

**ANALYSIS OF  
GOLD AND THE PLATINUM GROUP ELEMENTS  
IN GEOLOGICAL SAMPLES**

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# **ANALYSIS OF GOLD AND THE PLATINUM GROUP ELEMENTS**

## **IN GEOLOGICAL SAMPLES**

by

Riitta Juvonen

### **Academic Dissertation**

To be presented with the permission of the Faculty of Science of the University of Helsinki  
for public criticism in the Main Lecture Hall A110 of the Department of Chemistry  
(A.I.Virtasen aukio 1) at 12 o'clock noon on November 19<sup>th</sup>, 1999.

Geological Survey of Finland  
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**Juvonen, Riitta 1999.** Analysis of Gold and the Platinum Group Elements in Geological Samples. *Geological Survey of Finland, Espoo*. 54 pages, 12 tables and 5 figures.

For exploration and petrological studies low detection limits are necessary in the determination of gold and the platinum group elements in geological samples in order to differentiate anomalous concentrations from the background. The same holds true for samples in environmental studies. Analytical instrumentation has developed, allowing for the determination of this group of elements at the ng/g concentration level, however, preconcentration of the analytes and their separation from interfering elements prior to instrumental determination is usually required.

This thesis deals with the development of analytical methods for the determination of gold and the platinum group elements (PGE) — iridium, osmium, palladium, platinum, rhodium and ruthenium, with emphasis on the decomposition and preconcentration procedures used prior to instrumental determination. Preconcentration methods used for gold were the lead fire assay, aqua regia leach/mercury coprecipitation and sodium cyanide leach. The main method of preconcentration of the PGE was the nickel sulfide fire assay. The separation of the sulfide and the silicate phases was found to be incomplete after the nickel sulfide fire assay fusion in the case of black shale and magnetite-rich rocks. The interference in black shales, caused by graphite, was eliminated by roasting the sample or by adding potassium nitrate as oxidant to the fusion flux. The nickel sulfide fire assay fusion of magnetite proved successful after adding potassium tartrate or sulfur to the fusion flux.

The inductively coupled plasma-mass spectrometry (ICP-MS) has become the instrumental technique of choice for analysis of these elements in the recent years because of its capability of simultaneous determination of all of the elements at low detection limits. In addition to ICP-MS, the instrumental technique used in this study is atomic absorption spectrometry, both flame (FAAS) and graphite furnace (GFAAS) atomisation.

The repeatability of analytical results for the precious metals, especially for gold in geological samples presents a problem because of the inhomogeneous distribution of these elements in rocks. Sampling, sample preparation and the applicability of different methods of gold analysis to various types of ores was studied, using sample material from six Finnish gold ores.

Key words: (GeoRef Thesaurus, AGI): chemical analysis, gold, platinum group elements, rocks, soils, sampling, inductively coupled plasma methods, mass spectroscopy, atomic absorption, fire assay methods, aqua regia, cyanides, leaching, mercury, coprecipitation

## CONTENTS

|  |    |
|--|----|
| ACKNOWLEDGEMENTS .....   | 3  |
| ABSTRACT .....   | 4  |
| CONTENTS .....   | 5  |
| ABBREVIATIONS .....  | 6  |
| LIST OF ORIGINAL PUBLICATIONS .....                                  | 7  |
| 1. INTRODUCTION .....  | 8  |
| 2. ANALYTICAL METHODS FOR GOLD AND THE PLATINUM GROUP ELEMENTS ..... | 12 |
| 2.1 Sampling and sample preparation .....                            | 12 |
| 2.2 Commonly used analytical methods .....                           | 14 |
| 2.3 Decomposition and preconcentration methods .....                 | 15 |
| 2.3.1 The lead fire assay .....                                      | 15 |
| 2.3.2 The nickel sulfide fire assay .....                            | 17 |
| 2.3.3 Acid digestion .....   | 19 |
| 2.3.4 Cyanide leach .....  | 20 |
| 2.3.5 Chlorination .....   | 22 |
| 2.3.6 Sodium peroxide fusion .....                                   | 23 |
| 2.3.7 Separation and concentration procedures .....                  | 24 |
| 3. RESULTS AND DISCUSSION .....                                      | 28 |
| 3.1 The lead fire assay .....  | 28 |
| 3.2 Nickel sulfide fire assay .....                                  | 30 |
| 3.2.1 Reagent blank and recovery studies .....                       | 33 |
| 3.2.2 Fusion of black shale samples .....                            | 37 |
| 3.2.3 Fusion of samples with high magnetite content .....            | 39 |
| 3.3 The sodium cyanide leach .....                                   | 41 |
| 3.4 The sodium peroxide fusion .....                                 | 43 |
| 3.5 Observations on sampling for gold determination .....            | 44 |
| 4. CONCLUSION .....  | 46 |
| REFERENCES .....   | 49 |

**ABBREVIATIONS**

|          |   |
|----------|---|
| DCP-AES  | directly coupled plasma-atomic emission spectrometry            |
| EDXRF    | energy dispersive X-ray fluorescence                            |
| FAAS     | flame atomic absorption spectrometry                            |
| GFAAS    | graphite furnace atomic absorption spectrometry                 |
| HCl      | hydrochloric acid   |
| ICP-AES  | inductively coupled plasma-atomic emission spectrometry         |
| ICP-MS   | inductively coupled plasma-mass spectrometry                    |
| MC-ICPMS | multiple collector inductively coupled plasma mass spectrometry |
| NaCN     | sodium cyanide  |
| NiS      | nickel sulfide  |
| PGE      | platinum group elements   |

## LIST OF ORIGINAL PUBLICATIONS

The following previously published papers included in this study are:

**I Juvonen, R. and Väänänen, P.J., 1993.** Determination of gold in geological materials by atomic absorption after lead fire assay separation. In: (ed.) Kontas, E. Analytical methods for determining gold in geological samples. Geological Survey of Finland, Report of Investigation 114, 13 - 16.

**II Juvonen, R., Lakomaa, T. and Kallio, E., 1993.** Determination of the platinum group elements and gold in rock samples by nickel sulphide fire assay preconcentration and ICP-MS measurement. In: (ed.) Autio, S. Geological Survey of Finland, Current Research 1991 - 1992, Geological Survey of Finland, Special Paper 18: 101 - 105.

**III Juvonen, R., Kallio, E. and Lakomaa, T., 1994.** Determination of precious metals in rocks by inductively coupled plasma mass spectrometry using nickel sulfide concentration. Comparison with other pre-treatment methods. *Analyst* 119, 617 - 621.

**IV Juvonen, R., Kallio, E., Heiskanen, L. and Lakomaa, T., 1997.** Determination of the platinum group elements and gold in black shales by inductively coupled plasma-mass spectrometry using nickel sulphide fire assay pre-concentration. Reprint from: Papunen, Heikki (ed.), Mineral deposits: Research and exploration - where do they meet? - Proceedings of the fourth biennial SGA Meeting, Turku, Finland, 11 - 13 August 1997. 1008 pp., EUR.137.50/US\$162.00/GBP.97.00. A.A. Balkema, P.O. Box 1675, Rotterdam, Netherlands, 59 - 62.

**V Juvonen, R. and Kontas, E., 1999.** Comparison of three analytical methods in the determination of gold in six Finnish gold ores, including a study on sample preparation and sampling. *J. Geochem. Explor.* 65, 219 - 229.

These publications are referred to in the Summary with Roman numerals I-V.

The work was carried out at the Geological Survey of Finland (GTK) during the 1980s and 1990s in developing methods for the analysis of gold and the platinum group elements (PGE).



## 1. INTRODUCTION

Gold is the oldest known metal — man used metallic gold already 5000 - 6000 B.C. The ability to extract gold from its ores was known 4000 B.C. The oldest literature references of this activity are found in the Bible, where reference is made to the purification of gold by cupellation with lead. Platinum was used by Indians of Ecuador for making ornaments before the first Europeans arrived in South America. The metal, first thought of as being an inferior quality of silver, was brought to Europe in the 18th century. The other five platinum group elements — palladium, rhodium, iridium, osmium and ruthenium — were discovered in studying the chemistry of platinum at the beginning of the 19th century (Livingstone 1973).

The average concentrations of gold and the platinum group elements (PGE) in the continental crust are very low, at less than 3 ng/g (Reimann & de Caritat 1998). The PGE concentrations of meteorites are higher, at 100 - 1000 ng/g (Livingstone 1973). Rocks formed in collisions with meteorites, the impactites, exhibit elevated PGE concentrations. PGE concentration levels of some Finnish impactites have been in the range of 4 - 12 ng/g (Pipping 1991), which is slightly higher than the average concentration in other rocks.

**Table 1**

A section of the periodic table containing Au and the PGE.

|    |           |           |           |           |
|----|-----------|-----------|-----------|-----------|
| 7  | 8         | 9         | 10        | 11        |
| Mn | Fe        | Co        | Ni        | Cu        |
| Tc | <b>Ru</b> | <b>Rh</b> | <b>Pd</b> | Ag        |
| Re | <b>Os</b> | <b>Ir</b> | <b>Pt</b> | <b>Au</b> |

Gold belongs to the same group as silver and copper in the periodic table (Table 1), and it is commonly found to be associated with these elements in rocks. Gold is often found in nature as the metallic element and also in minerals with such elements as bismuth, antimony, arsenic and tellurium. Typical minerals of gold, in addition to native gold, are: calaverite  $\text{AuTe}_2$ , krennerite  $(\text{Au,Ag})\text{Te}_2$ , sylvanite  $(\text{Au,Ag})\text{Te}_4$  and petzite  $\text{Ag}_3\text{AuTe}_2$ . Common host minerals of gold are silver, tellurides and quartz



(Reimann & de Caritat, 1998). A mixture of silver and gold containing 45 - 75 % gold is known as electrum (Marsden & House 1992a).

In the periodic table, the platinum group elements appear in the same group as the transition elements iron, cobalt and nickel. Due to chemical similarity, the PGE have a tendency to become enriched with iron, cobalt and nickel in geological processes. They form chemically similar pairs: Ru-Os, Rh-Ir and Pd-Pt. The PGE are generally found in connection with sulfide ores of copper and nickel. The most common minerals are metals, metal alloys, sulfides, arsenides and tellurides. Because of isomorphic substitution among the PGE, the elements are often present as a group in various minerals. Such minerals are metal alloys, tellurides, selenides, arsenides, sulfarsenides, sulfides, oxides and silicates (Cabri 1981). Of all the PGE minerals, palladium minerals are the most abundant. Of the various PGE minerals, 48 % are palladium minerals, 21 % platinum, 9 % ruthenium and iridium, 8 % rhodium, and 5 % osmium. In 1990, there were 86 well-defined PGE minerals and about 200 inadequately-defined minerals, some of which may prove to be new PGE minerals. Mineral species vary depending on the ore type, but sperrylite (PtAs<sub>2</sub>) is the most common platinum mineral everywhere in the world (Cabri 1994). The relative abundances of the PGE in various ores are presented in Table 2.

