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***Nuclear analytical methods for  
platinum group elements***



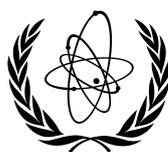
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## FOREWORD

Platinum group elements (PGE) are of special interest for analytical research due to their economic importance — chemical peculiarities as catalysts, medical applications as anti-cancer drugs, and possible environmental detrimental impact as exhaust from automobile catalyzers. Natural levels of PGE are so low in concentration that most of the current analytical techniques approach their limit of detection capacity. In addition, Ru, Rh, Pd, Re, Os, Ir, and Pt analyses still constitute a challenge in accuracy and precision of quantification in natural matrices. Nuclear analytical techniques, such as neutron activation analysis, X ray fluorescence, or proton-induced X ray emission (PIXE), which are generally considered as reference methods for many analytical problems, are useful as well. However, due to methodological restrictions, they can, in most cases, only be applied after pre-concentration and under special irradiation conditions.

This report was prepared following a coordinated research project and a consultants meeting addressing the subject from different viewpoints. The experts involved suggested to discuss the issue according to the (1) application, hence, the concentration levels encountered, and (2) method applied for analysis.

Each of the different fields of application needs special consideration for sample preparation, PGE pre-concentration, and determination. Additionally, each analytical method requires special attention regarding the sensitivity and sample type. Quality assurance/quality control aspects are considered towards the end of the report.

It is intended to provide the reader of this publication with state-of-the-art information on the various aspects of PGE analysis and to advise which technique might be most suitable for a particular analytical problem related to platinum group elements. In particular, many case studies described in detail from the authors' laboratory experience might help to decide which way to go. As in many cases nuclear techniques might not be available or might not be sufficiently sensitive, other non-nuclear techniques, such as atomic absorption spectrophotometer (AAS), voltammetry or inductively coupled plasma mass spectrometry (ICP-MS) are also included in the discussion. The complexity of the problem requires full exploitation of the analytical armoury to obtain reliable and accurate results.

The IAEA wishes to thank all the consultants for their valuable contributions. The IAEA officer responsible for this publication was M. Rossbach of the Division of Physical and Chemical Sciences.

## *EDITORIAL NOTE*

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## CONTENTS

1. INTRODUCTION .....	1
1.1. Definition and properties .....	1
1.2. Sources, production, uses and recycling .....	1
1.3. Economic impact .....	2
2. FIELDS OF APPLICATIONS AND RELATED ANALYTICAL APPROACHES .....	3
2.1. Geological samples .....	3
2.1.1. Case one: Mineral exploration .....	3
2.1.2. Case two: Analysis during extraction and production .....	4
2.1.3. Case three: Geochemical studies .....	4
2.2. Occupational exposure and medical applications .....	5
2.2.1. The use of urine for biomonitoring .....	5
2.2.2. Case one: Medical exposure .....	6
2.2.3. Case two: Occupational exposure .....	7
2.2.4. Case three: Uptake by humans due to dental PGE alloys and drug contamination .....	8
2.2.5. Case four: Background concentrations .....	8
2.3. Environmental monitoring .....	8
2.3.1. Case one: Road dust .....	9
2.3.2. Case two: Airborne particulate matter .....	11
2.3.3. Case three: Monitoring of water .....	12
2.3.4. Case four: Biological samples .....	13
2.3.5. Case five: Sludge and incineration monitoring .....	14
3. ANALYTICAL METHODOLOGY .....	14
3.1. Sample pretreatment .....	14
3.1.1. Digestion techniques .....	14
3.1.2. Separation and pre-concentration techniques .....	17
3.1.3. Fire assay .....	23
3.2. Analytical methods for PGE determination .....	25
3.2.1. Gravimetry, volumetry, UV/VIS absorption spectrometry .....	25
3.2.2. ICP-AES .....	26
3.2.3. Atomic absorption spectrometry .....	26
3.2.4. XRF analysis .....	28
3.2.5. Inductively coupled plasma-mass spectrometry .....	29
3.2.6. Electro-analytical techniques .....	33
3.2.7. Neutron activation analysis .....	34
3.3. Case studies/special applications .....	35
3.3.1. Determination of PGE in precious metal materials by means of ICP-AES .....	35
3.3.2. Pd concentration in Hg for TR-XRF-analysis .....	37
3.3.3. occupationally exposed personnel .....	38
3.3.4. Road dust .....	39
3.3.5. Ore analysis by fire assay and NAA .....	40

4. QA/QC AND REFERENCE MATERIALS .....	40
4.1. Reporting analytical results.....	40
4.2. Selection and application of reference materials .....	41
4.2.1. List of reference materials.....	41
4.3. Other tools for testing the accuracy of analytical results .....	46
4.3.1. Inter-method comparison .....	46
4.3.2. Proficiency testing (PT) .....	46
REFERENCES .....	49
CONTRIBUTORS TO DRAFTING AND REVIEW .....	53

## 1. INTRODUCTION

As a result of the rapid development of technology in recent years, platinum group elements (PGE) have gained tremendous importance, particularly because of their catalytic properties.

### 1.1. Definition and properties

PGE include iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh) and ruthenium (Ru). With an abundance of around  $10^{-6}$  to  $10^{-7}\%$  in the earth's crust, these noble metals belong to the rare elements. PGE can occur in various oxidation states and exhibit properties of typical transition metals such as catalytic effects, the tendency to form complexes and coloured compounds. The density of PGE is about  $12 \text{ g/cm}^3$  for the so-called light PGE: Ru, Rh, Pd and around  $22 \text{ g/cm}^3$  for the heavy PGE: Os, Ir, Pt. Noteworthy are the high melting points (ranging from  $1554 \text{ }^\circ\text{C}$  to  $3045 \text{ }^\circ\text{C}$ ) and the chemically inert character of the metallic forms.

### 1.2. Sources, production, uses and recycling

Up to a technologically attainable depth of 5 km, the amount of PGE is still enormous but only a small fraction of the ores is rich enough for commercially reasonable exploitation. Depending on the composition and accessibility, ores with a concentration of PGE higher than  $0.3 \text{ } \mu\text{g/g}$  can be considered worthy of exploitation. Basically there are three different sources for PGE: primary or secondary deposits, production as a by-product of Cu-, Ni-, for example, or noble metal production and recycling. The main commercially relevant PGE deposits are located in South Africa, Zimbabwe, North America, Russia and Australia. As Pt alloys well with Fe, large amounts of the PGE are assumed to be present in the iron rich centre of the earth. The PGE from primary or secondary deposits are pre-concentrated by flotation. For example, anode sludge from a Cu refinery is already a PGE concentrate. The subsequent processing is strongly dependent on the composition of the material. Essentially, the process begins with dissolution (e.g. in aqua regia) or by fusion (e.g. sodium peroxide). Then, if present, Ru and Os can be separated by an oxidizing distillation in the form of their tetroxides. The subsequent separation scheme applies by either precipitation or liquid-liquid extraction.

There are many application fields for PGE, such as their use for inert tools in the laboratory and the glass industry, for dental applications, in the electronics industry, for special alloys and some specific compounds as pharmaceuticals (cis- and carbo-platinum being currently the most important). However, the most pronounced application is due the specific catalytic properties. Here the PGE have been used in the chemical industry for many years in the production of hydrocarbons, and recently also for the production of fine chemicals and pharmaceutical compounds and in proton exchange membrane (PEM) fuel cells.

Since the introduction of the catalytic automobile exhaust gas converters in the 1970s in the United States of America and in the mid 1980s in Europe, the demand for PGE has risen tremendously. This is easy to understand because approximately 1 to 5 g of PGE (in various mixtures) is used in each converter. Since, usually, only a small amount of PGE is lost and introduced into the environment during the lifetime of an exhaust gas catalyst, the recycling of these catalysts is becoming increasingly important — particularly due to the extremely large quantity of systems. In 2000 around 25 tons of PGE were recycled from old automobile exhaust gas catalysts.

### 1.3. Economic impact

Having a wide range of applications in mind, the growing economic impact of PGE can be understood quite easily. PGE plays a very important role not only in jewellery, but also in financial investment, industrial applications (e.g. glass, electronics and catalyst industries) exhaust gas catalysts in automobiles and for medical purposes (dental metal and anti-cancer drugs), resulting in an increasing demand in the last few years. As the supplies of PGE could not be easily increased, prices did go higher. Prices for Pt increased from around US \$350 per oz (28.25 g) in 1999 to more than US \$600 at the end of 2000, and for Pd, from slightly above US \$300 in 1999 to around US \$900 at the end of 2000.

Future technological developments positron emission tomography (PET) tracer synthesis, fuel cells and automobile exhaust gas catalysts also for diesel cars) will lead to an increased application for PGE, which might further influence its market prices. Table I shows typical Pt levels in various matrices.

TABLE I. PLATINUM LEVELS IN VARIOUS MATRICES

Matrix		Pt
Elderberry leaves, next to motorway		800–2500 pg/g
Poplar leaves, unpolluted (Andes, Chile)		40 pg/g
Spruce shoots		100–550 pg/g
Gasoline		0.15–5.2 ng/L
Soil	Uncultivated	30–260 pg/g
	cultivated	150–3900 pg/g
	highway	15600–31700 pg/g
Air dust		5–130 ng/g; 0.3–30 pg/m <sup>3</sup>
Tap water		0.1 ng/L
Rainwater in Germany		0.2–0.08 ng/L
Sea water		0.3–2.4 ng/L
River water (Elbe, 1991)	dissolved	0.8–7 ng/L
	particulate	≤ 0.2–0.8 ng/L
Potato, peeled		100 pg/g
Salad		2100 pg/g
Flour		≤ 40 pg/g
Wine		≤ 0.4–2.4 ng/L
Honey		≤ 2 pg/g
Brussels sprouts	100 m beside highway	250 pg/g
Urine	unpolluted	0.5–14 pg/g
	polluted	2.1–2900 pg/g
Blood plasma	unpolluted	≤ 0.8–6.9 pg/g
	polluted	9.5–180 pg/g
	after Cis-Pt therapy	1100–1600 µg/L [1]
Whole blood	unpolluted	≤ 0.8–6.9 pg/g
	polluted	9.5–280 pg/g

## 2. FIELDS OF APPLICATIONS AND RELATED ANALYTICAL APPROACHES

### 2.1. Geological samples

Mining and mineral industries have a key interest in the accurate and precise measurement of the PGE in geological matrices, from exploration soils and sediments through ores, concentrates and slags in production, to assay of the final purified metal.

At the exploration stage, it is generally the case that there are large numbers of samples to be processed. Soils and sediments can be homogenized sufficiently that small samples sizes (up to a few grams) can be analysed. Acid digestion and atomic absorption spectrometer (AAS) or inductively coupled plasma atomic emission spectrometer (ICP-AES) can be used. In the case of ores and concentrates the distribution of the PGE will be inhomogeneous, requiring large samples (10 g and more) to provide representative analyses. In this case a pre-concentration stage, such as fire assay, will be necessary for mineralized samples prior to analysis by AAS, inductively coupled plasma (ICP) or neutron activation analysis (NAA).

Some minerals are quite difficult to dissolve and aggressive digestion techniques will be required. The full range of decomposition and preconcentration techniques applied to geological samples is reviewed in Ref. [19], including fire assay, chlorination and wet chemical attack. They include references to different methods such as digestion with multiple acids in open vessels, autoclave decompositions, microwave digestions and fusions with lithium borates, sodium hydroxide and sodium peroxide. Post irradiation radiochemistry can be used to remove unwanted matrix effects when NAA is used and these methodologies are reviewed in Ref. [20].

A number of reference materials for the PGE have been developed and distributed over the years for use in the mining industry. Agencies such as the Canadian Geological Survey in particular have a suit of ores and tailings with a range of Pt and Pd concentrations from ng/g to µg/g. These certified reference materials have been analysed by many laboratories over the years and provide a very good set a samples to validate laboratories and their methodologies. Therefore, geological mapping is one area in the determination of the PGE where good quality data can be assured by a laboratory setting up the methodology.

#### 2.1.1. Case one: Mineral exploration

Large numbers of samples are collected and analysed in mineral exploration as part of large surveys screening soils or stream sediments for PGE. Low concentrations of Pt and other PGE indicative of mineralized areas require detection limits down to 10–100 ng/g Pt and Pd and 1–10 ng/g Rh and Ir. Because the homogeneity of soil or sediment samples is generally poor and the sampling uncertainties will be high, it is recommended to use minimum sample sizes of 1–10g for analysis to obtain sufficient reproducibility. It is also possible to use vegetation as a biomonitor for exploration, but this technique is not widely used.

Whatever the matrix, a rapid and cost effective analytical technique is required with reasonable accuracy and precision. Techniques such as graphite furnace atomic absorption spectrometer (GF-AAS), ICP-AES, inductively coupled plasma-mass spectrometer (ICP-MS) and NAA can all provide adequate sensitivity, particularly if fire assay preconcentration has been used to remove interfering matrix elements.

Alternative preparation procedures include acid or alkali fusion, and total acid digestion or a partial leach. For this type of work acid digestion provides the most simple and rapid approach, even though acid extraction may not give complete recovery. The final solution can be determined by ICP-MS in a routine way. If fire assay is used to pre-concentrate the samples it is possible to analyse the NiS button directly (as a cheap and rapid method for exploration) using NAA [20] or laser ablation - inductively coupled plasma-mass spectrometer (LA-ICP-MS) [36]. The detection limits of between 1 and 10 ng g<sup>-1</sup> are adequate for exploration work in both cases.

### *2.1.2. Case two: Analysis during extraction and production*

Once the source of the PGE has been located, ore deposits will only be viable where Pt and Pd are present at concentrations above 100 ng/g. Most analytical techniques can be applied to these measurements but the key problem relates to the heterogeneity of the samples. Large sample sizes (10–50 g) must be processed to provide a representative analysis. Therefore ores and concentrates must be pre-concentrated with fire assay before analysis by ICP techniques, NAA or AAS. Lead fire assay is the method of choice for large assay houses associated with the mining industry, using a simple analytical finish such as AAS. It has been used with ICP-MS to determine PGE in sulphides and ultramafic rocks [26] and heavy mineral concentrates [11]. However, for complete determination of all the PGE it is most usual to use NiS collection to avoid losses of elements on cupellation. NiS fire assay has been used widely with ICP-MS and THE Ref. [19] provides many examples. The method has been refined for NAA and modified in particular for difficult material such as chromitite, which is one of the main sources of the PGE in South Africa.

