V., Pavlenko L.I., Petrukhin O.M., Seryakova I.V., Simonova L.V., Shevchenko V.N., (1974). Extraction of the noble metals for their group concentration and subsequent spectrographic determinations, *Zhurnal Analytic Khimii*, 29(3), 497-505.

Walsh A., (1955). The application of atomic absorption spectra to chemical analysis, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 7, 108-117.

Watson A.E., Moore G.L., (1984). Determination of traces of noble metals adsorbed onto an ion exchange resin by its direct injection into an ICP source, *South African Journal of Chemistry*, 37(3), 81-84.

Watters R.L.Jr., (1991). The use of standard reference materials for quality assurance in inductively coupled plasma optical emission and atomic absorption spectrometry, *Spectrochimica Acta, part B. Atomic Spectroscopy*, 46B(12), 1593-1605.

Webb P.C., Potts P.J., Watson J.S., (1990). Trace element analysis of geochemical reference samples by energy dispersive x-ray fluorescence spectrometry, *Geostandards Newsletter*, 14(2), 361-352.

Weiss H.V., Fresco J., (1983). Platinum group elements in seawater. 1. Palladium, *Canadian Journal of Chemistry*, 61, 734-436.

Wemyss R.B., Scott R.H., (1978). Simultaneous determination of platinum-group metals and gold in ores and related plant materials by ICP-OES, *Analytical Chemistry*, 50(12), 1694-1697.

Werbicki J.J., (1982). How much gold?, *Products Finishing (Cincinnati)*, 46, 42-53.

Westland A.D., (1981). Inorganic Chemistry of the platinum-group elements, in: L.J. Cabri (editor). Platinum group elements: mineralogy, geology, recovery. Canadian Institute of Mining and Metallurgy, Special Volume 23, 5-18.

Whitley J.E., Littlejohn D., (1987). Studies of transfer processes in GFAAS, Poster at Prof. Ottaway memorial meeting, Edinburgh.

Wilson S.M., Hoashi M., Brooks R.R., Reeves R.D., (1989). A method for the quantification of bismuth and palladium in geological materials including K-T boundary clays, *Chemical Geology*, 75, 305-310.

Wood S.A., Vlassopoulos D., Mucci A., (1990). Effects of concentrated matrices on the determination of trace levels of platinum and gold in aqueous samples using solvent extraction-Zeeman effect graphite furnace atomic absorption spectrometry and inductively coupled plasma-mass spectrometry, *Analytica Chimica Acta*, 229(2), 227-238.

Wright T.L., Fleischer M., (1965). Geochemistry of the platinum metals, *US Geological Survey bulletin*, **1214-A**, 24 pp.

Xie Xuejing, Wang Xueqiiu, (1991). Geochemical exploration for gold: a new approach to an old problem, *Journal of Geochemical Exploration*, **40**, 25-48.

Yoshikuni N., (1991). Rapid dissolution of chromite with sulphuric acid-lithium sulphate mixture containing ceric sulphate, manganese dioxide or periodate, and spectrophotometric determination of chromium, *Talanta*, **38(5)**, 515-519.

Yunan Lin, Jinxing Hu, Zhenxing Shen, Tiean Wu, (1988). A new fire assay of gold using antimony as a collector-determination of gold at ng/g levels in geochemical materials, *Fenxi Huaxue*, **16(1)**, 1-4.

Zhenru Zhang, Sixue Yang, Wen Yi, (1987). Studies of sub-micro gold and lattice gold in some minerals, *Journal of the Central-South Institute of Mining and Metallurgy*, **18(4)**, 355-361.

Zicheng Peng, Klinkenberg H., Beeren T., Van Borm W., (1991). Determination of germanium, palladium and platinum in highly concentrated solutions of phosphoric acid and ammonium nitrate by flow injection inductively coupled plasma mass spectrometry (FI-ICP-MS), *Spectrochimica Acta, part B. Atomic Spectroscopy*, **46B(6/7)**, 1051-1061.

Zientek M.L., Fries T.L., Vian R.W., (1990). As, Bi, Hg, S, Sb, Sn and Te geochemistry of the J-M Reef, Stillwater complex, Montana: constraints on the origin of PGE-enriched sulphides in layered intrusions, *Journal of Geochemical Exploration*, **37(1)**, 51-73.

Zolotov Yu.A., Petrukhin O.M., Shevenko V.N., Dinina V.V., Rukhadze E.G., (1978). Solvent extraction of noble metals with derivatives of thiourea, *Analytica Chimica Acta*, **100**, 613-618.