**Table 2**

Relative abundances (%) of the PGE in various ores around the world according to Crowson (Crowson 1994).

|                     | Pt | Pd | Ir | Rh | Ru | Os |
|---------------------|----|----|----|----|----|----|
| Columbia            | 93 | 1  | 3  | 2  | -  | 1  |
| Canada-Sudbury      | 43 | 45 | 2  | 4  | 4  | 2  |
| So. Africa-Merensky | 61 | 26 | 1  | 3  | 8  | 1  |
| -UG2                | 41 | 34 | 2  | 9  | 12 | 2  |
| -Platreef           | 44 | 48 | 3  | 1  | 4  | -  |
| Russia-Norilsk      | 25 | 67 | 2  | 3  | 2  | 1  |
| USA-Stillwater      | 20 | 78 | -  | 1  | -  | -  |
| -Duluth             | 18 | 78 | 1  | 2  | 1  | -  |

Platinum group metals are usually produced as by-products of copper-nickel ore refining. Even low concentrations of these elements may have an effect on the economical feasibility of such an ore. The world annual production of gold was 2000 tons and the

total production of the PGE was 300 tons in 1995 (Reimann & de Caritat 1998). World market prices play an important role in the production of these metals (Graham 1995).

Gold is used mainly for jewellery. Its chemical inactivity, ductility and good electrical conductivity also make it an excellent material for various applications in the fields of electronics, dentistry, decorations and other industrial applications (Crowson 1994). Platinum, palladium and rhodium have been used for the production of catalytic converters for automobiles in recent years. Other important uses for the PGE are in the fields of electronics, the chemical industry, oil refining and dentistry. They are often used as catalysts in chemical processes. Platinum coordination complexes are used in cancer chemotherapy, and gold salts are used in the treatment of rheumatoid arthritis (Van Loon & Barefoot 1991a).

Gold and the PGE are called noble metals because of their general resistance to chemical reactions. They do, however, react with numerous reagents. Osmium and ruthenium are the least resistant to chemical attack: osmium is slowly oxidised in air producing the gas osmium tetroxide, and ruthenium also produces the gas ruthenium oxide upon contact with an oxidising agent. The most easily soluble in acids is palladium. When heated at high temperature all of the PGE produce oxides. Chlorine and fluorine react with gold and the PGE upon heating, producing the respective halogenides, which are an important group of compounds of these elements (Van Loon & Barefoot 1991b, Cotton & Wilkinson 1988).

In the industrial production of gold, more than 85 % of all the new gold produced is extracted by the cyanide leach process (Fleming 1998). Environmental considerations are important in the process because of the toxicity of the cyanide solution. Accidents do, however, occur. A spill of cyanide-contaminated waste from a tailings pond from the Omai mine in Guyana was reported to have killed thousands of fish in the Omai River in 1995. The lethal concentration level for fish and other aquatic life is only 1 mg/l cyanide (McKeagney 1997).

There is international concern over mercury pollution caused by the traditional gold production method using mercury amalgamation by small-scale miners around the world. Various environmental projects have introduced simple procedures to the miners for distillation and collection of the mercury, but they have not found approval with the miners (Sassoon 1997).

Human activity has been shown to cause emission of gold and the PGE into the environment. Of the two types of automotive exhaust catalysts, the pellet type produces emissions of about 0.8 - 1.9  $\mu\text{g}$  of platinum for every kilometer driven. The amount of emission is dependant on the speed driven and declines with ageing of the catalyst. Emission rates of the monolith type catalyst are lower (Rosner et al. 1991). There is growing concern regarding the toxicity of these elements, especially of palladium compounds, and their possibility of entering into the food chain. The concentration levels in environmental samples are at the ng/g level or less in plant, soil and water samples (Pyrzynska 1998, Reimann & de Caritat 1998).

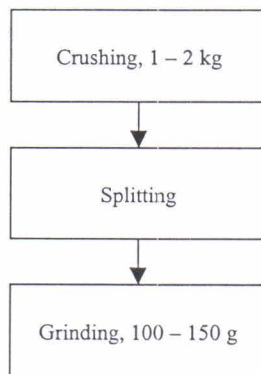
During the past decade, numerous occurrences of gold have been discovered in Finland. A recently published public database on Finnish gold deposits contains information on 131 mineralisations (Eilu 1999). Much of the success in the geochemical exploration can be attributed to the availability an analytical method suitable for the analysis of large quantities of samples at low detection limits and at fairly low cost in the laboratory (Kontas 1981, Kontas 1993).

The scope of this study is limited to methods, which are commonly used for the determination of gold and the platinum group elements in geological samples, with emphasis on sample pretreatment methods applicable to ICP-MS determination. Analytical methods required in recycling and in the monitoring of emission of these elements into the environment are also considered.

## 2. ANALYTICAL METHODS FOR GOLD AND THE PLATINUM GROUP ELEMENTS

### 2.1 Sampling and sample preparation

Because the concentration levels of these elements in rocks are low and because they are inhomogeneously distributed in rocks a large sample (10 - 50 g) is often used for analysis. The inhomogeneity is especially a problem with many gold ore samples. The rock sample is first crushed to a grain size of about 2 mm, then split repeatedly until the appropriate amount for grinding is obtained and then ground to a fine powder ( $\leq 100 \mu\text{m}$ ) with a swing mill (Fig. 1). During sample preparation, care is taken to avoid cross contamination of samples. It may not always be possible to produce a homogeneous sample in respect to gold and the PGE. Even certified reference samples at low concentration range are suspected of sample inhomogeneity (Plessen & Erzinger 1998).



**Figure 1**  
Preparation of rock sample for analysis.

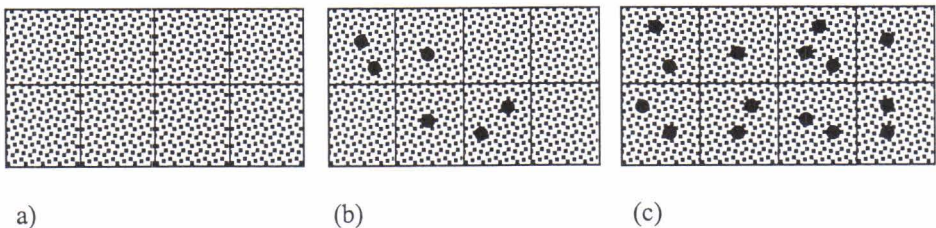
The mathematical methods employed by Clifton et al. and Ingamells are often quoted in connection with sampling for gold analysis. In establishing the minimum adequate sample size, using the method of Clifton et al., the important factors are the gold particle size and the number of particles in the sub-sample. If the particle size is not uniform, which is usually the case, a so-called effective particle size can be determined



on the basis of repeated analyses of a sample, or the effective gold particle diameter is determined by the distribution of gold values of sieve fractions. Numerous gold determinations of a single sample are required for establishing the adequate sample size by this method (Clifton et al. 1969). Ingamells defines three types of sampling constants which together permit the estimation of errors in sampling in the field and in the laboratory. The three constants are: (1) The laboratory sampling constant for describing the subsampling characteristics of a sample; (2) Gy's constant for controlling the reduction of field samples and (3) Visman sampling constants used for designing the sampling in the field (Ingamells 1974).

Defining the sampling constant as the amount of sample required, in grams, for a certain subsampling error, Malik and Parry calculated the sampling constants using the relative standard deviations of replicate gold determinations for the Canadian reference gold ore samples MA-1, MA-1b, MA-2 and MA-2a. They found that the MA-2 series is much more inhomogeneous than the MA-1 series. At least 6 g of MA-1 and 28 g of MA-2 ores are needed for a sub-sampling error of 3 % (Malik & Parry 1992).

In studying numerous gold deposits around the world, Xuejing and Xueqiu found that the finer than about 5  $\mu\text{m}$  gold particle size predominates in many ores, making the use of a large sample size for these samples unnecessary. They found that the largest variation in analytical results occurs in the middle range of gold content (Xuejing & Xueqiu 1992). The reason for this is depicted in Figure 2.



**Figure 2**

Variation of the sub-sample representativeness depending on the particle size distribution of the sample: (a) Fine grain size predominates, (b) some larger particles with fine grain size particles (c) abundant large particles with fine grain size particles (from Xuejing & Xueqiu 1992).



Kontas studied the contamination of the grinding vessel of the swing mill after grinding gold ore samples of various grades. After grinding the ore, the grinding vessel was washed with water and then pure quartz was ground in the same vessel. The quartz was found to contain traces of gold, the amount of which increased with the grinding time which had been used for the gold ore (Kontas 1993). The separation of gold to the bottom of the sample container upon transport and storage and the adhering of fine gold to the surface of plastic containers by electrostatic or other adhesive forces was observed by Hämäläinen and Kontas on a set of thirteen geochemical samples (Hämäläinen & Kontas 1992).

## **2.2 Commonly used analytical methods**

Gold and the PGE are usually enriched and at the same time separated from interfering elements either by a fusion or a dissolution procedure or by a combination of the two. There are various instrumental techniques available for the final determination of the elements. The oldest instrumental techniques are spectrophotometry and emission spectrography. The classical gravimetric method for the determination of gold is still widely used, especially in mine laboratories, around the world. Development of methods based on atomic absorption determination started in the 1960s (Simmons 1965, Olson 1965, Huffman et al. 1967), and today atomic absorption still holds its place as one of the most widely used instrumental techniques. Inductively coupled plasma emission spectrometry is also widely used for the determination of gold and the PGE (Van Loon & Barefoot 1989). Neutron activation analysis gained popularity in the 1970s and is still used in the 1990s (Hoffman et al. 1978, Borthwick & Naldrett 1983, Asif et al. 1992, Stone & Crocket 1993). Application of the inductively coupled plasma-mass spectrometry technique to gold and PGE determination began to develop in the 1980s. The technique enables the determination of gold and of all the PGE simultaneously at low detection limits, making it the method of choice today.

## 2.3 Decomposition and preconcentration methods

### 2.3.1 The lead fire assay

The classical lead fire assay is generally accepted as the most dependable analytical method for gold in geological samples. The method is used extensively by mine laboratories and geoanalytical laboratories all over the world for gold determination. Silver, platinum and palladium can also be determined after the fire assay preconcentration. Silver is usually determined gravimetrically, gold either gravimetrically or instrumentally, and platinum and palladium are determined instrumentally. Each laboratory has its own variation of the fusion and cupellation procedure.

The fire assay procedure begins with fusion of the sample — usually from 15 g to 50 g — with lead oxide, a reducing agent, sodium carbonate and sodium tetraborate. Silver is added to the fusion mixture either as metallic silver or in the form of silver nitrate solution. Silver acts as carrier for gold, palladium and platinum. The fusion takes place at about 1000 - 1100 °C. During the fusion, the noble elements are collected by forming droplets of the molten metallic lead as they fall through the melt to the bottom of the fusion crucible forming the lead regulus. After cooling, the lead regulus is separated from the slag and cupelled at about 960 °C in a magnesite or bone ash cupel. During the cupellation, the lead is oxidised and absorbed by the cupel as lead oxide. A small metallic bead remains on the cupel, which is composed of the added silver and the silver, gold and other noble metals extracted from the sample. The bead is hammered flat to facilitate handling and dissolution. For gravimetric determination, the bead is weighed with a micro-balance and then treated with dilute nitric acid to dissolve the silver. The remaining gold is then weighed to determine the amount of gold in the original sample. The amount of silver is calculated as the difference of the weights. If the sample contains platinum, palladium or other PGE, they will cause a positive error in the gold value because they will not be dissolved by the nitric acid treatment. For instrumental determination, the entire flattened bead is dissolved in aqua regia. Some laboratories continue cupellation of the silver bead at 1300 °C, whereby the silver is volatilised

(Robért et al. 1977). Gold is considered a better collector for rhodium and iridium than silver. The efficiency of the collection of ruthenium, iridium and osmium by the lead regulus depends greatly on the composition of the sample, the composition of the fusion flux and also on the fusion temperature. If silver is used as the collector, iridium and ruthenium are partly lost during cupellation because they are attached to the cupel. Osmium is lost as the volatile osmium tetroxide in the cupellation process. Osmium and ruthenium have been determined by dissolution of the lead regulus in perchloric acid, followed by distillation of osmium and ruthenium as tetroxides and their determination spectrophotometrically as the thiourea complexes (Van Loon & Barefoot 1991).