In the case of concentrates, where the PGE are present at high concentrations, it is possible to use direct methods of analysis such as X ray fluorescence (XRF), NAA or simple techniques such as AAS and ICP-AES, once the sample is in solution. Assay of final purified materials is a specialized field requiring high precision, since there is much at stake financially. Techniques such as NAA and ICP-MS, with uncertainties of several %, are not the most appropriate methodologies. Fire assay using a final gravimetric measurement is more appropriate.

XRF has been used to look at mattes using precipitates on a membrane filter or as solutions; it is not usual to carry out instrumental analysis on these types of samples. Total reflection X ray fluorescence is a fast technique and the detection limit of about 1 mg kg<sup>-1</sup> is sufficiently sensitive for this type of application.

### *2.1.3. Case three: Geochemical studies*

Mineralogical studies in museums and academic establishments have different requirements to the mining and minerals industries. Mineralogical phases may be identified using surface techniques such as scanning electron microscopy (SEM) and specialized procedure, such as the use of heavy liquids, magnetic fractionation or handpicking under a microscope, are used to separate the mineral phases, resulting in small sample sizes. Limited sample size, perhaps a few mg, will mean that high sensitivity is required to detect low concentrations of the PGE.

Radiochemical separation techniques following neutron activation can provide excellent sensitivity for geochemical studies [20]. Ion exchange, solvent extraction and precipitation have all been used to remove the matrix. In particular, there have been a number of procedures

for the isolation of Ir, to study the Cretaceous-Tertiary boundary, where the concentrations are as low as  $10^{-10}$  g. g<sup>-1</sup>. Sample types include silicate rocks, stony meteorites and iron meteorites. It is difficult to generalize about the detection limits of the analytical techniques available because they are so matrix dependent but there are many examples in the literature of applications with GF-AAS, ICP-AES, NAA and ICP-MS.

## 2.2. Occupational exposure and medical applications

Workers in the PGE mining, refining or processing industries are potentially exposed to high concentrations of the PGE and acute health effects, including allergy to platinum salts, have been observed. Patients undergoing cancer therapy and subjects with dental restoration, as well as personnel administering platinum based drugs, dentists and dental technicians, are exposed to PGE. It is therefore important to monitor PGE levels in exposed populations. This can be performed through the analysis of non-invasive samples, e.g. urine, blood or saliva, and the choice of an analytical technique depends on the concentration to be determined and therefore, on the exposure.

### 2.2.1. *The use of urine for biomonitoring*

The level of platinum in urine has been determined in a number of studies on occupational and medical exposure to platinum. Elevated concentrations have resulted from exposure. While both urine and blood concentrations would provide an assessment of the exposure to PGE, urine has the advantage of easy sampling and sample preparation compared, for example, with blood, but a number of precautions have to be considered:

- Personnel taking and handling samples should be aware of hygiene precautions and protected;
- Time of sampling should be considered carefully so that the urine sample represents an exposure period; 24 hour sampling is therefore recommended;
- Polyethylene containers are recommended and a new container should be used for each sampling;
- Sample contamination should be minimized, especially for the determination of platinum levels in non-exposed persons;
- Samples should be stored frozen.

In addition, it is preferable to normalize concentrations with the creatinine content in urine samples as concentrations vary with the volume of urine excreted. This can be done through the determination of creatinine in urine samples using commercially available kits.

The choice of techniques for PGE determination in urine depends on the expected concentration. Table II gives detection limits for GF-AAS, cyclic stripping voltammetry (CSV), total reflection X ray fluorescence (TXRF) and ICP-MS, while the concentrations measured in occupational exposure studies are provided in Tables III and IV.

TABLE II. ANALYTICAL TECHNIQUES USED IN THE DETERMINATION OF PGE IN URINE

Analytical technique	Detection limit	Sample preparation	Ref.
GFAAS	Pt: 50 $\mu\text{g L}^{-1}$	Dilution in 10% HCl to reach the analytical range of the instrument.	[2]
CSV	1 $\text{ng L}^{-1}$	UV irradiation with $\text{H}_2\text{O}_2$ and $\text{H}_2\text{SO}_4$	[3]
TXRF	Pd: 2.5 $\text{ng L}^{-1}$	High pressure ashing and Hg co-precipitation	[4]
ICP-SFMS	Pt: 0.03 $\text{ng L}^{-1}$ Pd: 0.25 $\text{ng L}^{-1}$ Rh: 0.03 $\text{ng L}^{-1}$	UV irradiation with $\text{H}_2\text{O}_2$ and $\text{HNO}_3$ , dilution (19x)	[5]

TABLE III. EXAMPLES OF Pt CONCENTRATIONS IN REPORTED MEDICAL STUDIES

Sample	Population	Concentration	Unit	Ref.
Urine	Control	6.2 $\pm$ 3.2	$\text{ng g}^{-1}$ creatinine	[7]
	With dental alloys	11.9 $\pm$ 8.5	$\text{ng g}^{-1}$ creatinine	
Saliva	Control	526 $\pm$ 871	$\text{pg g}^{-1}$	[7]
	With dental alloys	18.5 $\pm$ 3.6	$\text{pg g}^{-1}$	
Urine	After chemotherapy	0.74-77.24 depending on dose and time	$\mu\text{g g}^{-1}$ creatinine	[8]

TABLE IV. EXAMPLES OF Pt CONCENTRATIONS IN REPORTED OCCUPATIONAL EXPOSURE STUDIES

Sample	Population	Concentration	Unit	Ref.
Urine	Control	2.3 $\pm$ 10.4	$\text{ng g}^{-1}$ creatinine	[9]
	Medical personnel	4.35 $\pm$ 5.6 (up to 22.3)	$\text{ng g}^{-1}$ creatinine	
Urine	Platinum industry workers	up to 6270	$\text{ng g}^{-1}$ creatinine	[10]

### 2.2.2. Case one: Medical exposure

The discovery of the therapeutic properties of platinum against cancer has led to intensive medical research and the development of platinum based drugs [17]. These drugs now play an important role in the treatment of cancer. While cisplatin (cis-diammine-dichloroplatinum (II) carboplatin, oxaliplatin,) is the most commonly used drug in the treatment of cancer, new drugs including lobaplatin and nediplatin have received approval for clinical use either worldwide or locally. A further drug, JM213, is undergoing clinical trials.

While platinum based drugs are use extensively in cancer therapy, the drugs exhibit severe side effects including cytotoxicity and are only effective against a small number of cancers. It is therefore important to routinely monitor platinum levels in patients. Further

exposure to PGE which should be monitored includes the use of PGE-containing dental alloys, which are responsible for elevated platinum concentrations in saliva and urine [6].

The determination of total platinum concentrations is useful in the follow up of patients treated with platinum based drugs and should therefore be carried out on a routine basis. This can be performed through urine and blood analysis by GF-AAS, CSV, ICP-AES and ICP-MS. For urine, the procedures described in Table III can be applied. While similar procedures can be applied to the analysis of saliva, the analysis of blood requires a more difficult sample preparation.

A better understanding of the metabolism and mechanisms of the action of platinum based drugs would provide information useful to the development of new drugs with increased efficiency and lower side effects. Therefore, medical research has focused on the transformation of platinum drugs in biological fluids and on the mechanism by which platinum binds to DNA. The determination of platinum metabolites in biological fluids has been performed by chromatographic or electrophoretic separation with determination of the separated species by ultra-violet (UV) detection, ICP-MS and electrospray ionization tandem mass spectrometry (ESI-MS). While UV detectors can only provide information on the platinum content, ICP-MS and ESI-MS have provided information relevant to species determination in the binding of platinum to guanosine monophosphate. The binding of platinum to DNA was further studied by crystallography, nuclear magnetic resonance (NMR) and molecular models.

### 2.2.3. Case two: Occupational exposure

Workers in PGE related industries, dental technicians and nurses administering cancer therapy might be exposed to levels at which these metals exhibit toxic effects. It is therefore important to monitor both ambient PGE concentrations or potential sources and internal levels in occupationally exposed personnel. Table IV provides examples of concentration levels in workers with PGE related activities.

Exposure to platinum in mining, refining and processing industries has been the subject of extensive studies, which have led to the recommendation or legislation of limit values in a number of countries including Germany and the United States of America. It has been pointed out that it is important to monitor soluble platinum concentrations as soluble species exhibit acute toxic effects, while metallic platinum is virtually non-toxic. Therefore, a distinction has been made between total and soluble platinum levels with limit concentrations of  $1 \text{ mg m}^{-3}$  and  $2 \text{ } \mu\text{g m}^{-3}$ , respectively.

Sampling of airborne particulate matter can be performed through personal samplers or stationary devices composed of a calibrated pump drawing air through a filter. Procedures for the assessment of occupational exposure to airborne particles typically involve the dissolution of soluble species in weak acid and the dissolution of the remaining insoluble platinum in aqua regia. Analysis can be performed by GF-AAS.

Monitoring of workers with PGE related activities could be performed through the analysis of urine as described above. The analytical technique clearly depends on the exposure: for studies in which low concentrations are expected or control groups have to be studied, ICP-MS or CSV are recommended, while GF-AAS is suitable for higher concentrations.

#### 2.2.4. Case three: Uptake by humans due to dental PGE alloys and drug contamination

Both platinum and palladium are frequently used as components of dental alloys. Palladium basic alloys are relatively easy to handle and are cheaper than alloys with a high gold content. An increase of palladium in sewage sludge ashes of the German city of Stuttgart since the year 1984 has been traced back to the Pd emissions of dental laboratories and surgeries [24]. As a result, the Pt burden of a patient with Pt dental alloys has increased from 1,2 ng/L to 23,1 ng/L urine (average values), as measured by adsorptive voltammetry.

Pd emissions of Pd dental alloys have been quantified: While Pd alloys with a high gold portion revealed low solubility ( $< 0.2 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ ), Pd alloys with high copper and tin content exhibited much higher solubility with up to  $22,5 \mu\text{g cm}^{-2} \text{d}^{-1}$ . However, further desorption experiments, where the resulting fluids have been decomposed by pressurized microwave followed by solid phase extraction GF-AAS coupling, resulted in much lower values [48].

Due to the fact that many chemical reactions are mediated by PGE catalysts in the chemical industry, pharmaceutical products may also be contaminated. In certain medicaments, Pd contents of up to 130  $\mu\text{g}/\text{kg}$  have been detected.

#### 2.2.5. Case four: Background concentrations

Exposure studies rely to a great extent on the comparison of PGE levels in exposed and control groups. It is therefore important to provide accurate PGE concentrations in biological fluids of non-exposed persons. In addition, the increasing use of PGE in automobile catalysts and the release of these metals into the environment during vehicle operation have raised concern over potential health risks and there is now a need to monitor PGE in the general population.

However, the determination of background PGE concentrations in biological fluids is an analytical challenge, which requires careful sample handling and sensitive analytical techniques. PGE concentrations have been determined to be in the lower  $\text{ng g}^{-1}$  creatinine and  $\text{ng L}^{-1}$  ranges for urine and blood, respectively. Therefore, highly sensitive instrumentation is required. While ICP-MS [5] enables the determination of background Pt concentrations in biological fluids, the determination of Pd and Rh is difficult owing to severe interference and mathematical correction or matrix separation have to be applied. CSV [9] allows the determination of Pt and Rh in urine and blood. TXRF provides an interesting approach for the determination of background Pd concentrations [4].

### 2.3. Environmental monitoring

In this section the analytical questions of PGE determination in environmental samples will be discussed. As already mentioned in the introduction, concentration levels of PGE in environmental samples are very low, although a tendency to higher values is given due to anthropogenic impact. It can be seen in Table I that background concentrations of Pt in “unpolluted” samples are in the low  $\text{pg g}^{-1}$  range. As a matter of fact it is difficult to determine whether geogenic emissions, cosmic infall or anthropogenic emissions contribute to these values. In some cases the elemental and isotopic pattern of the PGE are used for tracing their origin.

Isotopic patterns work well for quantifying the contribution of cosmic infall to the environmental concentrations of Os and Ir [10], whereas elemental pattern are rarely

significant. For example a Pt/Rh ratio of 5 was found in unpolluted spruce shoots. This value corresponds to the Pt/Rh ratio in the earth crust <sup>1</sup> as well as to the Pt/Rh ratio in anthropogenic PGE emissions <sup>2</sup>.

In the last century, most environmental PGE background values have been determined for Pt, followed by Pd and Rh. In the case of Ir, Ru, and Os only rudimentary data are available. This is, on the one hand, due to the underestimation of their environmental importance, and on the other hand, due to the fact that their abundances are in most cases below the limit of detection of the analytical methods currently available. The fact that Os and Ru form volatile oxides complicates their analysis. This is an additional reason for the lack of environmental data.

The analysis of PGE in unpolluted environmental matrices is highly challenging. Very sensitive and selective instrumental methods have to be used in combination with pre-concentration or matrix separation (in the past, enrichment used to be the main objective of sample pretreatment procedures, but with the introduction of the highly sensitive techniques as NAA, GF-AAS, CSV and ICP-MS the analytical background changed and selective and quantitative separation of interfering elements became important).

In the following section several cases of environmental PGE-analysis will be described in detail.

### 2.3.1. Case one: Road dust

As a result of surface abrasion of the catalytic converters that are nowadays fitted to cars, Pt, Pd and Rh are released into the environment adsorbed on small particles [11]. Since the concentration of PGE in road dust is still very low at the present and moreover in samples of complex composition, the determination of these elements is still a special challenge to trace element analysis [11–14]. Typical concentration levels of environmental samples are two orders of magnitude lower than most geological samples, i.e. in the low ng g<sup>-1</sup> range. Generally, the detection of analytical trends requires a high expenditure of quality control, hence much effort has to be given to methodical and laboratory intercomparison.

Road dust can be collected by means of a commercial vacuum cleaner with special devices containing cellulose ester filters (7 cm diameter) [15]. Sample preparation has to account for the heterogeneous distribution of the PGE and for the difficult matrix [14]. Road dust is composed of a mixture of soil, soot and deposited dust. The major constituents of road dust are soil, organic matter derived from adjacent vegetation, and input from traffic. Additionally, there is salt and grit, debris from vehicle collisions, road construction materials, general waste, and animal deposits [13].

A minimum representative sample intake for subsequent analysis has to be critically assessed. Generally, this is depending on particle size distribution of the investigated dust. At a grain size < 90 µm obtained by milling, a minimum sample intake of 0.1 g was found sufficient for reproducible analysis results [16].