Each of the fusion reagents used in fire assay has its own function. Sodium carbonate is a basic reagent, which melts at 852 °C and dissociates at 950 °C. It reacts with the minerals of a rock sample producing sodium silicates and sodium aluminates. Lead oxide, PbO, is also a basic reagent, which melts at 883 °C and upon becoming reduced, produces the lead required for collection of the noble metals. Sodium tetraborate is a strongly acidic reagent, which melts most of the metal oxides. Quartz is always added if the sample itself does not contain quartz — it makes the flux less viscous. Calcium fluoride is sometimes used for the same purpose. Potassium tartrate, carbon powder, sugar and flour are alternatives commonly used as reducing agents for the reduction of the lead oxide. For samples with a high sulfide mineral content, potassium nitrate can be added to the fusion flux for the oxidation of the sulfides. Alternatively, the sample is roasted prior to the fusion. For best results in lead fire assay, the fusion flux is chosen according to the type of sample assayed (Haffty et al. 1977).

In most laboratories today, the noble metal bead obtained in fire assay is dissolved completely and the determination of gold, palladium and platinum is carried out by an instrumental technique, such as atomic absorption (Kallmann & Hobart 1970, Coombes & Chow 1977, Robért et al. 1977), inductively coupled plasma emission spectrometry, or ICP-MS (Hall & Bonham-Carter 1988, Hall & Pelchat 1994).



### 2.3.2 The nickel sulfide fire assay

The platinum group elements are almost always found enriched in nickel and copper sulfide ores as a result of geological processes. The same phenomenon is used in the nickel sulfide fire assay, where the sample, nickel, sulfur and fusion reagents are fused together at high temperature. Williamson and Savage first used the nickel sulfide collection on geological samples as a preconcentration and separation step before the spectrophotometric determination of osmium as the thiourea complex (Williamson & Savage 1965). They found the composition of the nickel sulfide button to be 69.3 % nickel and 27.9 % sulfur, which is close to the eutectic point between the sulfides  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_6\text{S}_5$ .

Preconcentration of the PGE by the NiS collection has been widely applied ever since. The fusion reagents are the same as in the lead fire assay procedure: sodium carbonate, quartz and sodium tetraborate. Nickel and sulfur are added as collectors for the PGE. The finely powdered rock sample is mixed with the reagents, transferred into a fusion crucible and fused at about 1000 °C. During the fusion, a silicate phase and a sulfide phase are formed in the melt. The sulfide phase, being heavier, settles at the bottom of the fusion crucible, and while falling through the melt, the sulfide phase collects gold and the PGE. In the usual analytical procedures, the amounts of nickel and sulfur contained by the sample are subtracted from the fusion mixture. The correct ratio of these elements is important to avoid the formation of  $\text{NiS}_2$ , which is difficult to dissolve in HCl. It would dissolve with the PGE sulfides in aqua regia and nickel would be in the final solution used for measurement and cause interference on Ru determination by ICP-MS (Jackson et al. 1990). If the sample contains copper, some laboratories increase the amount of sulfur in order to form copper sulfide along with the nickel sulfide (Paukert & Rubeška 1993). Asif and Parry replaced sodium tetraborate by lithium tetraborate in their small nickel sulfide button (Asif & Parry 1989).

The nickel sulfide button is dissolved in concentrated hydrochloric acid. The PGE sulfides remain undissolved and are separated from the solution by filtration. It has been found, that gold is partially dissolved by the hydrochloric acid treatment.

Coprecipitation of gold with tellurium from the hydrochloric acid solution is used for a better gold recovery (Shazali et al. 1987). The PGE sulfides are finally dissolved by the addition of nitric acid and hydrochloric acid.

The main problems involved with the method are the incomplete fusion of some types of samples and the high reagent blank values. Most commonly mentioned is the difficulty of fusing chromite-bearing samples, which leads to low recoveries of Au and the PGE (Borthwick & Naldrett 1984, Jackson et al. 1990). Some recommendations are given on the flux composition for chromite-bearing samples. Lithium tetraborate is sometimes substituted for sodium tetraborate in the fusion of the chromitites (Borthwick & Naldrett 1983; Borthwick & Naldrett 1984; Sun et al. 1993). Other recommendations have been such as adding silica as much as three times the sample mass (Paukert & Rubeška 1993) or adding iron oxide (Rice & Waldron 1994). McDonald et al. found that samples with unusually high magnesium or carbonate contents do not melt completely. They recommend addition of more silica to the magnesium-rich samples and more borax to the carbonate containing samples (McDonald et al. 1994). Most attempts to lower the reagent blank values have aimed at lowering the NiS button weight. Asif and Parry used only 0.35 g or 0.5 g of Ni (Asif & Parry 1989, Asif & Parry 1992). Paukert and Rubeska used a nickel sulfide button in which the amount of Ni was 1.9 g and the amount of S was 1.8 g (Paukert & Rubeška 1993). Frimpong and co-workers have studied the effect of lowering the button size on the recovery of the elements. They found that the recovery of Ir, Os and Au from a komatiite sample did not significantly depend on the mass of the button, whereas Ru, Rh, Pd and Pt recoveries were dependent upon the collector mass (Frimpong et al. 1995).

The nickel sulfide preconcentration has been used extensively since the 1970s as sample pretreatment for neutron activation analysis (Hoffman et al. 1978, Shazali et al. 1987, Asif & Parry 1989) and gained popularity as a preconcentration method for ICP-MS in the end of the 1980s. Paukert and Rubeška (Paukert & Rubeška 1993) have determined all of the PGE with the exception of osmium by GFAAS after the nickel sulfide preconcentration.

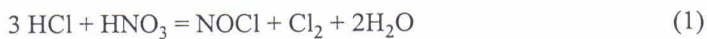


Iron, copper, tellurium and antimony sulfides have been used as alternatives for the nickel sulfide-collection. One disadvantage of iron sulfide is, however, that it is not as easily dissolved in acids as nickel sulfide is. Tellurium sulfide has proven to be less effective than nickel sulfide in collecting the precious metals (Shazali et al. 1987). Antimony sulfide collection is mentioned in the analysis of the new Chinese certified reference samples, the GPt 1-7 series, for the PGE (Yan et al. 1998).

### 2.3.3 Acid digestion

Dissolution of samples by aqua regia leach is commonly used in analytical procedures for gold and for some of the PGE in geochemical exploration. Gold and palladium are extracted from the samples almost quantitatively, whereas recoveries of the other PGE are less complete. Only some PGE minerals, such as stibiopalladinite, metallic platinum and palladium are dissolved in aqua regia. The PGE minerals sperrylite, laurite, cooperite, braggite, iridosmine, osmiridium and platiniridium are insoluble in aqua regia (Gowing & Potts 1991).

Gold is oxidised and dissolved by aqua regia. Both the elemental chlorine and the nitrogen (+III) in nitrosyl chloride, which are formed in aqua regia (1), take part in the overall reaction of oxidation of gold (2) (Šulcek & Povodra 1989a).



Platinum reacts similarly forming the hexachloroplatinate (IV) ion  $[\text{PtCl}_6]^{2-}$ . Palladium forms the hexachloropalladate (IV)  $[\text{PdCl}_6]^{2-}$  and rhodium the hexachlororhodate (III)  $[\text{RhCl}_6]^{3-}$  (Kivinen & Mäkitie 1988). A more efficient acid attack is obtained by adding hydrofluoric acid, which will attack the silicates and release the metals enclosed by the silicates (Terashima 1988).

An even more effective dissolution with aqua regia is obtained at elevated pressure. One such dissolution procedure is the Carius tube method, where a thick-walled Pyrex tube

(Carius tube) is sealed with the sample and acids and heated at 240 °C for 12 hours. One half to one third of the tube is left unfilled as a precaution against the tube bursting. The pressure within the tube rises to about 10 bar (Saikkonen 1999). The Carius tube method has been applied to sample dissolution for age determination based on the Re-Os isotopic system, using sample sizes of 0.1 - 5 g (Shirey & Walker, 1995). Microwave digestion is also used for a more complete digestion of geological materials (Totland et al. 1995). Insoluble residues after acid dissolution of the sample can be fused with sodium peroxide alone or with a combination of sodium peroxide and sodium carbonate (Grote & Kettrup 1987, Totland et al. 1995).

Most recently the use of a high pressure asher has gained popularity. This is a quartz tube into which the sample (0.3 - 0.4 g) and concentrated acids (5 ml HNO<sub>3</sub> and 2 ml HCl) are sealed and heated to 350 °C at 125 bars. Complete dissolution of chromites has been observed (Meisel & Moser 1999).

Dissolution by hydrobromic acid can also be used prior to the determination of gold in geological materials (Meier 1980, Benedetti et al. 1987).

#### 2.3.4 Cyanide leach

The leaching of gold ore with a basic solution of sodium cyanide is widely used in gold production. The process of cyanide extraction of gold from ores was described in a patent in 1840 (Fleming 1998). Oxygen is required for the reaction (3) to proceed. The rate of the reaction is dependent on the amount of oxygen dissolved in the aqueous solution used for extraction, which at 25 °C at sea level is 8.2 mg/l. The corresponding cyanide concentration is 0.002 M CN<sup>-</sup>, equivalent to 0.01 % NaCN. In leaching ore samples, however, there are other elements competing with gold for the cyanide, and for this reason a more concentrated solution of sodium cyanide is usually used. The sulfides, for example, are dissolved and produce metal ions, metal oxides or metal cyanide complexes and various sulfur-containing species, such as thiocyanate, sulfide and thiosulfate ions, as shown by reaction (4). Other factors effecting the rate of reaction are the temperature, pH, surface area of gold particles, agitation of the solution

and the accelerating effect of trace amounts of cations, such as lead, mercury, thallium or bismuth. The pH is kept above 9.4 to prevent loss of cyanide by hydrolysis (Marsden & House 1992b).



The cyanide leach has also been used as an analytical method for the quantitative determination of gold in geological samples. Because of the inhomogenous distribution of gold, the great advantage of this method is that, because of its simplicity, it allows for the use of a sample much larger than is normally possible with other methods. Using FAAS for gold determination, Olson and Simmons found that leaching the samples with a hot cyanide solution gives a precision superior to the fire assay method for siliceous limestone ores. Either sodium cyanide or potassium cyanide could be used (Olson 1965, Simmons 1965). In more developed procedures the cyanide leach is followed by solvent extraction, after which gold is usually determined by GFAAS. For the extraction, Huffman used methyl isobutyl ketone (MIBK). Fletcher and Horsky and Collis et al. used a solution of di-isobutyl ketone with 2 % trioctyl methyl ammonium chloride (Aliquat 336<sup>TM</sup>). Jain et al. claim that treatment of the acidified solution after cyanide leach with HBr and bromine water is necessary to oxidise Au(I) to Au(II) before the MIBK extraction for good recovery of gold. Variations of the cyanide leach method have been used extensively in geochemical exploration in various parts of the world (Huffman et al. 1967, Fletcher & Horsky 1988, Collis et al. 1991, Jain et al. 1987). Detection limits in the ng/g range are obtained.

Sample sizes used in the cyanide leach have been from a few grams to 500 g. The reaction takes place in an open bottle, the size of which is varied according to the sample size. The only reagents required for the gold extraction are a dilute solution of sodium cyanide and a base, such as calcium hydroxide or sodium hydroxide, for adjusting the pH of the solution.



### 2.3.5 Chlorination

The reaction of chlorine with the noble metals has been known since the identification of the metals. Chlorination was used in the 1800s prior to cyanidation in the production of gold and has also been used for the production of the chlorides of gold and the PGE. Van Loon and Barefoot have used dry chlorination as pretreatment for the precious metal determination of various types of sample materials for over 20 years. They recommend the method for various types of complex samples for which a fire assay would not be practical, such as automotive catalysts and precious metal-coated leads of alumina capacitors (Van Loon et al. 1984, Van Loon & Barefoot 1989).

Chlorine reacts with gold and the PGE at about 600 °C producing the following water-soluble chlorides: gold chloride,  $\text{AuCl}_3$ ; palladium chloride,  $\text{PdCl}_2$ ; rhodium trichloride,  $\text{RhCl}_3$ ; and iridium tetrachloride,  $\text{IrCl}_4$ . Platinum chloride  $\text{PtCl}_2$  is soluble in hydrochloric acid. There are two different forms of ruthenium trichloride: the  $\beta$  form is produced upon heating of ruthenium in the presence of  $\text{Cl}_2$  and CO at 370 °C, and the water-insoluble  $\alpha$  form is formed upon chlorination above 450 °C. The aqueous solution of osmium tetrachloride  $\text{OsCl}_4$  is unstable. The volatile osmium dioxide is formed (Van Loon & Barefoot 1991, Cotton & Wilkinson 1988).

Dry chlorination has also been proposed as a sample pretreatment method for the ICP-MS determination of gold and the PGE (Perry & Van Loon 1992, Perry et al. 1993). One advantage of the method is that because small amounts of the reagents — sodium chloride and hydrochloric acid — are used, the reagent blank values are low. Another advantage is the possibility to use a large sample, cit. 25 g and 250 g. Sodium chloride is mixed with the sample before the chlorination to avoid the formation of insoluble chlorides. During the chlorination, metals, alloys and minerals of gold and the PGE are transformed to soluble chlorides. The dry chlorination method is described as follows:

The sample and sodium chloride (0.5 g NaCl / 25 g sample and 1.5 g NaCl / 250 g sample) are placed in a Vycor tube. Both ends of the tube are closed with glass wool plugs, and the tubing for entrance and exit of the chlorine gas are attached. The tube is

placed in a tube furnace, which stands in a fume hood. The flow of chlorine is adjusted and the tube is heated and kept at 580 °C for 3.5 hours. The tube is agitated a few times during the heating. The tube is then allowed to cool down with the flow of chlorine continuing, after which the sample with the glass wool plugs are transferred to a beaker, and the tube is rinsed with 10 % HCl. The solution is warmed, whereby the chlorides are dissolved. The cooled solution is filtered with a cellulose nitrate membrane filter into a volumetric flask, from where it is further diluted for ICP-MS determination.

One disadvantage of the method is that it is not possible to determine osmium because of the instability of osmium tetrachloride in aqueous solution. In addition to the problems involved in working with the poisonous chlorine gas, one of the main difficulties may be the cleaning of the glassware between samples. Based on the experience in many laboratories, the glassware must be boiled in aqua regia after use in order to avoid cross contamination.

### 2.3.6 Sodium peroxide fusion

Fusion with sodium peroxide combined with acid dissolution is known as a method of decomposition for the precious metals. The PGE are oxidized to anions, whose compounds are readily soluble in water or acids (Šulcek and Povodra 1989b). The rock sample is roasted, fused with sodium peroxide and leached with acids. In the method of Boubertlová-Kosinová, the rock sample was sintered with sodium peroxide after which the precious metals were leached with 2 M hydrochloric acid. Platinum and palladium were adsorbed on activated carbon added to the solution, and the elements adsorbed by the carbon were determined directly by optical emission spectrography. Beta and gamma activity measurements of the isotopes  $^{197}\text{Pd}$ ,  $^{109}\text{Pd}$  and  $^{198}\text{Au}$  were also used to study the recovery (Boubertlová-Kosinová 1979). Stone and Crocket describe the determination of Pd, Pt, Ir, Au, Se, As, and Sb in small samples (<400 mg) by neutron activation analysis after sodium peroxide fusion and tellurium coprecipitation. The sample is fused in a nickel crucible with 1 g NaOH and 5 g  $\text{Na}_2\text{O}_2$  (Stone & Crocket 1993). Using ICP-MS determination, Enzweiler and co-workers carried out the sodium



peroxide fusion in a crucible of glassy carbon lined with a layer of sodium carbonate (Enzweiler et al. 1995).

### 2.3.7 Separation and concentration procedures

#### *Ion exchange*

Various ion exchange procedures have been proposed for the concentration and separation of gold and the PGE from the matrix elements after sample dissolution. Determination of Au, Pt and Pd in sulfide ores, concentrates and mattes was carried out with a directly coupled plasma emission spectrometer (DCP) after sample pretreatment by acid extraction, peroxide fusion and sorption and desorption on an ion-exchange resin containing S-bonded dithizone and dehydrodithizone as functional groups (Grote & Kettrup, 1987). Gold at the  $\mu\text{g/g}$  concentration level was determined by FAAS after dissolution of the sample with aqua regia and bromine and separation with Amberlite XAD-7 resin (Rivoldini & Haile 1989).

Jarvis and co-workers (Jarvis et al. 1997) have studied the behaviour of synthetic multielement solutions of the PGE (Ru, Rh, Pd, Ir and Pt) on Dowex 1-X8 anion exchange resin. A solution of thiourea in HCl was used for elution of Ru, Pd, Pt, Au and part of Rh. The remaining Rh and all of the Ir was eluted with 12 M HCl. High levels of total dissolved solids required either dilution of the solution or decomposition of the thiourea prior to ICP-MS determination. The thiourea was decomposed with nitric acid and the sulphate thus formed was removed by precipitation as barium sulphate. This led to low recoveries for all of the elements except Ir. In another study, the same group tried removal of the matrix elements from the sample solution — prepared by a combination of acid dissolution and fusion of the residue with sodium peroxide — by cation-exchange chromatography on AF 50W-X8 prior to analysis by ICP-MS. Good agreement with reference values for reference materials was obtained for Ru, Rh, Pd, Ir. Platinum recoveries were low at 63 - 75 % for the reference sample SARM7, and gold was lost on the ion-exchange resin (Jarvis et al. 1997). For preconcentration of gold, Amberlite XAD-16 resin at pH 2 and elution with KI in methanol has been used (Tunçeli & Türker 1997). A new Chinese anion exchange

resin HHY-10A has given good results in the separation of Au and Pt and made possible their determination by ICP-MS in Chinese reference materials of low concentration levels (0.4 - 6 ng/g) of the elements studied (Li et al. 1997).

Rehkämper and Halliday have combined an ion-exchange procedure with the nickel sulfide fire assay procedure. They first dissolved the NiS button in aqua regia and then loaded the solution onto an anion exchange column (Bio-Rad AG1X8). Two different sequences of elution were used, both employing rising concentrations of HCl and HNO<sub>3</sub> containing 10 % Br<sub>2</sub>. Recoveries for Pd, Ir, and Pt were about 85 - 95 % and for Ru about 70 - 75 %. Gold, rhodium and osmium were not determined. The elements were determined using the new multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS) (Rehkämper & Halliday 1997).

Ion exchange procedures are often used in the analysis of environmental samples with low concentrations of the elements to be determined. In the determination of gold in sea water by ICP-MS, gold has been retained as the cyanide complex on the AG 1-X2 anion resin after which it was eluted with concentrated nitric acid (Bakowska et al. 1989, Falkner & Edmond 1990).

Most recently the sorption of Au and the PGE onto a modified silicagel Separon™ SGX C18 column with cationic surfactant Septonex has been studied (Vlašánková et al. 1999) using samples of airborne particulates. The relative standard deviations of results for real samples were very high, but recoveries for pure solutions of Au, Pd and Pt are 100 % and of Os and Ir from 85 to 90 %.

Concentration on AG 1X-8 anion exchange resin, elution with a mixture of acetone and nitric acid, evaporation and extraction into MIBK has been used as a method of hydrogeochemical exploration for gold (Cidu et al. 1994).

#### *Concentration on activated carbon*

Adsorption on activated carbon as a means of concentrating and isolating the elements Au, Pd and Pt was already used in the 1960s in connection with spectrographic

determination of the elements as mentioned in section 2.3.6. According to Boubertlová-Kosinová, a solution of 2 M hydrochloric acid and 0.2 M Sn(II) chloride is the optimum medium for adsorption of Au and Pd, whereas Pt requires the presence of a neutral chloride such sodium chloride (Boubertlová-Kosinová 1970).

Thiourea solutions have been used as media for the adsorption of gold on activated carbon (Schmidt et al. 1988, Dajun & Guanghui 1992). Peräniemi and co-workers have used adsorption of Au on activated carbon and determination of gold by EDXRF after sulfuric acid/thiourea leaching of the ore sample, achieving detection limits as low as 38 to 45 ng/g (Peräniemi et al. 1992, Peräniemi 1995).

A method for hydrogeochemical exploration for precious metal deposits was developed in Canada in which a 200-fold concentration of the analytes is achieved. Surface water samples of one litre were collected, filtered through a 0.45 µm filter and acidified with 10 ml of concentrated hydrochloric acid. Activated charcoal, 300 mg, was added and the sample was stirred for 1 hour with a magnetic stirrer. The carbon was filtered under vacuum, and the filter paper with the carbon was ashed at 650 °C, after which the residue was leached with aqua regia. The aqua regia was partly evaporated, and the solution was diluted with water. Palladium and platinum were determined using the ICP-MS instrument with sample introduction by nebulization or by electrothermal vaporisation. The detection limits were in the range of 0.3 - 0.8 ng/l. The method has also been used for the determination of Au and Rh.

Lake and stream water samples were collected from various mineralized sites, and the method enabled the identification of dispersion patterns of the elements. Concentrations of the samples were generally below 5 ng/l (Hall & Pelchat 1993).

#### *Concentration by coprecipitation*

Since the beginning of the 1980s, the laboratory of the GTK has used a method of gold analysis for geochemical exploration, which is based on aqua regia leach and mercury coprecipitation of the elements to be analysed and consequent determination by GFAAS.

Along with gold, this method enables the determination of palladium and platinum (Kontas 1981).

*Concentration by organic solvent extraction*

There are a number of procedures for gold determination, which employ extraction into an organic solvent to increase the concentration of the analyte. The use of extraction of gold into an organic solvent after the cyanide leach has been mentioned in section 2.3.4. Many methods use extraction with MIBK after acid digestion of the sample followed by GFAAS determination of gold (Meier 1980, Benedetti et al. 1987, Terashima 1988).



### 3. RESULTS AND DISCUSSION

Analytical methods for the determination of gold and the PGE in rock samples have been developed. The main emphasis of the study is on the preconcentration of the analytes and their separation from interfering elements. Sample preparation and sampling for analysis have also been studied. The results obtained with the different methods were compared by analysing in-house samples and international reference materials.

The following dissolution and/or preconcentration techniques were used for gold:

- (1) lead fire assay
- (2) aqua regia leach/mercury coprecipitation
- (3) sodium cyanide leach

The final determination of gold in all three procedures was by FAAS.