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<sup>1</sup> The approximate PGE abundances in earth crust, hydrosphere and atmosphere are: Ir 1 ppb, Os 10 ppb, Pd 10 ppb, Pt 5 ppb, Rh 1 ppb, Ru 20 ppb.

<sup>2</sup> In anthropogenic emissions the ratios Pt/Rh and Pt/Pd are about 6 and 10, respectively.

Fire assay or wet chemical attack was shown to be suitable for sample preparation [13,15,16]. 20 g samples can be processed by the fire assay procedure accounting for representative sample size, efficient preconcentration and matrix separation. (Detection limits for NiS fire assay in combination with quadruple ICP-MS Rh  $0.165 \mu\text{g}\cdot\text{kg}^{-1}$ , Pt  $0.197 \mu\text{g}\cdot\text{kg}^{-1}$ , Pd  $0.204 \mu\text{g}\cdot\text{kg}^{-1}$ ) [13]. Complete sample digestion including the silicate matrix with HF was shown to be a prerequisite for total PGE analysis in road dust using a microwave system [15]. Leaching the sample with aqua regia can be applied provided a high pressure asher is used [12]. Suitable preconcentration procedures for road dust are, as already mentioned, fire assay, ion exchange and Te-coprecipitation.

The determination of Pt is by far the best developed technique among analytical techniques for the PGE [14,18,19]. A number of highly sensitive and powerful techniques are available [18]. The GF-AES and ICP-AES methods can be only applied to environmental samples in combination with preconcentration / matrix separation. Together with ICP-MS and NAA, the stripping voltammetry (SV) is the most sensitive technique for measuring Pt. However, when measuring Pt by ICP-MS the polyatomic interference of hafnium oxide has to be considered.

The problem can be overcome by different strategies: (1) the use of ultrasonic nebulization in combination with membrane desolvation for drastic reduction of oxide formation levels, (2) elimination by high mass resolution measurement, and (3) matrix separation by ion exchange.

Voltammetry requires a complete decomposition of organic substances, remaining C concentrations must be below 0.1 %. This can be achieved by high pressure ashing operated up to 130 bar. Furthermore the analysis is hampered by a species dependent response of detector [24]. NAA is performed after fire assay sample preparation. Depending on the expected concentration level, the collector button is dissolved or not dissolved for analysis. The key problem in the direct NAA determination is the interference posed by Sc and Au [14].

The determination of Pd is highly sophisticated. Determination of Pd by ICP-MS is strongly hampered by numerous interferences making an accurate analysis without tedious manipulations such as matrix separation or and mathematical correction procedures impossible [14]. Even, when measuring with the high resolution ICP-MS at resolution of 10 000, not all interferences can be separated from the Pd isotopes [16]. Furthermore it has to be kept in mind that the limit of detection increases with the increase of resolution.

As an alternative approach an on-line column preconcentration and separation system with GF-AAS detection was developed allowing selective Pd determination from the lower ng/L to the upper  $\mu\text{g}/\text{L}$  range even in such complex matrices [21]. The method employs a C18 column for concentration of N, N-diethyl-N'-benzoylthiourea (DEBT)-Pd complexes.

Determination of Rh in road dust can be performed by ICP-MS. However, the determination is hampered by ultra low concentrations in environmental samples and as regards ICP-MS by polyatomic interferences of the monoisotopic  $^{103}\text{Rh}$  [14]. Additionally, Rh may be analysed at ultratrace-levels by direct differential pulse cathodic stripping voltammetry after acid decomposition [9].

There is a road dust reference material available produced within the certification campaign of the European Commission (SMT4-CT98-2225 "PACEPAC"). The material was collected in 1994 from the ceiling of a tunnel in Styria (Austria). The grain size of the milled

dust was  $< 90 \mu\text{m}$  [18]. Table V shows the certified concentration value. For Pd a concentration with an uncertainty of 30% has been certified showing the difficulty of the analytical task.

TABLE V. CERTIFIED CONCENTRATION VALUES OF ROAD DUST, BCR 659

Element	Certified concentration value ( $\text{ng g}^{-1}$ )
Pt	$77.6 \pm 12.7$
Pd	$6.0 \pm 2.4$
Rh	$12.8 \pm 2.0$

### 2.3.2. Case two: Airborne particulate matter

Concerns have arisen that the PGE may have a deleterious effect on the health of the general population by direct contact with the dust, by inhalation of particulate matter and through food and water [22]. Therefore investigation into the exposure of man to these elements at the workplace and as it enters the environment is highly important. About 30 % of the particles emitted by car catalysts have a diameter  $< 10 \mu\text{m}$  and can be found as airborne particulate matter [15]. PGE concentrations in air are influenced by a variety of different factors which makes intercomparison difficult. This includes the volume of traffic on a particular roadway, the number of cars with catalytic converters, vehicle type and associated emission amounts, particle size of airborne matter, meteorological conditions, and driving conditions.

So far there is little literature available on the topic of PGE in air, and what has been published is mostly restricted to Pt. This lack of data on PGE content in aerosol particles can be explained by their extremely low concentration. Moreover, the determination by the most sensitive method, i.e. ICP-MS, is hampered by spectral interferences from monoatomic and polyatomic ions produced in the plasma from matrix constituents such as elements arising from atmospheric pollutants and gasoline.

Determination of the PGE content related to aerosol mass size distribution can be obtained by collecting airborne particles via an impactor (either cascade, rotating cascade or normal). The easiest means to collect aerosol samples is to filter a certain volume ( $10\text{--}80 \text{ m}^3$ ) of air over several hours (24–72 h). In most studies airborne particulate matter is collected using a rotative pump sampler with a PM10 sampling head (set up following the US EPA specifications, about  $1 \text{ m}^3/\text{h}$ , 24/48 h) and equipped with cellulose ester filters (47 mm diameter,  $0.8 \mu\text{m}$  pore size) [15]. For work place monitoring a personal passive sampler is the technique of choice.

Airborne dust particles are aerosols composed of various-sized particles. According to a number of studies, aerosols in ambient air are generally made up of soot (15%), inorganic ions such as sulphate, nitrate, carbonate, chloride and ammonium (43%), water (19%); organic compounds (19%) and various metal compounds (4%) [17]. Compared to road dust the sample digestion procedure is more straightforward.

The determination of PGE in aerosol particles is carried out by ICP-MS, mostly in combination with a separation/pre-concentration step [11, 23]. The techniques involve ion-exchange resins, fire-assay and co-precipitation.

Despite the effectiveness of a large number of separation methods, the application of such procedures to determine ultra-trace levels of PGE is not widespread. Spectroscopic interferences arising from more abundant constituents of the sample, as well as the risk of contamination during sample manipulation become increasingly serious with decreasing analyte concentration, especially in complex matrices. Pt and Rh can be determined by adsorptive voltammetry [24]. Ultratrace levels down to concentrations of ng/kg and pg/L can be measured. Pd can be measured by the above-mentioned GF-AAS technique.

Because Pt is so far the major PGE in catalysts, its concentration in particulate matter in urban areas is the most investigated among the relevant PGE. Moreover, as already mentioned the analysis technique of Pt is the most developed among PGE determination techniques. In a research project in Germany, Pt and Rh concentrations in aerosol collected by filtering air has been analysed after high pressure ashing using adsorptive voltammetry. Absolute detection limits of 3 pg for Pt and 10 pg for Rh have been found. Typical concentrations were found at the low pg m<sup>-3</sup> level. Background concentrations of 3 pg m<sup>-3</sup> for Pt and < 0.2 pg m<sup>-3</sup> for Rh were observed [16].

### 2.3.3. Case three: Monitoring of water

In environmental analysis, water — with the exception of sea and wastewater — is considered to be a straightforward matrix. Representative sampling is essential, therefore sampling in ground water wells or taps should be performed only after the effluent has reached constant pH, constant specific conductivity and constant temperature. Water samples should be conserved by acidification (pH 2 or lower) and analysed within some days after sampling, since longer storage of metal traces in glass or polyethylene containers may lead to losses due to wall absorption effects.

In most cases, water samples can be analysed without further sample pretreatment. Although, PGE concentrations reported for tap, rain, ground and surface water are below 1 ng L<sup>-1</sup>, which means that highly sensitive methods have to be applied. The concentrations in seawater are in the same range (Pt around 2 ng L<sup>-1</sup> and below, Os approx. 0.003 ng L<sup>-1</sup>), but the high salt concentration (3 % NaCl) may mitigate the direct determination of the elements. Higher concentrations (up to 3 orders of magnitude) can be expected in water contaminated due to hospital effluents, jewellery manufacturing or mill tailing.

In water analysis the selection of an appropriate analytical method is mainly depending on the concentration of the analytes. In the case of unpolluted samples CSV can be used without any analyte enrichment or matrix separation procedures for the determination of Pt and Rh. Since the detection limits of NAA and ICP-MS are in the range of PGE background concentrations, pre-concentration procedures for enrichment of the PGE are necessary. Depending on the achieved enrichment factors methods with lower sensitivity (GF-AAS, XRF) may also be applied. Co-precipitation, ion-exchange or pre-concentration by evaporation can be employed. For example Pd and Ir can be pre-concentrated by a factor of 2000 and more in acidified sea water samples by passing them through a column filled with a small amount (2 g) of strong basic anion exchange resin.

In contrast to the water samples described above, wastewater has to be regarded as a complicated matrix similar to sludge or soil. Depending on the content of solid matter, acid digestion (open or closed vessel treatment) in combination with high temperature and pressure is necessary. Heating may be accomplished by a hot plate (digestion block) or a microwave

oven. Aqua regia is essential for quantitative recoveries of Pt, Pd and Rh, and the use of HF is recommended in the presence of silica containing samples. For attacking all PGE the use of HClO<sub>4</sub> in combination with mineral acids is recommended. Again the necessity of pre-concentration and the selection of analytical methods depend on the expected concentration levels.

#### 2.3.4. Case four: Biological samples

Uncontaminated biological samples contain pg g<sup>-1</sup> amounts of PGE whereas the concentrations in contaminated samples may reach low ng g<sup>-1</sup> levels (see Table VI).

TABLE VI. PGE CONCENTRATIONS IN ENVIRONMENTAL MATRICES (ALL VALUES FROM [9] IF NOT INDICATED DIFFERENTLY)

Matrix	Pt	Pd	Rh
Wine	≤ 0.4 -2.4 pg/mL		
Honey	≤ 2 pg/g		
Flour	≤ 40 pg/g		
Poplar leaves (Andes, Chile)	40 pg/g		
Grass (Germany, unpolluted)	≤30 pg/g [30]		≤30 pg/g [30]
Potato (peeled)	100 pg/g		
Spruce shoots	100–550 pg/g		20 pg/g
Grass (Belgium, unpolluted)	700 pg/g [31]		
Brussels sprouts (100 m motorway distance)	250 pg/g		
Elderberry leaves, next to motorway	800–2500 pg/g		
Grass (Germany, polluted)	33–10000 pg/g	≤30–1300 pg/g	33–2100 pg/g
Poplar roots (Germany, polluted)		≤1000–13000 pg/g	

Acid digestion, with or without subsequent pre-concentration methods, followed by ICP-MS, GF-AAS, CSV, NAA, XRF or TR-XRF is proposed for solid samples. The decomposition step should include H<sub>2</sub>O<sub>2</sub> in order to decompose organic matter effectively. If the samples contain silica the use of HF is strictly recommended for complete digestion of Pd. HF in combination with HNO<sub>3</sub> will dissolve Pd quantitatively.

In order to get quantitative results for all PGE, again, the use of HClO<sub>4</sub> in combination with other acids is recommended. Ashing of the samples for decomposition of organic matter prior to digestion may be used alternatively to wet ashing, although some losses — not only of Ru and Os- have been reported [26, 27]. The methods can be applied to grass, tree leaves, tree barks, mosses, lichens, peat bog, animal tissues (mussels, fish, lung tissue, muscle tissue, etc.), hair, faeces and macro invertebrates. Liquid samples (urine, blood) can be concentrated by evaporation prior to digestion. The residue can be treated like a solid sample. The application of UV-photolysis for determination of PGE in urine is a fast and simple alternative to other digestion methods [28].

Sampling devices that allow contamination-free sampling are an important issue. If available, ceramic scissors, knives and tweezers for sampling are suitable to reduce the risk of contamination.

Special attention should be directed to determination of dry weight. A temperature of 105°C should not be exceeded. For accurate determination of Os and Ru the drying temperature should be kept under 50°C since OsO<sub>4</sub> and RuO<sub>4</sub> are highly volatile at higher temperatures.

#### 2.3.5. *Case five: Sludge and incineration monitoring*

Sludge samples form a difficult matrix comparable with road dust [29]. The analytical procedures are adapted accordingly. Because of the high organic content of this sample type, ashing is a prerequisite.

So far studies on PGE in sewage sludge mainly focus on Pt. Like other heavy metals, Pt is enriched in sewage sludge originating from catalysts applied in various production lines, electro-technology and anticancer drug production. Measurements by ICP-MS (after drying and microwave digestion) reveal typical concentrations ranging between 80 µg/kg and 600 µg/kg [30]. Another study involved Pt, Rh and Pd determination in sewage sludge incineration ashes [29]. A nickel sulphide fire assay (NiS-FA) was carried out for ICP-MS analysis. Very high Pd contents up to 450 µg/kg were found. The Rh content was very low with 5–10 µg/kg compared to approximately 100 µg/kg of Pt.

### 3. ANALYTICAL METHODOLOGY

#### 3.1. Sample pretreatment

Prior to analysis a digestion of Pt metals from natural materials and pre-concentration steps are necessary to determine naturally occurring concentration levels with current analytical techniques.

##### 3.1.1. *Digestion techniques*

The ‘acid digestion’, ‘fusion’, and ‘chlorination’ as sample preparation steps to make Pt metals accessible for analysis are discussed below.

##### 3.1.1.1. Acid digestion

In order to employ most of the analytical determination methods recommended below (such as voltammetry, atomic absorption spectrometry, and ICP techniques) solid samples need to be dissolved. Also, for certain techniques, e.g. voltammetry, aqueous samples need to undergo a decomposition step to reduce the carbon content to a minimum, which may require an acid digestion. Additionally, an acid digestion may be necessary prior to the application of a pre-concentration method such as the enrichment of Pd traces in mercury.