Four dissolution and/or preconcentration techniques were used for the determination of the platinum group elements (PGE):

- (1) lead fire assay for platinum and palladium
- (2) aqua regia leach with mercury coprecipitation for palladium
- (3) nickel sulfide fire assay for all of the PGE
- (4) sodium peroxide fusion for platinum, palladium and rhodium

The final determination of the PGE was either by GFAAS (Pd and Pt) or by ICP-MS.

The problems of sample representativeness and the correct choice of analytical procedure for a specific gold ore were studied by comparing the three methods for gold in a study on six Finnish gold ores.

#### 3.1 The lead fire assay

The lead fire assay procedure has been used at GTK for decades. The fusion flux differs from fluxes used in other laboratories in that in addition to sodium carbonate, it also contains potassium carbonate. The fusion flux has been found effective in the fusion of most types of rock samples. Samples with high sulfide content (over 6 %) are roasted at 600 °C before fusion.

Gravimetric gold determination, which had been traditionally used, was replaced by determination by FAAS. An important aspect was to make the procedure more productive. A dissolution procedure was developed for the final product of the lead fire assay fusion procedure — the silver bead — which contains the gold, platinum and palladium extracted from the sample. In the first dissolution attempts, silver was dissolved with nitric acid and washed out, after which the remaining gold was dissolved in aqua regia, diluted with water and measured by FAAS. Washing out the silver and trying to avoid losses of gold was found to be very tedious and time consuming. For this reason it was decided to dissolve the entire bead in one operation in a graduated test tube. The main problems encountered were overboiling and precipitation of the silver as silver chloride. The overboiling was controlled by slow heating and the precipitation of silver by a sufficiently high concentration of hydrochloric acid. Gold is determined by FAAS atomic absorption and platinum and palladium by GFAAS atomic absorption. The silver present in the solution has not been found to interfere with the determination of any of these three elements.

Before adapting the new method to routine use, comparisons with the gravimetric determination of gold were made, and the method was also tested on reference materials. For routine quality control, a reference sample, as well as a reagent blank, is analysed with every batch of samples. Results of gold, platinum and palladium determinations of reference samples are given in Table 3. In publication I, the revised method is described in detail.

**Table 3**

Results of reference samples by lead fire assay. All determination by GFAAS except the Au results of WG1 by FAAS. n = number of determinations

| Reference sample      | n  | Mean $\pm$ sd<br>$\mu\text{g/g}$ | Reference value*<br>$\mu\text{g/g}$ |
|-----------------------|----|----------------------------------|-------------------------------------|
| SARM 7 (platinum ore) |    |                                  |                                     |
| Au                    | 14 | $0.39 \pm 0.18$                  | $0.31 \pm 0.015$                    |
| Pd                    | 11 | $1.55 \pm 0.11$                  | $1.53 \pm 0.032$                    |
| Pt                    | 11 | $3.46 \pm 0.43$                  | $3.74 \pm 0.045$                    |
| WG1 (gold ore)        |    |                                  |                                     |
| Au                    | 85 | $1.446 \pm 0.0633$               | $1.42 \pm 0.02$                     |
| SU-1a (Ni-Cu-Co ore)  |    |                                  |                                     |
| Pd                    | 13 | $0.379 \pm 0.02$                 | $0.37 \pm 0.03$                     |
| Pt                    | 11 | $0.327 \pm 0.09$                 | $0.41 \pm 0.06$                     |

\*Certificate value of the reference material

SARM7: South African Bureau of Standards

WG1: Rocklabs, Ltd., New Zealand

SU-1a: Canada Centre for Mineral and Energy Technology

Sutarno and Steger recommend using the following inequality for testing whether the result which the laboratory obtains is accurate:

$$|\bar{x} - A_c| < 2 s_{LC}$$

where  $\bar{x}$  is the mean concentration obtained by the laboratory,  $A_c$  the certified or equally well defined concentration, and  $s_{LC}$  is the between laboratory standard deviation of certification or recommendation process. If the inequality is true, the results for the certified reference material do not differ from the certified value by more than can be accounted for by within- and between-laboratory statistical fluctuations (Sutarno & Steger 1985). According to the Sutarno-Steger test, all results of Table 3, with the exception of gold and platinum for the SARM7 reference sample, are accurate.

### 3.2 Nickel sulfide fire assay

Publications II - IV deal with the nickel sulfide preconcentration and ICP-MS determination of gold and the PGE in geological samples. In the nickel sulfide fire assay, as in the lead fire assay procedure, the finely ground rock sample is fused with the fusion reagents at high temperature. Nickel and sulfur are added as collector to the fusion charge in place of the lead. During the fusion, a silicate phase and a sulfide phase are formed. Gold and the PGE are enriched in the sulfide phase of the melt, which falls to the bottom of the crucible forming the button of nickel sulfide upon cooling.

We compared three procedures in practice before making the choice for a routine method to be used in the laboratory. A report of the method comparison is given in Publication II. The chosen procedure was that of Jackson and co-workers (Jackson et al. 1990). According to our results, tellurium coprecipitation improves the recovery of the PGE in addition to improving the recovery of gold. We have observed that covering the crucible during fusion gives a larger nickel sulfide button. Without the cover some of the sulfur is obviously oxidised and is not available for the formation of the nickel sulfide button. The weight difference with or without cover is about 0.5 – 1.0 g. This does not seem to have any effect on the recovery of the analytes.

In both Publications II and III, lowering the reagent blank values was mentioned as an important target for further method development. We have applied the method to

silicate rocks and chromites. There are many references to the difficulties in the nickel sulfide fire assay fusion of chromitite samples. However, the chromitite reference samples, CHR-Pt+ and CHR-Bkg containing 13.91 % and 19.80 % of chromium respectively (Govindaraju 1994a), have produced nickel sulfide buttons of the normal size and a homogeneous silicate slag with our routine method on a 15 g sample. The nickel sulfide fire assay results of the analyses of these two reference samples are given in Table 4. The results agree well with the reference values with the exception of the gold value for sample CHR-Bkg. Our recovery for gold using three independent analytical methods was 29 - 32 %. On the basis of this, we suspect that the sample portion received by our laboratory did not contain 28 ng/g of gold due to sample inhomogeneity.

**Table 4**

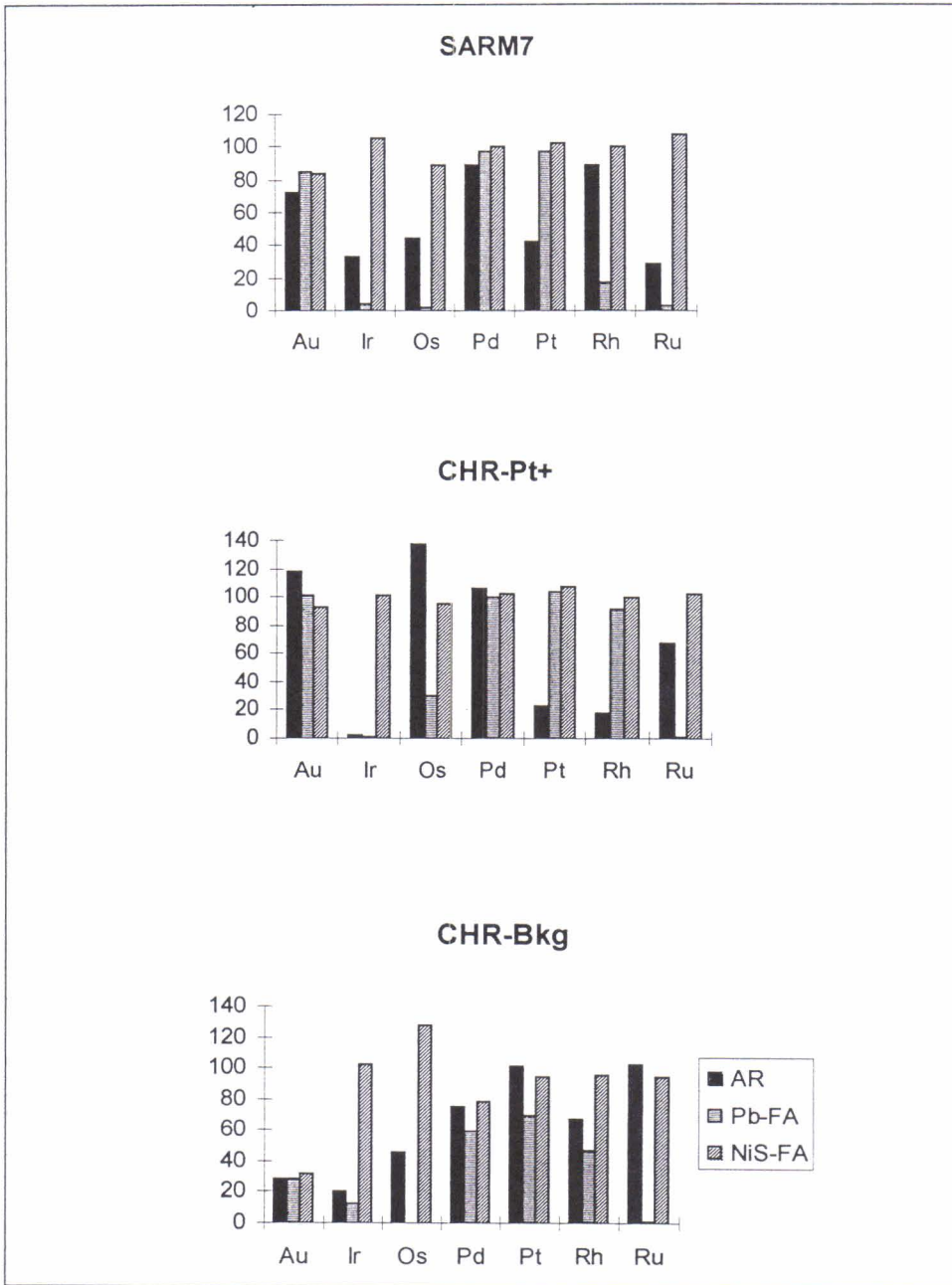
Gold and the PGE results by NiS fire assay /ICP-MS determination for chromitite reference samples CHR-Pt+ and CHR-Bkg. Results are mean values of four determinations.

| Reference sample | Mean of four determinations | Reference value* |
|------------------|-----------------------------|------------------|
| CHR-Pt+          | µg/g                        | µg/g             |
| Au               | 4.0                         | 4.3              |
| Ir               | 6.3                         | 6.2              |
| Os               | 1.8                         | 1.9              |
| Pd               | 82.2                        | 80.8             |
| Pt               | 62.0                        | 58               |
| Rh               | 4.7                         | 4.7              |
| Ru               | 9.4                         | 9.2              |
| CHR-Bkg          | ng/g                        | ng/g             |
| Au               | 9                           | 28               |
| Ir               | 29                          | 28               |
| Os               | 34                          | 27               |
| Pd               | 55                          | 70               |
| Pt               | 47                          | 50               |
| Rh               | 9                           | 9                |
| Ru               | 63                          | 67               |

\* Govindaraju 1994b

In Publication III, a method comparison was made to see which of the PGE could be analysed after a pretreatment method other than NiS fire assay. Gold was also analysed. The recoveries for the reference samples of this comparison are presented in Figure 3. The lead fire assay compares well with the NiS fire assay in the determination of Au, Pd and Pt. The aqua regia leach results for the PGE are dependent on the sample type. Interferences caused by the sample matrix are suspected for causing the high results for rhodium and ruthenium. Reliable results were obtained for gold and palladium.