Employing an acid digestion, different acids and mixtures of acids can be used. This must be adjusted with respect to the detection method applied afterwards. For example, solutions with nitric acid are usual in atomic spectroscopy since parts of some instruments may be not resistant to aqua regia and hydrofluoric acid.

On the other hand, mixtures of digesting acids must be chosen with respect to the individual PGE quantified due to a different complex chemistry. Pt and Rh need to be stabilized by hydrochloric acid while nitric acid is also added to perform oxidation and

mineralization of the matrix. This way, Pt and Rh are quantitatively extracted from a matrix like soil or grass, although a silicate residue may remain in the decomposition vessel.

Pd, on the other hand, shows a stronger association with silicate. Matrices with low silicate content such as urine may be decomposed with a mixture of nitric acid and hydrochloric acid for subsequent Pd analysis [4]. Matrices with high silica content, however, need to be treated with higher effort: undigested residues of a silica matrix lead to a loss of Pd from 10–90%, depending on the period of time between decomposition and measurement. Hence a "total decomposition" of silica containing samples (grass, sludge ashes, dust, reference material SARM 7) is required to mobilize Pd: prior to the total decomposition carbon-containing samples such as grass and dust were dry ashed at 500°C in a muffle oven. The ashes or ores (50 mg up to 1g) are mixed with a 1–10 fold excess of sodium peroxide and melted for 1 h at 495°C in a zirconium crucible (the use of nickel crucibles refers to radioactivity only).

***IMPORTANT NOTE: NEVER USE NICKEL CRUCIBLES IN ANALYSIS FOR PGE, THEY ARE HIGHLY SUSPECTED OF CAUSING PGE CONTAMINATION.***

The crucible is allowed to cool down for two minutes and the sample is then transferred into a 600 ml beaker. After the addition of 50 ml of warm bi-distilled water (60°C) the crucible is rinsed with water (10 ml) and 6M HCl (2 ml). The precipitate is then totally dissolved by the addition of 20 ml of 6M HCl.

Generally, open digestion should be avoided. There is a strong danger of losing Pt as e.g. higher volatile chlorides.

For evaporation tasks, temperatures must not exceed 100°C to prevent losses. Evaporation to dryness must generally be avoided. Any processes performed in open vessels have to be particularly controlled by recovery tests.

Acid digestion can be performed in Teflon<sup>®</sup> or in quartz vessels due to the fact, that both are suitable for higher temperatures. Teflon<sup>®</sup> vessels may be used with temperatures of up to 250°C, while quartz vessels can be used at even higher temperatures. A heating step is needed to achieve a quantitative oxidation and dissolution of the matrix. A minimum memory effect is required which can be assured by only a few materials. PFA, for example, has a low memory effect but is stable only up to 100°C.

In order to achieve sufficient decomposition quality, pressure digestion is needed. Equipment is available for pressurized decomposition employing Teflon<sup>®</sup> and quartz vessels. Quartz vessels possess the lowest memory effects. Due to possible memory effects, Teflon<sup>®</sup> vessels can be used only if the PGE concentrations in the samples do not differ too much. Otherwise the samples have to be decomposed in different vessels adjusted to the order of concentration magnitude. Quantification of the vessel blanks is necessary in every case.

There are three technical principles of pressurized decomposition devices: First, a vessel (Teflon<sup>®</sup> or quartz) filled with the acids together with the sample can be introduced to a steel device which is then heated to up to 250°C. Second, vessels can be irradiated by microwave. In order to achieve a maximum quality of decomposition in a short time, the mixtures of acids have to be specially optimized to the matrix in this case.

Third, the quartz vessels may be mounted in a pressure-proof chamber. Before heating, the chamber is filled with high pressure nitrogen gas. This high pressure, together with temperatures of up to 320°C, ensures maximum decomposition quality (HPA = high pressure ashing), which is required for a subsequent voltammetric analysis. Lower pressure acid decomposition may supply sufficient decomposition quality for detection methods like AAS and ICP.

The amount of the subsample introduced into the acid digestion/ decomposition step has to be aligned with respect to the expected concentration level and to the size of the vessels. Typically, up to 0.5 g of soil, dust or organic matrix can be digested in vessels of up to 100 ml of volume.

Adjusting the appropriate acid mixtures is particularly sensitive prior to the voltammetric determination of Pt and Rh. Decomposition must be performed with a specially adapted mixture of nitric acid and hydrochloric acid [24]. Since any remaining nitric acid will interfere during the voltammetric measurement following the decomposition step, it needs to be carefully evaporated after adding additional sulphuric acid and hydrochloric acid. This is a critical step since platinum may be lost.

#### 3.1.1.2. Fusion

Fusion has mostly found applications in the analysis of geological materials. As opposed to fire assay, fusion describes high temperature digestion procedures in small crucibles leading to the formation of water-soluble PGE salts. The method is suitable for small samples, with sizes ranging from 0.25 to 1 g samples and is typically performed in a Na<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>- Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>O<sub>2</sub>-NaOH flux [31, 32].

The fusion in a Na<sub>2</sub>O<sub>2</sub> flux is usually performed with zirconium crucibles, while glassy carbon crucibles are recommended for a Na<sub>2</sub>O<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub> flux. For Na<sub>2</sub>O<sub>2</sub> fusion, the amount of sample is placed in a zirconium crucible together with about 5 times the amount of Na<sub>2</sub>O<sub>2</sub>. Fusion has been performed using a reducing flame or a furnace with temperatures up to 600°C. Mixing of the sample with the fusion flux and swirling the crucible during the fusion is important. Once the sample is fused into a bead, it is cooled down and dissolved by a drop-by-drop addition of water and 6M HCl (the dissolution can lead to a vigorous reaction and therefore, eye-glasses and suitable protection should be used). The solution is then taken into dryness and redissolved for analysis.

Potential drawbacks of fusion include the high salt content of the final solution and the possible introduction of contaminants. Fusion is therefore often followed by sample purification through co-precipitation, solvent extraction or ion exchange.

#### 3.1.1.3. Chlorination

Chlorination was developed as a means of pre-concentration for the determination of trace PGE and gold concentrations in geological samples. Chlorination involves the conversion of precious metals into water-soluble chloro-complexes by heating the samples in the presence of chlorine. It offers the possibility to handle large sample sizes of up to 250g [32].

Powdered samples are mixed with a small amount of sodium chloride and heated at 580°C in a current of chlorine gas. Separation of precious metal salts is performed by

dissolution of the salts in water or a weak HCl solution, followed by filtration of insoluble, chlorination resistant matrix components. Residues can be further digested by acid digestion or another digestion method. The method has been used in combination with ICP-MS with detection limits below  $1 \text{ ng g}^{-1}$  and could be used with other techniques depending on the sensitivity required [32].

The method has proved useful for native metals, natural alloys and sulphide minerals. However, some minerals such as silicates are resistant to chlorination and another digestion procedure would be required.

### *3.1.2. Separation and pre-concentration techniques*

A number of pre-concentration techniques have been developed for the enrichment of Pt metals. Among these are several ion-exchange techniques, the application of high performance liquid chromatography (HPLC) using various columns, several extraction techniques (liquid/liquid, solid), and electro deposition, amalgamation and fire assay methods. The main aspects of these different pre-concentration techniques are discussed in this section.

#### *3.1.2.1. Ion exchange procedures*

Platinum group elements are known for their unique complex chemistry in mineral acid solution. They form stable anionic chloro complexes, in contrast to most transition metals, alkali and alkaline earth metals forming weaker anionic or stable cationic complexes. Both the high affinity of the chloro complexes for strong basic anionic exchange resins and their low affinity for cationic exchange resins can be exploited for matrix separation. Several elution protocols have been investigated with respect to analyte recovery, matrix separation, low blank levels and separation among the different elements of the platinum group [17, 18].

Separation among the PGE into different solution fractions is desirable in terms of improved sensitivity since fewer elements can be analysed in the same or smaller volume of solution. Maintaining low procedural blank levels was found to be problematic (1) with elution protocols using concentrated, hot acids or (2) with sample solution containing HF, since in both cases the resin material is literally digested during elution [34]. As a key advance, ion exchange procedures offer reduction of the total dissolved solid content and pre-concentration accomplished within one step.

For determination of PGE by ICP-MS, ion exchange has been recognized as the method of choice for elimination of spectral interferences. However, non-reproducible loss or release of the analytes is often an unavoidable feature of these ion exchange preparation steps and recoveries have to be specifically addressed for each investigated sample type.

Quantification by isotope dilution ICP-MS is the most elegant procedure to circumvent the problem and has long been regarded as the most accurate means of measuring PGE concentrations in the low and sub  $\text{ng g}^{-1}$  level by ICP-MS [23].

No studies have been done of simultaneous chromatographic separation of PGE including Os, because Os can be easily lost by forming the highly volatile species,  $\text{OsO}_4$ , if oxidizing agents are present [18].

(a) *Cationic exchange*

The use of cationic exchange for PGE analysis has been extensively investigated. All studies employ a strong cationic exchanger resin. The anionic chloro complexes pass straight through cationic columns, whereas in diluted acids most other metals are quantitatively absorbed. PGE yields are very high especially when mixed organic-solvent acids are used. A drawback is that relatively large amounts of sample resin are necessary to absorb non-PGE metals. This implies lengthy cleaning of the resin with a large volume of clean acid. In addition, quantitative elution of PGE from the column requires relatively large amounts of eluent, which enhances the risk of elution of other metals that do not form strong cation complexes [35,36]. However, the major obstacle of the cationic exchange strategy is that it is difficult to obtain separation among the PGE. Approximately simultaneous elution of PGE from the cation resin is (1) limiting the opportunity for removal of potential interferences and (2) increasing the number of masses that must be measured from a single solution. Moreover, the separation from Hf and Zr is not effective which poses severe problems to subsequent ICP-MS and NAA analysis. These elements tend to form stable anionic complexes depending on sample and sample digestion procedure. The problem is especially associated with samples obtained by digestions using HF.

*Example of cation exchange elution protocol [34]*

Dowex AG 50 W-X8 (H<sup>+</sup> form, 200–400 mesh), a strong cation exchanger, is used as resin. The mesh size is selected to reduce flow rate through the column allowing better separation of the base metals from the PGE. The columns are packed with 4 mL (3.2 g) of resin and cleaned by passing 100 mL (25 bed volumes) of 6 M HCl through the columns before being repacked and equilibrated with 50 mL of the 0.6 M HCl matrix (Table VII).

TABLE VII. THE ELUTION PROGRAM FOR CATIONIC EXCHANGE

Step 1	0.6 M HCl
Step 2	0.75 M HCl
Step 3	1 M HCl
Step 4	2 M HCl
Step 5	3 M HCl
Step 6	4 M HCl
Step 7	6 M HCl

The PGE pass directly through the cation exchange resin. A 10 ng /g standard solution flushed with the above shown gradient elution of successive 5 mL washes has shown recoveries of nearly 100 % in the 0.6 M HCl fraction. However, when applied to rock samples, each sample is required to pass through 8 mL of resin (i.e. through the columns twice) in order to ensure adequate separation of the PGE from the matrix.

(b) *Anion exchange*

Anion exchange procedures are more widely used than the cation exchange approach [33]. All applications employ strong anionic exchanger resins for the determination of PGE. The selectivity of anion exchange is enhanced because the separation is governed

by the valance state and moreover by the possible formation of stable ion pairs between the chloro complexes and quaternary ammonium groups.

Several combinations of eluents are possible. As with cation exchange the separation from Hf and Zr is not effective, but can be overcome by the introduction of an HF-HCl step (see Table VIII) [38, 39]. Mo, V, Cr are also found to be problematic. The affinity of  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}$  to AG1-X8 resin is very high, with distribution coefficients ( $K_d$ ) > 1000, so stripping of these complexes requires anions with stronger affinity such as perchloric acid or concentrated nitric acid. In some studies hot 12 M  $\text{HNO}_3$  has been used for elution of Pd [38, 39]. In this elution step the resin is being literally digested. A negative implication of this, regarding the procedural blank levels, is that it is not possible to remove Pd-contaminations from the resin by the applied cleaning procedure. Moreover, additional unidentified interferences can be introduced in this step.

Another approach for efficient removal of PGE from the resin is complexation using thiourea or other equivalent complexing agent [19]. In other studies in-situ reduction of Ir has been applied to aid elution [38]. It is well known that Ir forms 2 stable chloro complexes,  $\text{IrCl}_6^{3-}$  and  $\text{IrCl}_6^{2-}$ , which show different affinity to the anion exchange resin. The former shows weak adsorption on the resin, but the latter shows strong adsorption. To achieve high adsorption, strong oxidizing agents, such as  $\text{Cl}_2$  gas and  $\text{Br}_2$  water are used.

TABLE VIII. SEPARATION STEPS OF THE OFF-LINE ION-EXCHANGE PROCEDURE [38] (The resin used for the Anion exchange was AG50W-X8 200–400 mesh)

Step		
a	5 mL	0.2 M HCl
b	5 mL	0.8 M $\text{HNO}_3$
	20 mL	0.1 M $\text{H}_2\text{SO}_3$ Reduction of Ir
c	10 mL	1 M HF-HCl      Removal of Hf, Zr
d	20 mL	2 M HCl      Elution of Ir
f	20 mL	6 M HCl      Elution of Pt
h	20 mL	4 M $\text{HNO}_3$ Elution of Ru/ (Re)
j	20 mL	14 M $\text{HNO}_3$ (hot)      Elution of Pd

The anion exchange procedure described in Table VIII has been applied to the analysis of geological RM (komatiite WITS-1) after acid digestion of 1 g sample in Carius tubes (furnace for 24 h at 210°C). After digestion the samples are submitted to chlorination in order to obtain for all PGE the highest oxidation state. In another study the elution program has been modified with respect to the on-column reduction by  $\text{H}_2\text{SO}_3$ , the chlorination step having been removed from the sample preparation procedure [40]. The modified procedure has been applied to Ir determination in geological samples and to Pd in geological reference material. Ir could be analysed analogously in the 2 M HCl fraction, however Pd is already eluted in the 4 M  $\text{HNO}_3$  fraction.

(c) HPLC

The use of mixed bed columns, providing both anionic and cationic functional groups has been evaluated for the determination of Pd in geological reference materials [34]. The method provides an on-line fast separation of the matrix elements from Pd for ICP-MS detection. The detection limits are higher compared to the off-line ion exchange procedures due to the low absolute sample intake (injection volume restricted to 100  $\mu\text{L}$ , due to limited capacity). Moreover, the instrumentation is very expensive.

A metal-free HPLC system (DX500, Dionex Corp., Sunnyvale, CA, USA) is used. The system is equipped with a mixed bed ion exchange column (IonPac CS5A, Dionex Corp., Sunnyvale, CA, USA) supplying a heterogeneous system, which allows both cation and anion exchange. Table IX summarizes the HPLC settings.

TABLE IX. HPLC OPERATING PARAMETER AND CHROMATOGRAPHIC CONDITIONS

HPLC column	Dionex CG5A-CS5A	Eluent A	H <sub>2</sub> O
Flow rate	1.2 mL min <sup>-1</sup>	Eluent B	500 mmol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>
Injection volume	100 $\mu\text{L}$	Eluent C	12 mmol L <sup>-1</sup> PDCA <sup>a</sup>
Oven temperature	45°C		100 mmol L <sup>-1</sup> CH <sub>3</sub> COOH
Makeup solvent	1% HNO <sub>3</sub>		100 mmol L <sup>-1</sup> CH <sub>3</sub> COONa
Makeup flow rate	1 mL min <sup>-1</sup>		pH = 4.5
Time	A	B	C
[min]	[%]	[%]	[%]
0.0	35	0	65
7.0	35	0	65
7.2	0	100	0
9.6	0	100	0
9.8	35	0	65
14.5	35	0	65

<sup>a</sup> 2,6-pyridinedicarboxylic acid.

With 2,6-pyridinedicarboxylic acid (PDCA), transition metals form very stable divalent or monovalent anionic complexes  $[\text{Me(II)(PDCA)}_2]^{2-}$  or  $[\text{Me(III)(PDCA)}_2]^-$ , therefore anion exchange is the predominant separation mechanism [41]. Since there is almost no interaction between  $\text{Rb}^+$ ,  $\text{Zr}^{4+}$ ,  $\text{Mo}^{6+}$  and PDCA, these elements are separated by cation exchange. The  $\text{H}^+$  ion concentration of the initial eluent suffices to elute the single charged  $\text{Rb}^+$ , the higher charged  $\text{Zr}^{4+}$  and  $\text{Mo}^{6+}$  elute only after switching to 500 mM  $\text{H}_2\text{SO}_4$ . For  $\text{Y}^{3+}$  anion exchange is governing the separation. The long retention time is caused by the formation of strongly retained  $[\text{Y(PDCA)}_3]^{3-}$ .

### *Quality assurance*

Separation procedures have to be checked in terms of separation efficiency, recovery and blank levels using standards (prepared as the samples) or reference material (commercial or in-house), which are prepared according to the sample preparation scheme (see Section 4).

#### 3.1.2.2. Co-precipitation

Co-precipitation is performed in order to separate the PGE from the host matrix and/or pre-concentrate the PGE in case of sensitivity problems. The technique may be applied to geological samples [42], environmental or biological samples. An appropriate digestion method ending up in a solution, which is suitable for the described co-precipitation method, has to be selected.

To collect the PGE a dilute Te/Se salt solution may be added to the PGM-containing solution. Reduction of Te/Se is achieved by adding  $\text{SnCl}_2$ . The precipitate is redissolved in  $\text{HNO}_3$  and can be measured using different techniques depending on the sensitivity, which is needed. A detailed procedure for Te co-precipitation is described in Ref. [32]. The sample has to be present in HCl ( $2\text{--}6 \text{ mol L}^{-1}$ ). For a sample size of 0.5 g with PGE levels from 5–4000  $\text{ng g}^{-1}$ , 2 mg of Te ( $1 \text{ mg L}^{-1}$  Te as  $\text{TeCl}_4$  in  $2 \text{ mol L}^{-1}$  HCl) are added. Precipitation of metallic Te is achieved by means of 10 mL of a  $\text{SnCl}_2$  solution ( $1 \text{ mol L}^{-1}$   $\text{SnCl}_2$  in 2 M HCl). Ru, Pd, Ir and Pt are determined by ID-ICP-MS in different reference materials.

A recently described technique uses mercury nitrate as co-precipitation reagent. Hg is reduced by formic acid and collects Pd quantitatively in urine, roots and dust samples after a high pressure decomposition step (see special application #7 in Ref. [4]).

Thiourea and thioacetamide may also be used as precipitants for the group concentration of Pt, Pd, Rh, Ir and Ru, making use of copper as a collector.

When using co-precipitation for enrichment, the recovery of the different PGE has to be evaluated carefully for the investigated matrix. If available, IDMS in connection with ICP-MS would be the best choice for getting reliable results. If IDMS is not available (which is certainly the case for the monoisotopic element Rh) standard addition should be applied for determination of the recoveries. The use of reference materials similar to the matrix of the sample is strongly recommended.

### 3.1.2.3. Extraction

#### (a) Liquid-liquid extraction (LLE)

PGE in solutions can be separated and concentrated from other elements by means of liquid-liquid extraction. Methyl isobutyl ketone (MIBK) in the presence of potassium iodide [43], dithizone in  $\text{CCl}_4$  [44], dibutylsulphide, tributyl phosphate and trialkylphosphine oxide are some of the common reagents [44]. The antipyrine derivatives of Pt, Pd, Ir and Os are used for their pre-concentration in chloroform [45]. Bis(2-ethylhexyl) sulphoxide (BESO) has a strong extraction ability towards Pd. Trace and macro amounts of Pd can be quantitatively and selectively extracted from acidic solutions ( $8 \text{ mol HNO}_3 \text{ L}^{-1}$ ) by BESO in toluene [46]. A method for selective extraction of Pd has been described in Ref. [47]. Pd is pre-concentrated by extraction from water at pH 3.5 with bismuth diethyldithiocarbamat in chloroform (aqueous/organic ratio 20:1). The organic phase is evaporated to dryness. The residue is irradiated for NAA.

$\text{OsO}_4$  and  $\text{RuO}_4$  can be selectively extracted with chloroform from solutions of mineral acids; this is an alternative to the distillation of the oxides.

As mentioned in the section above, for pre-concentration procedures method evaluation (i.e. the determination of procedural blank values, recovery factors, etc.) is highly important.

#### (b) Solid phase extraction (SPE)

SPE of PGE is based on liquid-solid extraction of PGE-complexes whose ligands have a high affinity to unpolar solid phase materials (i.e.  $\text{C}_8$  or  $\text{C}_{18}$  reversed phases). In this context several dithiocarbamates have been used as complexing agents, although their application is restricted to non-oxidising, weakly acidic or neutral solutions. Recently a more robust method using N,N-dialkyl-N'-benzoylthiourea (DEPT) as highly selective complexing agent has been described [58]. Pd is determined employing on-line column pre-concentration and GF-AAS. Quantitative and selective extraction out of a solution containing 6.5 % nitric acid and up to  $10 \text{ g L}^{-1}$  of matrix elements (Co, Ni, Cu, Zn, etc.) is demonstrated.

The procedure begins with the loading of the complexing agent onto a microcolumn ( $1.0 \text{ mm} \times 13.0 \text{ mm}$ ,  $10.2 \mu\text{L}$   $\text{C}_{18}$  material with a particle diameter of  $40\text{--}63 \mu\text{m}$ ). Subsequently the sample solution is moved onto the column. After complex formation, a wash step with nitric acid (6.5% v/v) is performed to remove interfering matrix constituents. The Pd complex and the excess ligand are then eluted with  $60 \mu\text{L}$  of ethanol and directly introduced into the graphite tube of the GF-AAS. Quantification is performed via internal calibration, meaning that the standards are running through the same procedure as the samples. For an injection (loop) volume of  $4.85 \text{ mL}$  a detection limit of  $13 \text{ ng L}^{-1}$  Pd has been reported. The detection limit is determined by the calibration graph method [59]. This is noteworthy, since this method yields more reliable values as quantifying detection limits by the three fold standard deviation of several blank determinations. The method is suitable for trace and ultra trace analysis in environmental and geological matrices as well as in medical samples. It is evident that the enrichment process can be performed by both, on-line and off-line procedures. The technique is also variable concerning the method of detection, which means that ICP-MS and CSV may be higher sensitive alternatives to GF-AAS.

### 3.1.2.3. Electrodeposition

Electrodeposition has not found wide distribution as a separation/preconcentration step for PGE determination. The use of electrodeposition requires the sample to be in liquid form. Electrodeposition of Pt on to a graphite tube prior to its determination by GF-AAS has been described by Beinrohr, et al. resulting in a LOD 0.3 ng Pt. Au has been separated from other elements in solutions of biological materials by electrodeposition onto a niobium cathode to be subsequently determined by RNAA [50].

### 3.1.2.4. Amalgamation

The reductive co-precipitation of trace and ultra-trace elements together with mercury followed by complete evaporation of the mercury enables a sensitive determination of Pd [4]. First, samples have to be decomposed with the aid of nitric acid and hydrochloric acid operating a high pressure asher at a temperature of 320 °C and a pressure of 130 hPa [4]. Subsequently, Pd and Au are separated from the matrix: The digested sample solution is heated together with mercury. From a droplet of metallic mercury containing enriched Pd and Au, Hg is evaporated on a quartz-glass target suitable as a sample carrier for TXRF [4].

### 3.1.3. Fire assay

Fire assay is the quantitative determination of metals in ores using heat and dry reagents. It is a digestion technique that can be applied to large (up to 50 g) samples of geological material and therefore is particularly useful for preconcentration of the PGE to provide a representative analysis and where good sensitivity is required. It involves the attack of the sample, usually but not exclusively a silicate, at high temperature with a reducing flux of sodium carbonate and sodium tetraborate, with extraction of the base metals in the silicate-borate slag, and concentration of the PGE into a collecting button, which is usually lead or nickel sulphide.

Fire assay is a reducing fusion, using a dry flux to render the sample molten at a reasonable temperature. Sodium carbonate is a basic reagent and provides a very viscous flux. Silica and sodium tetraborate are both acidic and the reaction of sodium carbonate with silica provides sodium silicate slag, with the evolution of carbon dioxide. Sodium tetraborate is used to lower the melting point of the flux so that fusion can be carried out at a reasonable temperature. The usual applications involve 10–50 g samples, where an equal volume of sodium carbonate and twice the mass of sodium tetraborate is added to the sample in a clay crucible. Complete fusion can be achieved in 1–2 h. The normal temperature of fusion is 1 000°C but for the digestion of chromitite it is necessary to use temperatures of up to 1 200°C and to use lithium tetraborate to ensure that a fluid melt is achieved.

Fire assay is generally confined to a few expert laboratories. However, it is not difficult for an analytical laboratory to develop fire assay capability with the correct specialized equipment and with adequate staff training. Expertise can be developed for particular applications, such as exploration soils or road dust, using the well known certified reference materials to demonstrate quality assurance. A good laboratory technician can be trained to develop the skills for pouring the molten slag into the cold iron mould, and the dissolution stage is simple wet chemistry. What is much more difficult is developing the skills to handle a wide range of geological samples types such as sulphides, carbonates and chromites, where the flux composition and quantities must be varied according to the matrix.

### 3.1.3.1. NiS collection

Nickel sulphide collection is the most commonly used method for preconcentration of all the PGE, whether followed by AAS, ICP-AES, ICP-MS or NAA. It can be applied to geological material with high PGE content or for environmental studies where low concentrations are to be measured. The preconcentration of the PGE by fire assay results in a high degree of purification which is of great advantage for NAA and for ICP-MS. It removes species that interfere with ICP-MS determinations, in particular Pb that is ubiquitous in the roadside environment.

Ni and S are added to the fusion flux in the ratio Ni/S of 1:0.7 to give a total button size of up to a few grams. It is essential that Ni produced by the INCO carbonyl method is used since it is the form of Ni free from high levels of PGE contamination. Provided that this Ni is used, the blank values are extremely low (0.06 ng/g Pt and Pd, 0.007 ng/g Rh). During fusion the PGE are quantitatively collected in the NiS button that is formed. The molten flux is poured into a cold iron mould to chill the glass and on cooling the NiS button is separated from the slag. The button can be analysed directly using NAA or LA-ICP-MS. Detection limits for direct NAA of the button are about 20 ng/g Pt, Pd and Os, 2 ng/g Rh, 0.2 ng/g Ir and 200 ng/g Ru. LA-ICP-MS gives detection limits of 8.3 ng/g Pt, 3.3 ng/g Pd, 1.3 ng/g Os, 5 ng/g Ru, 0.7 ng/g Ir and 1 ng/g Rh.

Normally the NiS button is crushed to form a fine powder and dissolved in concentrated HCl. The NiS dissolves with the evolution of H<sub>2</sub>S and the insoluble PGE sulphides remain undissolved. These sulfides are filtered off and analysed by NAA directly or dissolved in aqua regia for analysis by GFAAS, ICP-AES or ICP-MS. The PGE sulfides may be partially dissolved in the HCl and this may lead to losses of up to 20% of all the PGE. It is possible to re-precipitate the PGE using a tellurium co-precipitation method which requires the addition of Sn and Te solutions. The addition of Sn can have a detrimental effect on the gamma ray spectrum after neutron activation but is of advantage in ICP analysis.

### 3.1.3.2. Lead collection

Lead oxide is a basic flux and can be reduced to provide the lead for collection of Pt, Pd and Rh, which form as alloys in the lead button. Ir, Ru and Os are only partially collected. Separation of the button from the slag containing the unwanted elements is based on the large difference in the specific gravity of the two phases. The PGE are separated from the lead button by an oxidising fusion process called cupellation. The lead button is placed on a small cupel of magnesium and calcium phosphate and heated at above 900°C. The lead is partially evaporated as the oxide, but mainly percolates into the cupel. The gold-silver button that remains, which contains the PGE, is dissolved in acid. If necessary, silver is added at the cupellation stage to ensure that a button is formed. On cupellation, some of the Ru, Os and Rh are oxidized and lost.

Most measurements with lead collection are made with ores and concentrates, and alternative collectors are used where the danger of losses are more serious at lower concentrations. However, a very cheap screening technique has been used with a silver collecting button to analyse samples weighing between 10 and 30g [26]. The cost of analysis is very low and for exploration work the possibility of small losses may be outweighed by the ability to analyse very many samples.

### 3.2. Analytical methods for PGE determination

From the large array of analytical techniques that have been applied for PGE analysis the most promising and widely used such as gravimetry, volumetry, UV/VIS spectrometry for high level concentrations, ICP-AES, AAS and XRF for medium to low level concentrations, and NAA, ICP-MS and electro-analytical techniques for the ultra low level concentrations in natural biological systems are discussed below.