**Figure 3**

Recovery % of Au and PGE using the sample decomposition and preconcentration methods: aqua regia leach (AR), lead fire assay (Pb-FA) and nickel sulfide fire assay (NiS-FA) before ICP-MS determination for reference samples SARM7, CHR-Pt+ and CHR-Bkg.

We have had difficulties in fusing some rock types, such as black shales and rocks containing high quantities of magnetite. The difficulty being in both cases that the nickel sulfide does not separate completely from the silicate phase. It is often possible to avoid this type of interference by lowering the sample mass, but this will have an effect on the detection limits and the representativeness of the sample. There is limited information available on how the fusion procedure should be varied according to the type of sample fused. Some of our observations are presented in the following sections.

### 3.2.1 Reagent blank and recovery studies

One of the main problems in the nickel sulfide fire assay method is the high concentration level of the reagent blank. In petrological and environmental studies it would be important to be able to determine gold and the PGE below ng/g level. This would require lower detection limits than obtained with our routine method described in Publications II and III. From the beginning, great care has been taken in trying to avoid all possibilities of cross-contamination of samples in the analytical procedure. Glassware has been washed with boiling aqua regia. Spoons and spatulas are reserved especially for this method only.

We have analysed some of the reagents for Au and the PGE in search for the source of the contaminants. The tellurium solution, used for coprecipitation, was analysed by ICP-MS: no detectable amounts of the analytes were found. The Sn(II)chloride and nickel were analysed by GFAAS for gold and palladium: detectable concentrations were not found.

Reagent blanks were prepared using alternative fusion procedures and by making some changes in the routine procedure, in an effort to find a method which would yield lower reagent blank values than the routine method. The modifications to the routine procedure were: (1) the button was dissolved directly in the hydrochloric acid without grinding; (2) filtration by gravity using a glass fibre filter was changed to vacuum filtration by a mixed cellulose acetate and nitrate membrane filter (Millipore HA 0.45  $\mu\text{m}$ ); (3) the final solution was made up with Suprapur™ acids; (4) the fusion reagents were reserved for this procedure only and not used in the lead fire assay procedure as previously; (5) the amount of HCl for dissolving the NiS button was lowered from 600 ml to 400 ml. This modified routine method is Method A' in Tables 5 and 6, where Method A is the routine method.

The other procedures (B-C) tested use less reagents than the routine method. The composition of the fusion charge of each method and the amount of HCl used for dissolution of the NiS button are summarised in Table 5. The reagent blanks were prepared by mixing all of the fusion reagents in the fusion crucible and fusing according to the method, but without sample or sample substitute. All results are calculated as if there had been the amount of sample indicated for each method in Table 5.

**Table 5**

Reagents used in variations of the NiS fire assay method. Method A is the routine method of the GTK laboratory. Method A' is the routine method with alterations described in the text. In Method B, the Ni and S amounts are half of those of Method A. Method C is the method of Paukert and Rubeška, and Methods D and E are of Asif and Parry.

|   | A   | A'  | B   | C   | D    | E    |
|---|-----|-----|-----|-----|------|------|
| Sample, g   | 15  | 15  | 15  | 20  | 25   | 25   |
| Na <sub>2</sub> CO <sub>3</sub> , g               | 10  | 10  | 10  | 12  | 10   | 10   |
| Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , g | 20  | 20  | 20  | 24  | -    | -    |
| Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , g | -   | -   | -   | -   | 20   | 20   |
| SiO <sub>2</sub> , g                              | 5   | 5   | 5   | -   | 2    | 2    |
| Ni, g   | 5.0 | 5.0 | 2.5 | 1.9 | 0.5  | 1.0  |
| S, g  | 3.0 | 3.0 | 1.5 | 1.8 | 0.35 | 0.70 |
| HCl, ml   | 600 | 400 | 150 | 50  | 50   | 50   |

**Table 6**

Reagent blank values for Au and the PGE in ng/g using different variations of the nickel sulfide preconcentration method and ICP-MS determination.

|    | Method A     | Method A' | Method B | Method C | Method D | Method E |
|----|--------------|-----------|----------|----------|----------|----------|
|    | Min-max      | n = 3     | n = 2    | n = 2    | n = 2    | n = 2    |
|    | n = 80       |           |          |          |          |          |
| Au | 0.686-3.998  | 0.228     | 0.664    | 0.891    | 0.307    | 0.695    |
| Ir | 0.024-0.514  | 0.043     | 0.0485   | 0.0125   | 0.028    | 0.103    |
| Os | 0.186-3.075  | 0.000     | 2.85     | 0.630    | 1.89     | 1.26     |
| Pd | 0.342-8.390  | 0.119     | 3.00     | 3.38     | 6.92     | 5.76     |
| Pt | 0.054-1.224  | 0.101     | 0.064    | 0.032    | 0.45     | 0.134    |
| Rh | 0.0057-0.134 | 0.000     | 0.038    | 0.043    | 0.380    | 0.156    |
| Ru | 0.0879-1.082 | 0.065     | 0.533    | 0.543    | 3.14     | 1.88     |

The results of the ICP-MS determinations of the reagent blank samples are presented in Table 6. The values for the modified routine method, Method A', are much lower than the

the mean values given in Publication III. With a few exceptions, Method A' gives the lowest reagent blank values. The acids are commonly suspected of causing a major part of the blank problem. However, if HCl were a major cause of the high reagent blank values, there should be a clear difference between Method A and Methods B - E, but this is not the case. Variation of the amounts of nickel and sulfur also does not give a significant difference in the blank values. Reference sample SARM 7 and real rock samples were also analysed by the five procedures. Results for SARM 7 are presented in Table 7. Lowering the amounts of nickel and sulfur to one half of the routine method lowered the recoveries significantly (Method B). The original method of Paukert and Rubeška (Paukert and Rubeška 1993) was modified by adding tellurium coprecipitation to improve the recovery of gold. The gold result is low. The results for gold, however, have had a tendency to vary, and this is suspected of being caused by inhomogeneity of the sample with respect to gold (Kontas 1999). Comparing results of real samples at 10 – 100 ng/g concentration level gave lower recoveries with Method C than Method A.

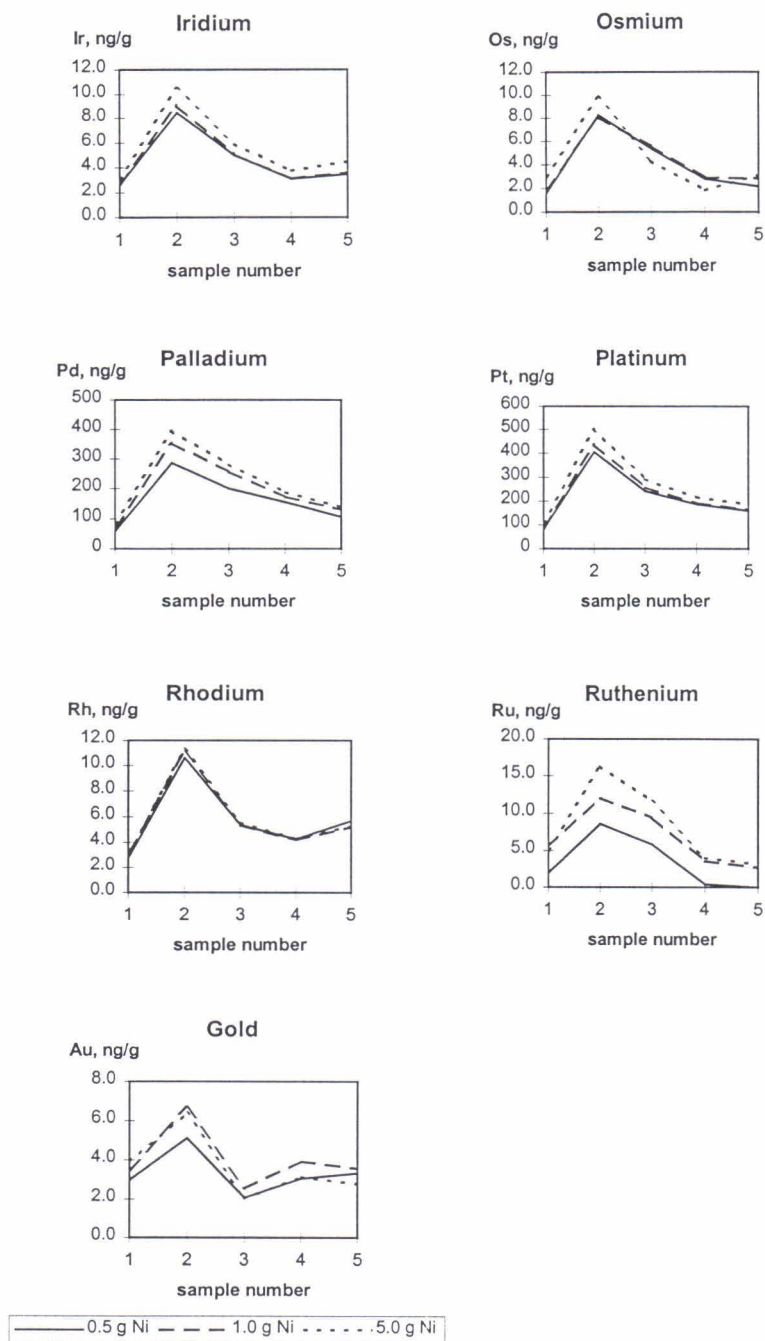
**Table 7**

Results for reference sample SARM 7, µg/g, by ICP-MS determination of solutions prepared by five different fusion procedures.

|    | Method A          | Method B | Method C | Method D | Method E | Reference value    |
|----|-------------------|----------|----------|----------|----------|--------------------|
|    | mean $\pm$ SD     |          |          |          |          |                    |
|    | n = 148           |          |          |          |          |                    |
| Au | 0.256 $\pm$ 0.035 | 0.12     | 0.18     | 0.35     | 0.27     | 0.31 $\pm$ 0.015   |
| Ir | 0.080 $\pm$ 0.005 | 0.039    | 0.087    | 0.079    | 0.085    | 0.074 $\pm$ 0.012  |
| Os | 0.065 $\pm$ 0.016 | 0.057    | 0.053    | 0.105    | 0.111    | 0.063 $\pm$ 0.0068 |
| Pd | 1.46 $\pm$ 0.078  | 0.64     | 1.55     | 1.62     | 1.63     | 1.53 $\pm$ 0.032   |
| Pt | 3.82 $\pm$ 0.229  | 1.62     | 4.28     | 3.65     | 4.21     | 3.74 $\pm$ 0.045   |
| Rh | 0.23 $\pm$ 0.012  | 0.10     | 0.27     | 0.27     | 0.27     | 0.24 $\pm$ 0.013   |
| Ru | 0.46 $\pm$ 0.044  | 0.21     | 0.55     | 0.50     | 0.54     | 0.43 $\pm$ 0.057   |

Asif and Parry recommend a very small nickel sulfide button (< 1 g). In Methods D and E their procedure was studied. Good recoveries were obtained for reference sample SARM 7, as can be seen in Table 7. However, for real samples of lower concentration range than the SARM 7 sample results for the PGE were systematically lower by Methods D and E than by the routine method. Results for real samples by the three methods are given in Figure 4.





**Figure 4.** Analysis of five samples for gold and the PGE using the routine method (5 g Ni) and the Asif-Parry methods with 0.5 g Ni and 1.0 g Ni.