#### 3.2.1. Gravimetry, volumetry, UV/VIS absorption spectrometry

In this section the applicability of classical analytical methods (i.e. gravimetry, volumetry) and UV/VIS absorption spectrometry will be described. The three methods need relatively simple and low-cost equipment and provide fast and easy determination of PGE at higher concentration ranges (upper  $\mu\text{g g}^{-1}$  to per cent range). From the analytical point of view, the three methods have in common that — after sample preparation — the PGE must be present in a defined ionic state. The quantitative transfer of the analytes into the ionic state indicated by a method is a prerequisite for their selective and accurate determination. For decomposition and pre-concentration of PGE in various matrices, see 3.1.1.

##### 3.2.1.1. Gravimetry

Gravimetric methods can be used for accurately checking and confirming the concentration of PGE-rich standard stock solutions and other PGE-rich samples from fields like jewellery or pharmaceutical industry. In order to obtain reliable results, PGE concentrations should range around 0.1% and above [37]. The metals can be quantitatively precipitated with an appropriate reagent (e.g. Pd with 2-hydroxy<sup>-1</sup>-acetonephthone oxide [51]) or reduced to their metallic state using a reduction agent (e.g. noramidopyrine for Pt, Pd, Ru, Rh [52]). After precipitation, the residues are dried and weighed. It is evident that losses during precipitation, cleaning of the residues and drying are the main sources of error. Assessment of recovery rates via standard addition and utilization of CRM are the most important QA-tools for evaluation of gravimetric methods.

##### 3.2.1.2. Volumetry

A variety of volumetric methods using chemical and physico-chemical endpoint detection for PGE contents of 0.1 % and above have been described in the last years. In the following section two selected examples for determination of Pd will be presented.

###### (a) Complexometric determination of Pd in presence of other PGE [64]

The acidic solution should contain about 50 mg Pd. Matrix elements and other PGE do not interfere.

- 10 mL  $\text{Na}_2\text{-EDTA } 0.1 \text{ mol L}^{-1}$  are added.
- pH 3 is adjusted by ammonium acetate.
- 100 mg xylenolorange indicator are added.
- back-titration of excess EDTA by a thorium nitrate solution ( $0.1 \text{ mol L}^{-1}$ ).
- end-point is reached when colour changes to red.
- $1 \text{ mL Na}_2\text{-EDTA } 0.1 \text{ mol L}^{-1} = 10,642 \text{ mg Pd}$ .

*(b) Determination of Pd in solutions free of matrix elements and other PGE*

Hexadecylpyridiniumchloride (HDPCl) is used as a precipitant for potentiometric titration of Pd. The acidic solution should contain about 6 mg Pd.

- 40 mL of a solution containing  $0.5 \text{ mol L}^{-1}$  HCl and  $0.02 \text{ mol L}^{-1}$  NaCl are added.
- the solution is titrated to the end-point with  $0.02 \text{ mol L}^{-1}$  HDPCl using an ion surfactant electrode and an Ag/AgCl reference electrode.
- $1 \text{ mL HDPCl } 0.02 \text{ mol L}^{-1} = 1.0642 \text{ mg Pd}$ .

### 3.2.1.3. UV/VIS absorption spectrometry

UV/VIS spectrometry for the determination of PGE is widely used since it is a cheap, relative selective and sensitive method. In recent years various organic reagents, forming UV/VIS-active complexes with PGE, have been synthesized. In an excellent review, Yi Bin Qu lists about 20 UV/VIS spectroscopic methods and refers to several other published reviews on this topic. Most of the methods are suitable for the determination of one or two PGE in special matrices with limits of detection in the  $\mu\text{g g}^{-1}$  range.

### 3.2.2. ICP-AES

Optical ICP is a relatively easy method for the analysis of PGE. The decomposition quality required prior to analysis is much lower compared with other methods. During the decomposition step it is necessary to convert the metals into solution. Alternatively, a stable suspension may also be analysed if this fits to the architecture of the nebulizer and if the deposition of salt on the torch is controlled. Anyway, it is necessary to quantify the analytical recovery in the range of detected values, particularly, if Pd is analysed in a silica containing matrix. The detection sensitivity is related to the detection technique operated: simultaneous instruments can analyse lower concentrations due to the fact that smaller volumes are needed.

The higher the volume uptake by the system, the higher dilution is needed, the worse is the detection sensitivity with respect to the original matrix. Consequently, reported detection limits are varying [19]: between 54 and 110  $\mu\text{g/L}$  for Pt, Pd, Ru, Ir and Rh, while Os is detected with a limit of 0,7  $\mu\text{g/L}$ . Other researchers have been reported a detection limit of 10  $\mu\text{g Pd/L}$  [64]. The same concentration range has been reached for Pt in a study employing a simultaneous ICP-AES. Application, consequently, is limited to matrices with high PGE concentrations: Mined ores containing between 0.01 and 1000 mg/kg Pt may be analysed by ICP-AES after acid decomposition. Pt has been quantified by ICP-AES on catalytically active membranes of fuel cells after pressurized acid digestion.

However, coupled to a preconcentration method detection limits may be considerably lower [19]. For example, if Pt and Pd are enriched from a 30g sample by a fire assay, subsequent ICP-AES analysis is possible down to 10  $\mu\text{g/kg}$  for both metals [63].

### 3.2.3. Atomic absorption spectrometry

For many years both flame-AAS (FAAS) and graphite furnace-AAS (GFAAS) have been popular instrumental methods for the determination of the elements [18, 37]. Work involving FAAS includes the determination of Au in geological materials and of Pt in natural water.

GFAAS has been used for determination for precious metals in related materials, Au in related materials and rocks, Pt, Pd and Au in vegetation, and Pt in environmental samples and water [18]. Most applications involve separation and pre-concentration prior to AAS determination, because of the complex nature of interferences and the low concentration of the analytes. These are vital steps in many procedures, owing to the very low concentration, the complexity of the matrix and the refractory nature of some metals. Among the FAAS methods developed, the determinations for Ag, Au, Pd and Rh are relatively sensitive. Generally, the sensitivity of the elements of the platinum group in GF AAS depends largely on their melting points [54]. Table X summarizes the analytical characteristics for determination of PGE by FAAS.

TABLE X. SUMMARY OF THE ANALYTICAL CHARACTERISTICS FOR DETERMINATION OF PGE BY FAAS [19]

Element	Flame type	Detection limit ng mL <sup>-1</sup>	Wavelength nm	Interferences
Pt	Air-acetylene (lean flame)	100	265.9	Complex cationic interferences (suppressed by 1% La)
Pd	Air-acetylene (lean flame)	20	244.8	Several cationic interferences; 1% La suppresses these effects
Rh	N <sub>2</sub> O-acetylene (reducing)	10	343.5	Complex cationic interferences (suppressed by 1% La); 3 % NaSO <sub>4</sub>
Ru	Air-acetylene (reducing)	100	349.9	No significant cationic interferences in dilute solutions
Ir	Air-acetylene (reducing)	600	208.9	Diverse interferences. Minimal cationic interferences
Os	N <sub>2</sub> O-acetylene (reducing)	100	290.9	Minimal cationic interferences in dilute solutions

Pt is best determined in a sharp, oxidizing air-acetylene flame. It exhibits a multitude of analytical lines. The best characteristic concentration of around 1 mg/L is obtained at the 265.9 nm line. Inter-elemental effects in the presence of other noble metals can be eliminated by adding 10 g/L each of Na and Cu, which at the same time was found to enhance sensitivity of Pt determination by 50%. Alternatively, 5 g/L of Li or 5 g/L each of Cu and Cd as buffer can be added. Another approach for elimination of interferences is the use of the nitrous oxide-acetylene flame, however at the expense of sensitivity [54].

The determination of Pt by GFAAS is straightforward, although the sensitivity is rather low. A pyrolysis temperature of 1300°C can be applied. Characteristic masses of 100 pg and 200 pg are reported for longitudinally-heated atomizer with atomisation temperatures of 2650°C and transversely-heated atomizer and 2200°C, respectively [54].

Rh can be determined in the nitrous oxide-acetylene flame with a characteristic concentration of 0.8 mg/L at the 343.5 nm resonance line. A sharp, fuel-lean air-acetylene flame exhibits markedly better sensitivity, but substantial matrix effects must be expected [54].

Since the melting point of Rh of 1970°C is not especially high, it can be determined relatively well by GFAAS. The characteristic masses are 10 pg and 24 pg depending on the heating of the atomizer. Pyrolysis temperatures of 1300°C and atomization temperatures of 2400°C are reported. However, inter-elemental interferences with the other noble metals have been observed due to the formation of alloys. Consequently it is recommended to separate and pre-concentrate the analyte.

Ru can be determined in the air-acetylene flame with a characteristic concentration of 0.7 mg/L and in the nitrous oxide-acetylene flame with a characteristic concentration of 2.5 mg/L at the 349.9 nm resonance line. Different reagents were found to reduce interferences and enhance sensitivity; e. g. addition of La 20 g/L and 1 mol/L HCl, addition of mixture of 5 g/L Cu and 5 g/L Cd as the sulphates. Owing to its relatively high melting point of 2310°C, Ru can only be measured with typical absolute amounts of 31 pg and 45 pg depending on longitudinal or transversal heating [54].

Pd can be measured in a very sharp fuel-lean air acetylene flame with a characteristic concentration of 0.15 mg/L. The analytical lines at 247.6 and 244.8 nm exhibit approximately the same sensitivity. Different strategies can be applied for elimination of interferences, addition of Na and Cu (10g/L each), addition of Li (5 g/L), or addition of Cu and Cd (5 g/L each). Pd can be determined by GFAAS in a longitudinally-heated atomizer with a characteristic mass of 22-24 pg at an atomisation temperature of 2650°C. For a transversally-heated atomizer the parameters are 2200°C and 50 pg [54].

The determination of Ir by GFAAS is hampered by substantial interferences from the ubiquitous elements present in environmentally relevant samples: Ca, Fe, K and Na. Hence separation and preconcentration by ion exchange, extraction or sorption is an absolute prerequisite. Ir can only be atomized from the tube wall in a longitudinally heated atomizer at a temperature of 2650°C and characteristic mass of 250 pg. The transversely heated atomizer is slightly better; it can be used at 2400°C and 230 pg [54].

Despite its refractory character, Os can be determined by GFAAS. However, it is among the elements exhibiting the poorest sensitivity. Due to the volatility of the tetroxide a pyrolysis temperature in excess of 200°C cannot be applied, making a determination in the presence of higher concentrations of concomitants more difficult. To date a modifier that could stabilize Os has not been described [54].

#### 3.2.4. XRF analysis

Preparation for XRF is simple because samples can be analysed in the solid or liquid states. Therefore air filters or samples of metals and alloys can be analysed directly, while soils and sediments can be prepared as pressed powders. Energy-dispersive XRF (ED-XRF) is widely used in environmental and industrial applications because it is applicable to a wide range of elements over a large dynamic range. However, the use of total reflection XRF (TXRF) is increasing, particularly because it has the advantage of being more sensitive than ED-XRF, allowing for ultratrace analysis. Because only small (or dilute) samples are required,

interferences are minimized. It has been applied to the determination of trace elements in drinking water, airborne particulates, plants and soils [66].

Surprisingly, there appear to be few examples of where XRF has been applied to PGE analysis in the published literature. However, it is used in the minerals industry for the assaying of ores [17], mattes and metal alloys, although the work is generally not published. XRF has been applied to the analysis of catalytic converter material [12], which was crushed and milled to <0.063 mm. The analysis resulted in an initial mean bulk concentration of 2045 mg/kg Pt and 420 mg/kg Rh, with an elemental ratio of 5:1. In-vivo XRF has been used to determine the uptake and retention of platinum in patients treated with cis-platin for tumour therapy of patients. A roentgen apparatus was operated at 155 kV and 25 mA, in conjunction with a high-purity germanium detector arranged to minimize scatter. This system could detect down to 8 mg/kg of Pt, with a measuring time of 30 min and an organ depth of 4 cm.

### 3.2.5. Inductively coupled plasma-mass spectrometry

The coupling of inductively coupled plasma to mass spectrometry was first realized in the late 1970s. Since the development of ICP-MS, the potential of this technique for the determination of PGE in geological, biological and environmental samples has been clear. ICP-MS is based on the vaporisation, atomisation and ionisation of a sample in a plasma for subsequent mass spectrometric analysis (Figure 1). The plasma is a very efficient ion source and provides the technique with a high sensitivity allowing the determination of most elements at trace concentrations.

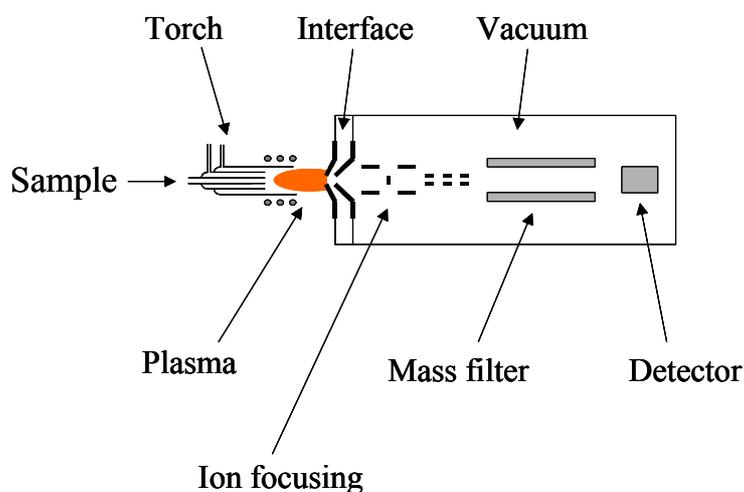


FIG. 1. Cross section of a quadrupole-ICP-MS instrument.

ICP-MS typically employs an argon plasma. Argon is supplied through a torch with three concentric gas flows. The main gas flow provides Ar to the plasma, the auxiliary gas flow controls the position of the plasma and pushes it away from the torch, thereby preventing it from melting, and the central channel presents the sample to the plasma. The plasma is ignited by a short electric discharge and is maintained by an electromagnetic field generated by a copper load coil to which a radio frequency is applied. In the electromagnetic field, electrons are accelerated and their collision with Ar atoms and further collisions of Ar atoms results in the formation of a plasma.