During the course of about 3 years, the SARM7 sample has been analysed with every batch of samples for gold and the PGE. It was the only PGE reference sample available until recently. A reference sample of lower PGE content would have been preferable. Data on 164 analyses has thus been collected. A 5 g sample size was used. The distribution of the analytical results is not normal for any of the elements. It is therefore difficult to treat the outliers. The results were sorted into rising order, and 5 % of the results from both extremes were cut off before calculating the mean and the standard deviation which are presented in Table 7. According to the accuracy test of Sutarno and Steger (3.1), with the exception gold and palladium, the results for all the elements are accurate. The SARM7 reference material was supplied to the laboratory in containers of 3 kg. According to the supplier, inhomogeneity occurs for gold when samples of 1 g or less are used. It is possible, however, that the inhomogeneity of the sample increases during shipment and upon standing. The sample has not been rehomogenized in the laboratory.

### 3.2.2 Fusion of black shale samples

The problems encountered in the nickel sulfide fire assay procedure with black shale samples are discussed in Publication IV. During fusion of this type of a rock sample, the sulfide and the silicate phases do not always separate clearly. Depending on the sample, the fusion sometimes results in a number of small nickel sulfide pebbles and sometimes an inhomogeneous slag is formed. It is impossible to follow the routine method for these samples. The high graphite content of the black shales seems to interfere with the formation of the nickel sulfide button. Roasting of the sample prior to fusion helped to overcome the problem. Roasting, however, was considered tedious and as shown in Publication IV, losses of certain elements, such as osmium and ruthenium occur. An alternative to roasting was therefore sought. Potassium nitrate is used in lead fire assay as an oxidant for samples containing sulfides. In this study, it was considered as a possible oxidant for the graphite in black shale samples.

Four reagent blanks were prepared, using one fifth of the fusion reagents of Method A (Table 5). As in the previous section, the fusion charge was prepared by mixing all of

the fusion reagents in the fusion crucible without a sample or a sample substitute. Graphite and potassium nitrate were added to the reagent blank samples according to Table 8. The graphite was added to cause a similar interference as occurs with the black shale samples and the potassium nitrate to overcome this interference. The graphite was obtained from a graphite electrode (Ringsdorff, Spectralkohlen). The greatest mass for the nickel sulfide button was obtained using the ratio of 6:1 for potassium nitrate to graphite. Real samples of black shale with known contents of noncarbonate carbon were fused with potassium nitrate added to the fusion charge of the routine method. Results on the nickel sulfide button formation are given in Table 9.

**Table 8**

The effect of graphite and potassium nitrate on the nickel sulfide button formation. Varying the ratio of graphite to potassium nitrate varies the size of the button.

|   | S, g | Ni, g | C, g | KNO <sub>3</sub> , g | KNO <sub>3</sub> /C | Mass of NiS button, g |
|---|------|-------|------|----------------------|---------------------|-----------------------|
| 1 | 0.6  | 1.0   | 0.2  | 1.0                  | 5                   | 0.946                 |
| 2 | 0.6  | 1.0   | 0.1  | 0.6                  | 6                   | 0.991                 |
| 3 | 0.6  | 1.0   | 0.2  | 2.0                  | 10                  | 0.735                 |
| 4 | 0.6  | 1.0   | 0.1  | 1.5                  | 15                  | 0.524                 |

**Table 9**

Formation of the nickel sulfide button in black shale samples of known graphite content with potassium nitrate added as oxidant. A 15 g sample is used.

| Sample | C, %  | KNO <sub>3</sub> , g | KNO <sub>3</sub> /C | Mass of NiS button, g |
|--------|-------|----------------------|---------------------|-----------------------|
| 503    | 7.19  | 6.5                  | 6.0                 | no button             |
| 504    | 5.82  | 5.5                  | 6.3                 | 7.4                   |
| 505    | 9.53  | 9.0                  | 6.3                 | 7.3                   |
| 507    | 6.97  | 6.5                  | 6.2                 | 7.2                   |
| 508    | 4.59  | 4.5                  | 6.5                 | 7.3                   |
| 228    | 16.2  | 17.0                 | 7.0                 | no button             |
| 233    | 13.50 | 14.0                 | 6.9                 | no button             |
| 238    | 12.3  | 13.0                 | 7.0                 | small button          |
| 262    | 11.1  | 12.0                 | 7.2                 | no button             |
| 1384   | 4.33  | 3.9                  | 6.0                 | 7.1                   |
| 1402   | 4.9   | 4.4                  | 6.0                 | 7.4                   |

According to the results obtained in Publication IV, the ratio of the masses of KNO<sub>3</sub> to graphite between 5:1 and 8:1 produced good nickel sulfide buttons. When the ratio was

above 8:1, poor fusions clearly resulted. When the ratio was below 4:1, the button size decreased. It seems on the basis of these studies that the ratio of potassium nitrate to noncarbonate carbon in the sample should be between 6 and 8. Results with the real samples, however, are not completely consistent. Roasting of the sample prior to fusion, instead of the potassium nitrate addition, remains an alternative when osmium and ruthenium are not to be determined.

### 3.2.3 Fusion of samples with high magnetite content

Besides the black shales there are other types of samples, for which the routine nickel sulfide fire assay procedure is not suitable. The product of the fusion is an inhomogeneous slag as with the black shales. One such sample was found to contain large amounts of magnetite,  $\text{Fe}_3\text{O}_4$  (Hanski 1997).

About 1 kg of a magnetite rock was homogenised for studying the behaviour of this sample type upon fusion. Upon fusion according to the routine procedure, the button weight was only 4.5 g (normally 6.8 - 7.0 g), and there were numerous pebbles of NiS dispersed in the inhomogeneous slag. The fusion flux was altered in three different ways in an attempt to obtain a homogeneous slag and a nickel sulfide button of normal size. Since magnetite contains more oxygen than most other minerals, this rock differs from the average rock composition with respect to its high oxygen content. The first idea was to add a reducing agent and see if this would help in the fusion. Another thought was that the high viscosity of the flux may inhibit the nickel sulfide pebbles from settling to the bottom of the crucible and forming one single button. The flux was altered by adding calcium fluoride, which is known to make the melt less viscous and in this way facilitate the separation of the two phases. The third alternative to the routine fusion procedure was based on the idea that adding more sulfur would help to separate the iron from the slag as iron sulfide.

From the results of Table 10 it can be seen that addition of a reducing agent does improve the result. The size of the button increases systematically as the amount of reducing agent, either potassium tartrate or wheat flour, is increased. The addition of sulfur also brings about the expected result, where the button size is greatly increased



because of the formation of iron sulfide. The Ni-Fe-S-button was analysed and found to contain 23.9 % Fe, 28.9 % Ni and 31.7 % S. From the fact that both the addition of a reducing agent and the addition of sulfur helped in producing the nickel sulfide button, it could be concluded that the reason for the difficulty in formation of the nickel sulfide button may be the oxidation of the sulfur, because both additions provided more sulfur into the melt. The addition of calcium fluoride did not bring about the expected result. The button was small and numerous small pebbles of nickel sulfide were dispersed in the slag. The NiS buttons of Table 10 were analysed for Au and the PGE and it was found that their concentrations were very low.

Since the additions of either potassium tartrate or sulfur helped in producing the nickel sulfide button, the study was continued by checking their effect on the recovery of gold and the PGE. The test sample containing magnetite and low concentrations of Au and the PGE was spiked by mixing it with reference sample SARM7. Samples containing 1 %, 5 % and 10 % (w/w) of the reference sample were prepared according to Table 11, where also the results of ICP-MS determination of the elements are presented. From the results of Table 11 it can be seen that the recovery is not clearly dependent on the composition of the fusion flux. In general, all of the recoveries were low.

**Table 10**

Additives in the NiS fire assay fusion charge of a magnetite sample and their effect on the weight of the NiS button. A 15 g sample was used. Other reagents used in the fusion are: 5g nickel, 3 g sulfur, 10 g sodium carbonate, 20 g sodium tetraborate, 5 g quartz.

|    | Addition to the fusion flux | Weight of NiS button, g |
|----|-----------------------------|-------------------------|
| 1  | 0.5 g potassium tartrate    | 5.3                     |
| 2  | 1.0 g potassium tartrate    | 5.6                     |
| 3  | 1.5 g potassium tartrate    | 5.6                     |
| 4  | 2.0 g potassium tartrate    | 6.0                     |
| 5  | 3.0 g potassium tartrate    | 6.3                     |
| 6  | 4.0 g potassium tartrate    | 7.0                     |
| 7  | 1.0 g flour                 | 5.5                     |
| 8  | 5.0 g flour                 | 6.8                     |
| 9  | 3.0 g S                     | 10.0                    |
| 10 | 5.0 g S                     | 12.4                    |
| 11 | 1.5 g CaF                   | 5.8 + numerous pebbles  |

**Table 11**

The results of ICP-MS determination of the reagent blank samples, the magnetite sample and the magnetite sample spiked with reference sample SARM7. The NiS fusion of the sample was altered by adding 1.5 g of potassium tartrate, 4.5 g of potassium tartrate or 3 g of sulfur.

|                         | NiS<br>Button<br>Weight, g | Au<br>ng/g | Ir<br>ng/g | Os<br>ng/g | Pd<br>ng/g | Pt<br>ng/g | Rh<br>ng/g | Ru<br>ng/g |
|-------------------------|----------------------------|------------|------------|------------|------------|------------|------------|------------|
| <b>Magnetite sample</b> |                            |            |            |            |            |            |            |            |
| 1.5 g tartrate          | 6.1                        | 5.56       | 0.121      | 0.000      | 0.159      | 0.203      | 0.006      | 0.045      |
| 4.5 g tartrate          | 7.3                        | 4.38       | 0.036      | 0.000      | 0.108      | 0.079      | 0.002      | 0.071      |
| 3 g S                   | 10.0                       | 5.51       | 0.126      | 0.008      | 0.162      | 0.206      | 0.005      | 0.046      |
| Mean                    |                            | 5.15       | 0.094      | 0.003      | 0.143      | 0.163      | 0.005      | 0.054      |
| <b>SARM7 1 %</b>        |                            |            |            |            |            |            |            |            |
| 1.5 g tartrate          | 5.9                        | 19.4       | 0.55       | 0.58       | 10.7       | 17.2       | 1.6        | 4.0        |
| 4.5 g tartrate          | 6.9                        | 6.74       | 0.53       | 0.31       | 11.9       | 14.1       | 1.8        | 3.1        |
| Expected value*         |                            | 3.1        | 0.74       | 0.63       | 15.3       | 37.4       | 2.4        | 4.3        |
| <b>SARM7 5 %</b>        |                            |            |            |            |            |            |            |            |
| 1.5 g tartrate          | 5.6                        | 12.48      | 2.81       | 1.98       | 56.4       | 69.4       | 8.9        | 19.4       |
| 4.5 g tartrate          | 7.5                        | 15.60      | 3.81       | 2.74       | 64.3       | 121        | 11.1       | 17.6       |
| 3 g S                   | 9.7                        | 28.45      | 2.74       | 1.80       | 64.3       | 160        | 9.5        | 16.6       |
| Expected value*         |                            | 15.5       | 3.7        | 3.15       | 76.5       | 187        | 12.0       | 21.5       |
| <b>SARM 7 10 %</b>      |                            |            |            |            |            |            |            |            |
| 1.5 g tartrate          | 5.0                        | 13.19      | 4.98       | 2.96       | 94.9       | 131.6      | 14.87      | 28.05      |
| 4.5 g tartrate          | 5.6                        | 18.17      | 5.79       | 4.44       | 127        | 214.4      | 20.05      | 31.41      |
| 3 g S                   | 9.4                        | 22.94      | 6.13       | 4.40       | 157        | 259.1      | 20.44      | 37.25      |
| Expected value*         |                            | 31.0       | 7.40       | 6.30       | 153        | 374        | 24.0       | 43.0       |

\*Expected value is calculated on the basis of the certificate values for SARM7 given in Table 6.

### 3.3 The sodium cyanide leach

The method of sodium cyanide leach followed by the FAAS determination of gold is described in Publication V. It is a simple method for gold determination and applicable to various types of ores. Its major advantage is the possibility of using a large sample — samples from 500 g to 1000 g are normally analysed, but even larger samples can be treated. The major disadvantage of the method is the inability of the cyanide solution to extract gold from enclosures within silicate or sulfide minerals.

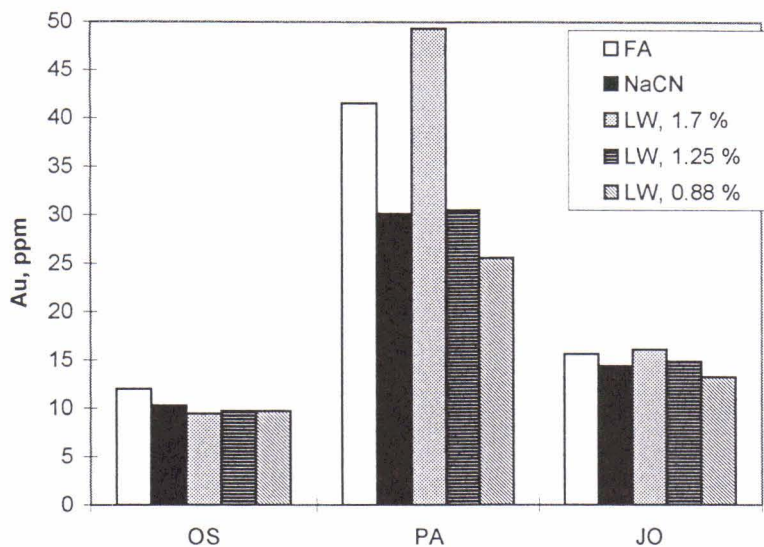
The required reaction time and optimum concentration of the cyanide solution depend on the type of ore being treated. In our studies we have exclusively used a 0.3 % NaCN solution and a reaction time of 24 hours. This has been sufficient for the ores studied,

but a much lower concentration of NaCN and a shorter reaction time may also be adequate for some types of samples (Section 2.3.4). The rate of gold extraction was studied with five samples of the Pampalo ore. After 30 minutes, from 34 % to 61 % of the gold was extracted, after 10 hours 67 % to 81 % was extracted, and after 24 hours 96 % to 98 % was extracted. Silver and copper were also extracted, but the recoveries for these elements were much lower.

In a modification of the NaCN leach procedure, an oxidant, the Leachwell™ patented reagent was added to the cyanide solution. This reagent allows for the reaction vessel to be closed during the reaction, contrary to the simple sodium cyanide leach, described in Publication V, where the oxygen needed for the reaction is supplied by the surrounding air. The reaction time can be considerably shortened by the use of this reagent. The oxidant used in the patented reagent is not known, but it was found to contain soluble lead, which is known to speed up the cyanidation reaction (2.3.4).

We compared fire assay and simple NaCN leach with the accelerated NaCN leach, using samples of the same gold ores which were used in Publication V. The reaction time was kept constant at three hours, for which the recommended NaCN concentration is 1.7 % (w/v) and Leachwell concentration is 0.72 % (w/v). Leaching at lower than the recommended concentrations — 1.25 % and 0.88 % NaCN — was also carried out to see how this would effect the recovery of gold. The ratio of NaCN to Leachwell™ was kept at the recommended 2.5 : 1 ratio.

Recoveries using the accelerated leach in closed vessels appear similar to the simple NaCN leach in open vessels. Inhomogeneity of the samples with respect to gold makes it difficult to draw conclusions on the effect of lowering the reagent concentrations from the recommended level. The results are given in Fig. 5.



**Figure 5**

Comparison of gold results by fire assay (FA) and 0.3 % NaCN leach (NaCN) with 1.7 % NaCN + 0.72 % Leachwell (LW, 1.7 %), 1.25 % NaCN + 0.5 % Leachwell (LW, 1.25 %) and 0.88 % NaCN + 0.35 % Leachwell (LW, 0.88%). The samples are Finnish gold ores: OS (Osikonmäki), PA (Pahtavaara) and JO (Jokisivu). Reaction time with Leachwell reagent was 3 h for all three concentrations.

### 3.4 The sodium peroxide fusion

Sodium peroxide fusion was used in sample dissolution prior to ICP-MS determination of palladium, platinum and rhodium in automotive catalysts. The method was tested on two certified reference materials. Because lead is also a certified element in these reference materials, it was also determined. Sodium peroxide fusion was performed in zirconium crucibles on a flame of a Bunsen burner, using a 0.1 g sample weight and about 1.0 g of sodium peroxide. After the fusion, the solutions for ICP-MS determination were prepared by dissolving the melts in diluted hydrochloric acid and transferring them into volumetric flasks. The results of the ICP-MS determination given in Table 12 indicate that good recoveries (94 - >100 %) are obtained with this method for the three PGE. Preparation of the same samples by aqua regia digestion resulted in low recoveries.



**Table 12**

Results obtained for reference samples of automotive catalysts with the sodium peroxide fusion/ICP-MS determination.

| Reference sample | Rh<br>mg/kg | Pd<br>mg/kg | Pt<br>mg/kg | Pb<br>mg/kg |
|------------------|-------------|-------------|-------------|-------------|
| NIST2556*        | 49.0        | 307         | 711         | 5989        |
| Reference value  | 51.2 ± 0.5  | 326 ± 1.6   | 697.4 ± 2.3 | 6228 ± 49   |
| NIST2557**       | 134         | 230         | 1182        | 12871       |
| Reference value  | 135.1 ± 1.9 | 233.2 ± 1.9 | 1131 ± 11   | 13931 ± 97  |

\*used auto catalyst (pellets), Standard Reference Material 2556 National Institute of Standards and Technology, USA.

\*\*used auto catalyst (monolith), Standard Reference Material 2557 National Institute of Standards and Technology, USA.

### 3.5 Observations on sampling for gold determination

The problem of the inhomogeneous distribution of gold in geological samples was studied in Publication V. In weighing the samples for analysis, each of the six pulverised gold ore samples (about 3 kg) were emptied onto a sheet of hard-surfaced paper (about 40 x 60 cm<sup>2</sup>). The sample was spread evenly on the paper, and opposite corners of the paper were lifted causing the sample to roll over. The sample was spread again, and again opposite corners were lifted. This was repeated several times. Finally the sample was spread evenly on the paper and lines were drawn through the sample with a spatula forming about 20 - 24 squares. When weighing for analysis, sample material was taken evenly from each square so that the analysed sample would be as homogenous as possible.

The separation of gold after pulverisation was found to be especially pronounced with the Pampalo ore sample, which had a high gold content. The sample had been homogenised after grinding, as described above, and analysed for gold by the three methods — fire assay, aqua regia leach and sodium cyanide leach. The gold results of five replicates of the sample by the three methods were all over 300 ppm. The sample was then stored in the laboratory in a 5-litre plastic container for a few months, after which it was re-analysed using the sodium cyanide leach method. For the repetitions, the sample was weighed directly from the container without spreading it on the paper.

The five repetitions of the Pampalo sample gave results close to 100 ppm gold, indicating that although the weighing had been done with great care by spooning sample from all parts of the container, the gold had settled to the bottom of the container, and it was not possible to get a homogenous sample.

The possibility of separation of gold to the bottom of the container must always be kept in mind, although the problem is seldom as severe as was observed here. The methods of sampling, sample preparation and analysis should be chosen individually for each ore type to achieve the best possible results with least effort, as is pointed out in Publication V.

#### 4. CONCLUSION

It was shown by studying sampling and comparing methods of gold determination using six Finnish gold ore samples that for some ores a small sample size may be representative, and sample pre-treatment by a method other than lead fire assay, such as the aqua regia leach or sodium cyanide leach, can give good recoveries.

A method for gold, palladium and platinum determination by lead fire assay with AAS finish was developed. The silver bead obtained after cupellation was dissolved by aqua regia, and gold was determined by FAAS, palladium and platinum by GFAAS. Results for reference samples are in good agreement with the reference values.

Gold and the six platinum group elements were determined by ICP-MS after preconcentration by NiS fire assay. Three versions of the NiS fire assay method were compared using previously analysed samples and reference sample SARM7 for evaluating the accuracy and precision of the results. All three fusion procedures were found to give good recoveries for the elements analysed. Tellurium coprecipitation improved recoveries for gold and possibly also for the PGE. Some advances were made in the lowering of reagent blank values and thereby the detection limits for the analytes. Great care is required throughout the procedure to avoid contamination of the sample solutions. In refining the procedure, we found that filtration of the PGE sulfides by a membrane filter gives the best results, however, it is still difficult to name the main cause of the high reagent blank values. Some solutions were found to overcome the difficulties encountered in the fusion of black shale and magnetite-containing rock samples. Adding an oxidant to the fusion flux for black shale samples and a reducing agent for magnetite-containing rock samples was found to improve the formation of the NiS button.

In a comparison of sample pretreatment by NiS fire assay, lead fire assay and aqua regia leach, it was found that both fire assay procedures give equivalent values for Au, Pd and Pt for the reference samples. The results by the aqua regia leach for the PGE are variable and depend on the rock type of the sample.

For gold analysis in geological samples, the lead fire assay with an instrumental finish, most often FAAS, will hold its place as the method of choice when the determination of total gold content is required. The leaching procedures, aqua regia or sodium cyanide, remain good alternatives for the fire assay, often giving equivalent recoveries. Sampling for gold and PGE analysis requires great care because these elements and their minerals are often unevenly distributed in geological samples and because, after homogenisation, separation easily occurs due to the heavy weight of the particles.

The ICP-MS instrumental detection limits are extremely low, allowing for determination of the elements at lower concentration levels than has been possible before. This has set new demands for the procedures which come before the instrumental measurement: sampling, sample decomposition and preconcentration. Work will continue in refining these procedures.

The ideal method for gold and PGE analysis would be one which uses small amounts of easily purified reagents and reaction vessels which could be easily cleaned. The methods employing sample digestion by acids in closed vessels under pressure are promising in this respect.

Much work has been done in various laboratories on ion exchange separations of gold and the PGE from the matrix elements in order to obtain solutions with less interferences on the analytes during instrumental determination and consequently lower detection limits. So far, success has been quite limited. Only some of the elements have been separated, recoveries are generally poor for real samples, and the procedures are extremely complicated leading to losses of analytes and contamination.

The nickel sulfide fire assay is at present the only known method for the concentration and separation of gold and all of the PGE from rock samples, and ICP-MS is the instrumental technique of choice for their determination. The routine procedures used in many laboratories are not applicable to all types of rock samples. The study on which is the correct fusion flux for a particular rock type still requires much more investigation.



Through increasing use of gold and the PGE in consumer products, such as the automotive catalysts, recycling becomes of increasing importance in the production of these metals, and analytical methods for various types of materials will be needed. There will also be an increase in the burden of these elements on the environment, and already there is growing concern over the possible toxicity of these elements and their enrichment in the food chain. Analytical methods for environmental monitoring of gold and the PGE must be further developed in the near future.

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