Once introduced into the plasma, the sample is vaporized, atomized and ionized. The ions formed are then extracted into a mass spectrometer. Ion extraction is critical to ICP-MS with ions being transferred from high temperature and atmospheric pressure plasma into a mass spectrometer operating at room temperature and under vacuum. The interface is composed of two successive cones (the sampling cone and the skimmer) with millimetre orifices through which the ions are extracted from the plasma. After the interface, ions are focused through ion lenses and introduced into the mass filter where they are separated based on their mass-to-charge ratio ( $m/z$ ). The most common mass filter is a quadrupole, which consists of four metallic or metallized rods suspended parallel to a central axis and with opposite pairs connected together. Direct current and radio frequency voltages are applied to each pair. The ions to be analysed are introduced along the axis. For a given voltage, only ions with a specific  $m/z$  ratio will have a stable trajectory and emerge at the other end of the quadrupole, where they are detected. Other mass filters used with an ICP include sector field and time-of-flight mass spectrometers.

The sample can be introduced into the plasma as gas, micro droplets or solid micro particles. Different sample introduction techniques can be used for this purpose. When liquid samples are analysed, a nebulizer has to be used to form the droplets. A range of nebulizers exists including pneumatic, ultrasonic and micro concentric, each one having its own advantages. In the case of solid samples, the sample is converted to micrometer sized particles or vaporized. Laser ablation or electro thermal vaporization are examples of introduction techniques for solid samples.

#### 3.2.5.1. Interferences in ICP-MS

Interference is a major problem in the determination of trace elements by ICP-MS. Two different interferences can be distinguished.

- Spectral interference, which occurs when several ions have the same or a similar mass-to-charge ratio and are not differentiated by the mass filter.
- Non-spectral interference or matrix effects.
- Spectral interferences can further be divided into three different types: isobaric overlap, polyatomic ions and double charged ions. The isotopic pattern of elements is well known and as a result, spectral interferences are easily predicted.
- An isobaric overlap occurs when two elements have isotopes of essentially the same mass. In principle, isotopic overlaps can easily be corrected using the isotopic pattern of the interfering element and the signal of one of its isotopes, providing that it is not subject to interference.
- Reactions in the plasma and ion extraction can lead to the formation of polyatomic ions, including argides and oxides, and double charged ions. Ar, O and N are the dominant ions in the plasma and may combine with each other or with other elements to form polyatomic ions. These polyatomic ions can have the same mass-to-charge ratio as the element to be determined, resulting in spectral overlap. Other elements present in solvents and acids, such as Cl and N, also participate in the formation of polyatomic ions for solution analysis.
- Most ions produced in the plasma are singly charged. However, double charged ions can form when the second ionisation energy of an element is lower than the first ionisation energy of Ar. The mass-to-charge ratio of these ions is half the ratio for single charged ions and therefore, interference might occur if an element has to be determined at this mass-to-charge ratio.

The main spectral interference in the determination of PGE by ICP-MS is listed in Table XI. These include argides, oxides and doubly charged species.

TABLE XI. MOST COMMONLY USED ISOTOPES IN THE DETERMINATION OF PGE BY ICP-MS, INTERFERENCE AND THE INSTRUMENTAL RESOLUTION REQUIRED FOR THE SEPARATION OF THE ANALYTE FROM THE INTERFERENTS

Element	Interfering species	Minimum resolution required ( $\Delta m/m$ )
<sup>103</sup> Rh	ArCu <sup>+</sup>	8040
	ArZn <sup>+</sup>	10100
	Pb <sup>2+</sup>	1248
	SrO <sup>+</sup>	102900
	RbO <sup>+</sup>	147000
<sup>105</sup> Pd	ArCu <sup>+</sup>	7300
	YO <sup>+</sup>	27600
	SrO <sup>+</sup>	1000000
	RbO <sup>+</sup>	28400
<sup>195</sup> Pt	HfO <sup>+</sup>	8100

There are several approaches to reduce spectral interferences, including the use of a sector field instrument with a sufficient mass spectral resolution, matrix separation prior to analysis, alternative sample introduction systems and mathematical correction.

Interferences can be corrected mathematically by estimating the contribution of interfering species to the PGE signals through the analysis of standard solutions [55]. Corrections can be calculated through equations 1–3.

$$I_{Pt} = I_{Pt,s} - (I_{Hf,s} \times R_{HfO,Hf}) \quad 1$$

$$I_{Pd} = I_{Pd,s} - (I_{Cu,s} \times R_{ArCu,Cu} + I_{Y,s} \times R_{YO,Y} + I_{Sr,s} \times R_{SrO,Sr} + I_{Rb,s} \times R_{RbO,Rb}) \quad 2$$

$$I_{Rh} = I_{Rh,s} - (I_{Cu,s} \times R_{ArCu,Cu} + I_{Pb,s} \times R_{Pb^{2+},Pb} + I_{Sr,s} \times R_{SrO,Sr} + I_{Rb,s} \times R_{RbO,Rb}) \quad 3$$

Where for equation 1:  $I_{Pt}$  is the corrected Pt intensity;  $I_{Pt,s}$  is the apparent Pt intensity in the sample;  $I_{Hf,s}$  is the Hf intensity in the samples;  $R_{HfO,Hf}$  is the ratio of  $HfO^+/Hf^+$  determined previously in Hf containing standard solutions. The same nomenclature applies to Equations 2 and 3.

Pt and Rh can generally be determined accurately providing that the interference ratios are measured and that the influence of the interfering species on the signal of the element of interest is controlled carefully. The determination of Pd is more difficult and remains a challenge in most samples.

The successful analysis of PGE in environmental samples is primarily dependent on the level of spectral interferences in the matrix and it would be preferable to overcome these, rather than correct mathematically. Mass spectral interference can be avoided if sufficiently

high resolution is applied. ICP-MS instruments using a sector field mass spectrometer can achieve resolutions up to 10000 ( $\Delta m/m$ ). Table XI gives the minimum resolution required to separate interferences from the PGE signal. While interference from HfO on  $^{195}\text{Pt}$  can be avoided at a resolution higher than 8100 ( $\Delta m/m$ ), interferences remain for Pd and Rh. At a resolution of 10102 ( $\Delta m/m$ ), SrO and RbO still interfere with the determination of  $^{103}\text{Rh}$ , while YO, SrO and RbO interfere with the determination of  $^{105}\text{Pd}$  [56]. However, a loss of sensitivity results from the application of a high resolution and therefore, mass spectrometers are usually operated in the low resolution mode with matrix separation or mathematical correction [57].

Non-spectral interferences are more complex and less understood. They include signal suppression or enhancement effects and physical effects caused by dissolved solids. Non-spectral interferences can be overcome by the use of an internal standard that closely matches the properties of the analyte.

### 3.2.5.2. Quadrupole and interference correction

PGE have been determined in acid digested road dust by means of quadrupole ICP-MS with mathematical correction of interference using equations given in Section 3.2.5.1 [58]. A careful control of interference and correction is required to ensure good quality of the results and results with too high interference should be discarded. The method has been successfully applied to the determination of Pt and Rh, while results for Pd were only considered indicative.

### 3.2.5.3. High resolution and IDMS

Mass spectral interference can be avoided if sufficiently high resolution is applied. However, while the use of a sector field instrument provides sufficient resolution for the interference free determination of Pt, the resolution required for the determination of Pd and Rh exceeds that of commercial instruments and therefore, either matrix separation or interference correction should be applied [56].

While sector field instruments provide better ion transmission and focusing compared with quadrupole instruments, the major drawback associated with a high resolution is a loss of sensitivity resulting from narrower slits in the mass spectrometer and therefore most studies have used sector field instruments in the low resolution mode with matrix separation or interference correction [57]. Matrix separation includes sample introduction systems using a desolvation membrane, which enables the removal of oxide interference and therefore, the interference-free determination of platinum [58].

Online and offline matrix separation has recently been applied to the determination of Pd by ICP-SFMS [58]. Online matrix separation was performed using an ion chromatographic column coupled to ICP-MS using a microconcentric nebulizer and a cooled spray chamber. Off-line matrix separation was through ion exchange. For both approaches, quantification was by isotope dilution mass spectrometry (IDMS). The method is based on spiking the sample with a solution, which has an altered isotopic pattern. This avoids recovery problems in the matrix separation and provides a highly precise quantification method.

#### 3.2.5.4. Laser ablation-ICP-MS

Laser ablation-ICP-MS enables direct trace element measurement in solid environmental samples. While sample preparation is kept to a minimum, calibration is a major difficulty in LA-ICP-MS since it is based on the preparation of solid, matrix-matched standards [58].

A method has been developed for the LA-ICP-MS determination of PGE in road dust. The method is based on the use of uncontaminated road dust, which is collected before the introduction of catalysts and spiked with PGE, both as solution and as solid certified reference material (NIST 2557). These samples with known PGE concentrations are then used to calibrate the instrument. The same principle can be applied to standard addition in the sample to be analysed.

All samples are mixed thoroughly and pressed without binder. Samples are then placed in the ablation cell and the laser is used to scan across the surface, while recording the signal with the ICP-MS. The method allows the determination of Pd, Pt and Rh with estimated detection limits in the lower  $\text{ng g}^{-1}$  range. Interferences were controlled by measuring the isotope or concentration ratios in the model samples. The ablation of a dry sample is known to result in lower oxide formation due to lower oxygen concentration compared with solution analysis. Therefore, interference of HfO on Pt determination is not a problem when using LA-ICP-MS. The method also enables the determination of Rh, while Pd is found to be interfered when low concentrations have to be determined.

#### 3.2.6. *Electro-analytical techniques*

The improved equipment for electrochemical analysis, which is still quite inexpensive (compared to ICP-MS-, ICP-AES or AA-spectrometer), has renewed the interest in these techniques. Efforts have been made to overcome interference and sensitivity problems. Electro-analytical techniques have found a wide range applications not only for typical elements of electrochemistry such as cadmium or copper. Also for the determination of PGE, a variety of different methods have been described in literature, some of which are mentioned here [59].

Amperometric titration has been described for the determination of Ruthenium(IV) in Cu-based sludge and Ni concentrates using 8-quinolineethiocarboxylate in 1-2 M HCl and 2 polarized electrodes [60]. Adsorptive stripping voltammetry has been used according to Ref. [61] for the determination of Pt (II) and Ru(III) in a solution containing 1-(2-pyridylazo)-2-naphthol of pH 9.3 with LOD of around 65 ng/L for Pt and 65 ng/L for Ru. The most sensitive method for the determination of platinum using the catalytic effect of the formazone complex with platinum in  $\text{H}_2\text{SO}_4$  medium at a static mercury-drop electrode requires completely decomposed solutions without residual organic carbon or other surface active components. This can either be achieved by UV-irradiation [62] or high pressure ashing (HPA) with subsequent removal of the interfering nitric acid, depending on the sample type [62, 63]. A further improvement of this system, slightly modified, allows the simultaneous determination of platinum and rhodium at the pg/mL-range and below [62]. These two systems have gained wide spread attention in the determination of Pt and Rh in various environmentally related and technical samples. Other less sensitive systems are described for the determination of rhodium in ore concentrates, slags or anodic mud [63].

### 3.2.7. Neutron activation analysis

Activation analysis, in general, is a method of elemental analysis based on the activation of a stable nuclide to an unstable radionuclide [44, 66]. The mode of decay of the product radionuclide is used to identify the target element, and the activity of the product can be used to calculate the original concentration of the element. There are several activation analysis methods, characterized by the source of activation, such as charged particles, neutron or photon activation. Neutron activation is the most widely used activation method, principally because neutrons can penetrate a thick target and hence it is a bulk method, in contrast to photon or charged particle activation, which are surface techniques. Elements are activated by thermal, epithermal or fast neutrons. The PGE produce at least one radionuclide on interaction with thermal neutrons and the resulting radionuclides decay with half lives ranging from seconds to years.

NAA laboratories generally use a nuclear reactor to provide a high flux of thermal neutrons. Irradiation devices give access to a constant flux of thermal neutrons for the required irradiation time, from a few seconds to several weeks, to generate sufficient activity in the sample for detection and measurement. The analysis of the radionuclide will depend on its mode of decay. A single element target, with only one radioactive product, can be detected directly for its beta emissions but it is usually necessary to separate out the element of interest to measure the activity from a particular radionuclide in the presence of others. Gamma ray emissions from the PGE are easily identified in the presence of other emitters using high resolution spectrometry with a semiconductor germanium detector. The gamma ray spectrum from a typical environmental or industrial sample may contain peaks at over one hundred energies, all readily resolved from one another using sophisticated software, which can be used on a standard personal computer.

The normal programme of irradiation for the PGE starts with a short irradiation, for example 5 min in a thermal neutron flux of  $10^{16} \text{ m}^{-2} \text{ s}^{-1}$ . The sample is allowed to decay for 5 min and counted for  $^{104\text{m}}\text{Rh}$  at 51 keV and  $^{109\text{m}}\text{Pd}$  at 188 keV. This is followed by a longer irradiation, for example 10 h in a thermal neutron flux of  $10^{16} \text{ m}^{-2} \text{ s}^{-1}$ , and then counted after an overnight (16 h) decay and again after 5 days. This allows the optimized detection of  $^{109}\text{Pd}$  at 88 keV, Pt as  $^{199}\text{Au}$  at 158 keV,  $^{192}\text{Ir}$  at 316 and 468 keV,  $^{103}\text{Ru}$  at 497 keV and  $^{191}\text{Os}$  at 129 keV (Table XII).

If the PGE are present at high concentrations it is possible to use instrumental NAA to measure samples such as catalysts containing the PGE on silicates, pharmaceuticals containing PGE, stable tracers, and even iron meteorites. The only significant nuclear interference is the production of  $^{199}\text{Au}$  via the  $(2n,\gamma)$  reaction on  $^{197}\text{Au}$ , which is also used to determine Pt via activation of  $^{198}\text{Pt}$  to  $^{199}\text{Pt}$ , followed by decay to  $^{199}\text{Au}$ . The interference is significant in high flux reactors and appropriate corrections should be made. The main interfering radionuclides are those originating from nuclear reactions on Ti or Ca, appearing as  $^{47}\text{Sc}$  close to the Pt peak of  $^{199}\text{Au}$  at 158 keV. The detection limits for direct analysis of geological material are restricted by the interfering background from elements such as Al, Si, Na and Sc. These can be removed using a pre-concentration stage or by using a post-irradiation separation. Fire assay has been used as a pre-concentration step and then the NiS button containing the PGE has been irradiated directly for gamma ray spectrometry. This provides a detection limit that is adequate for many exploration and industrial applications and is even sufficient for road dust in an urban environment: 20 ng/g Pt, Pd and Os, 2 ng/g Rh, 0.2 ng/g Ir, and 200 ng/g Ru.

TABLE XII. SELECTED NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF PLATINUM ELEMENTS

Element	Abundance of target nuclide	Nuclide	Half life	Cross-section	$\gamma$ -energy [keV]
Ru	31.6 %	<sup>103</sup> Ru	39.6d	1.3 ± 0.15 b	497.1
Rh	100 %	<sup>104</sup> Rh	4.35m	11 ± 1 b	51.4, 555.8
Pd	26.7 %	<sup>109</sup> Pd	13.5h	12 ± 2 b	88.1
Os	26.4 %	<sup>191</sup> Os	15.3d	13 ± 0.3 b	64.0, 129.4
Ir	37.4 %	<sup>192</sup> Ir	74.3d	924 ± 53 b	316.5, 468, 308.4, 296,
	62.6 %	<sup>194</sup> Ir	19.4h	112.5 ± 7.5 b	328.5, 293.6
Pt	7.2 %	<sup>199</sup> Pt	30.8m	3.7 ± 0.2 b	542.7, 317,
	7.2%	<sup>199</sup> Au	3.13d	3.7 ± 0.2 b	158.4, 208.2

Radiochemical separation has a number of benefits including the ability to add a stable tracer, which also acts as a carrier. This allows the analyst to determine the recovery of the radionuclides and hence correct for losses during the separation stage. Once the interfering activities have been removed from the samples, the sensitivity of neutron activation analysis provides a powerful tool for analysing geological, biological and environmental systems. Very small samples, including blood samples, air particulates and separated mineral phases can be analysed to determine ng/g concentrations of the PGE using radiochemical separation techniques such as ion exchange, solvent extraction or precipitation. The recovery can be determined from the stable tracer added at the start of the procedure, using gravimetric analysis or by re-irradiation to activate the stable PGE for determination by instrumental NAA.

### 3.3. Case studies/special applications

The following methods have been used for the determination of precious metals in geological materials. The determination of  $\mu\text{g g}^{-1}$  and  $\text{ng g}^{-1}$  amounts of Ru, Rh, Pt, Ir, Pd, Ag and Au is accomplished by attacking the samples with HF and aqua regia, removing the interfering elements with a cation exchange resin and measuring in a simultaneous multi-element graphite-furnace atomic absorption spectrometer equipped with a Zeemann-effect background correction device. A GFAAS method is applied for the determination of Pt, Pd, Rh, Ir and Ru in chromite ores using a modified NiS fire assay pre-concentration procedure in which  $\text{CaF}_2$  is added to increase the flux temperature. Among the pre-concentration techniques for the determination of precious metals in metallurgical intermediate products are the following: synergistic extraction of Pd (in copper anodic slime) with quinolin-8-ol and TBP in  $\text{CHCl}_3$  and back-extraction with dilute HCl containing thiourea; extraction of Pt and Pd in sulphate solutions with alkyylaniline hydrochloride and petroleum sulphide in toluene and measuring in the organic phase.

#### 3.3.1. Determination of PGE in precious metal materials by means of ICP-AES

Instruments based upon inductively coupled plasmas as atomisation and ionisation sources for analytes have been applied to the determinations of precious metals in a variety of

matrices [65] (Table XIII). ICP-AES has been used for many years, while applications of ICP-MS are of more recent origin. Many studies have been concentrated on the determination of impurities in fine precious metals and their alloys. Attention has also been paid to the determination of these metals in ores and materials of industrial importance.

TABLE XIII. SUMMARY OF PGE CONCENTRATION LEVELS DETERMINED IN MATTE LEACH RESIDUES, HIGH-GRADE CONCENTRATE, MATTES, FLOTATION CONCENTRATE, TAILINGS AND FEED MATERIALS [65]

Materials	Approximate concentrations of total precious metals [g.t <sup>-1</sup> ]
Concentrates	250,000–450,000
Feed materials	2–8
Flotation concentrates	50–300
Mattes	1500–2000
Matte leach residues	250,000–650,000
Tailing	0.5–2.5

ICP-AES is used on a routine basis for the PGE analysis in these samples. Sample preparations involve fusions and dissolutions in acid depending upon the sample type (see Table XIV) and the concentration of the PGE. Sc is used as an internal standard [65].

TABLE XIV. PREPARATION PROCEDURES FOR PGE ANALYSIS BY ICP-AES

Sample type	Preparation procedure
Matte leach residue and high grade concentrate	Fusion of 0.5 g sample with 5 g of sodium peroxide, leaching the melt in aqueous solution of HCl and HNO <sub>3</sub> . Dilution to 500 mL (Sc concentration 50 mg/L)
Mattes	Treatment of 10 g sample with NH <sub>4</sub> Cl-HCl for 1 h. Treatment of residue with H <sub>2</sub> O <sub>2</sub> -HCl-HF mixture Evaporation to dryness Treatment of the residue with HCl Filtration (retain the filtrate 1) Residue in Zr crucible at 450°C Fusion with Na <sub>2</sub> O <sub>2</sub> Leaching the melt with filtrate 1 Evaporation to 25 mL Dilution to 50 mL (Sc concentration 50 mg/L)
Flotation concentrate, tailings and feed materials	NiS fire assay  (Sc concentration 50 mg/L)

The PGE are measured according to the operating conditions listed in Table XV [65]:

TABLE XV. OPERATING PARAMETER FOR THE ICP-AES

Flow rates	
Plasma gas (L min <sup>-1</sup> )	19, Ar
Carrier gas (L min <sup>-1</sup> )	2.5, Ar
Coolant gas (L min <sup>-1</sup> )	50, N <sub>2</sub>
Power input (approx.)	11 kW (5.2 kV)
Observation height above coil (mm)	15
Measurement wavelength (nm)	
Pt	270.2
Pd	248.8
Ru	269.2
Rh	252.0
Ir	322.0

### 3.3.2. Pd concentration in Hg for TR-XRF-analysis

The following application is based on a method described in Ref [4].

Ultratraces of Pd are determined in biological matrices by means of total reflection X ray fluorescence (TXRF) after high pressure digestion followed by collection via reductive co-precipitation with mercury. An absolute detection limit of 50 pg Pd can be achieved by the method. Relative detection limits for urine (sample intake of 20 g) and poplar roots (sample intake 0.05 g) are 2.5 pg g<sup>-1</sup> and 1 ng g<sup>-1</sup> respectively. The method has also been successfully tested for air dust and road dust samples.

#### 3.3.2.1. Sample preparation

20 mL of urine and 1 mL of HNO<sub>3</sub> (p.a. 65%) are mixed in a 70 mL quartz-vessel. The volume of the solution is reduced to about 2 mL on a hot plate. Then 4 mL of HNO<sub>3</sub> (p.a. 65%) and 0.5 mL of HCl (p.a. 37%) are added. Afterwards the vessels are transferred to a high pressure asher (HPA<sup>®</sup>, Kürner, Rosenheim, Germany) for closed vessel sample digestion (50 min, 320°C, 13 MPa). The resulting solution is evaporated to approx. 0.5 mL. For co-precipitation, the solution is transferred to 10 mL centrifuge tubes using about 2 mL ultrapure H<sub>2</sub>O. Subsequently, 0.2 mL of a mercury nitrate solution (3 g of reagent grade mercury for polarography dissolved in 4.5 mL 30% HNO<sub>3</sub> and brought to 20 mL using ultrapure H<sub>2</sub>O) and 0.5 mL of formic acid (p.a. 98–100%) are added. The tubes are heated to 80–85°C for 45 min. Afterwards, the temperature is increased to 115–120°C and after 10 min of weak boiling the reduction step is finished. The residual solution containing 1–2 mercury droplets is decanted (the supernatant is removed) and the droplets are cleaned with 3 mL of 0.4 M HCl and centrifuged in order to get one single droplet. The solution is filtered and the collected Hg-droplet is cleaned with a small amount of ultrapure H<sub>2</sub>O followed by some mL propan-2-ol (p.a.). For TXRF the droplet is transferred to a siliconized quartz-carrier and Hg is evaporated on a hot plate at 300°C.

CAUTION! — A mercury absorber, e.g. iodized activated carbon or zinc chips, must be used for collection of the highly toxic mercury fumes.

Prior to TXRF, the residues on the target are spiked with 2 ng of Y (internal reference element).

### 3.3.2.2. Results and discussion

The method quantitatively (yield > 95%) collects Pd, whereas matrix elements present in the original samples are reduced to negligible amounts. Absolute limits of detection are in the range of 50 pg. The precision of the method depends on sample intake and matrix. It must be evaluated by repeated analysis of a sample or reference material. Recoveries should be checked frequently via standard addition. Standard addition should be performed prior to the first sample preparation step; liquid standards may only be used for liquid matrices. It is noteworthy that method recoveries for solid matrices cannot be checked via addition of liquid standards.

Collection via reductive co-precipitation can be used for various sample types after complete digestion and after the sample is present in 0.5 mL of an HNO<sub>3</sub>/HCl mixture. The method can also be used for enrichment of ultratrace amounts of gold (yield > 95%).

### 3.3.3. *Occupationally exposed personnel*

Exposed personnel in PGE processing industries have been investigated for several of years now. This way it has been verified that they incorporate considerable amounts of PGE. For example, urine Pt concentrations of workers employed in a platinum refinery as well as of workers employed in the catalyst industry are higher by up to a factor of 1000 compared with the background level [8]. Therefore there is a maximum workplace concentration (MAK) imposed by German law of 2 µg Pt/m<sup>3</sup>. Also, urinary Pd concentrations of personnel from a palladium refinery showed values of up to 5,5 µg/L while urinary Pd concentrations of unexposed persons were below the detection limit of 36 ng/L [6]. Due to the fact that the automobile catalyst industry has partly shifted to Pd as the catalytically active component during recent years, investigations of this element are missing presently. It has even been found elevated Pt concentrations in urine of pharmaceutical and hospital personnel connected with the handling of Pt-containing anti-cancer drugs [8]. Although the increased Pt concentrations are much lower compared with industry workers, it must be kept in mind that the drug cisplatinum (and similar chemicals) are mutagenic and carcinogenic.

For Pt measurements in urine, adsorptive voltammetry as well as ICP-MS have been employed. Pd has been analysed in urine by FI-GF-AAS after microwave-assisted pressurized decomposition and solid phase extraction.

#### 3.3.3.1. Platinum in hospital effluents

Pt from excreted anti-cancer drugs yielded concentrations of up to 601 ng Pt/L in hospital effluents, while the background level is below the detection limit of 10 ng/L. Interestingly, Pt releases from hospitals are minor sources compared with e.g. Pt emissions of automobile catalysts in European countries. However, they are of the same order of magnitude. Pt has been analysed in these matrices by adsorptive voltammetry subsequent to high pressure ashing.

### 3.3.4. Road dust

Research on the environmental impact of catalysts has been performed through extensive analysis of environmental samples. Road dust plays an important role in the environmental pathways of PGE as particles emitted from the catalysts deposit on the road surface or roadside soil. Therefore, road dust has been analysed in a number of studies on the environmental impact of PGE.

#### 3.3.4.1. Road dust sampling

Road dust has been collected using a brush or a wet/dry vacuum cleaner. While brushing is attractive because of its simplicity, vacuum cleaners enable the collection of particles in porosities of the road, especially fine particles that would not be collected by brushing. The vacuum cleaner should be equipped with a filter in order to avoid losing fine particles.

#### 3.3.4.2. Sample handling and preparation

Once in the laboratory, road dust samples should be dried. This is typically done placing the samples in an oven at 105°C for 3 hours. Samples are then sieved in order to eliminate large stones and different particle size fractions can be selected (e.g. <63µm and 63-250µm). Dry samples can then be kept in polyethylene containers until further preparation.

Microwave digestion is by far the most commonly used sample digestion technique for trace element analysis. Commercially available microwave digestion systems typically use closed Teflon vessels with control of temperature and pressure in the vessels. A method for road dust digestion [65] is described below:

- Weigh 250 mg of sample into PTFE reactor
- Add 8 ml aqua regia (HCl:HNO<sub>3</sub>, 3:1)
- Digest with the controlled temperature programme in Table XVI
- Take to dryness on hot plate using acid-washed crucibles or beakers
- Redissolve in 5 ml of 2% HCl and dilute if necessary.

TABLE XVI. TEMPERATURE PROGRAMME FOR THE DIGESTION OF ROAD DUST

Step	Power (W)	Temperature (°C – control parameter)	Ramp (min)	Holding (min)	Maximum pressure (psi)
1	300	110	5	2	50
2	600	140	5	2	100
3	600	170	5	2	200
4	1200	200	5	6	300

The use of HF has been recommended for the determination of Pd [57]. HF can be added in the digestion vessel in a 3:1 aqua regia HF proportion, resulting in the digestion of silicates in the sample. Risks associated with the use of HF have been reported and it is therefore important to take all necessary precautions, e.g. availability of an antidote in case of contact.

### 3.3.5. Ore analysis by fire assay and NAA

Fire-assay, with nickel sulphide bead collection, is used to concentrate the PGE and gold from large rock samples, prior to neutron activation analysis. The technique is very sensitive and therefore it is widely used in geochemical studies of the PGE. The rock powder is fused with a flux at 1000°C and the PGE and gold are collected in the nickel sulphide button which separates from the slag. The button is crushed and the nickel sulphide matrix is dissolved in concentrated hydrochloric acid. The insoluble residue containing PGE and gold is filtered off and analysed by neutron activation and gamma ray spectrometry. This method was implemented at Imperial College London to enable large and representative samples of chromitite from the Merensky Reef, South Africa, to be analysed for Pt, Pd Rh, Ir, Ru, Os and Au. A modification was used where lithium tetraborate replaced sodium tetraborate to ensure dissolution of the chromitite, and sodium hydroxide was added to the flux to reduce the viscosity of the melt. The temperature of the fusion was 1150°C to ensure complete dissolution of the chromite grains. Samples weighing 50 g, to provide a representative sample, were mixed with 100 g of di-lithium tetraborate, 50 g of lithium carbonate, and 50 g of sodium hydroxide.

Three sets of irradiations were performed:

1. A 5 min irradiation in an epithermal neutron flux, followed by 5 min decay and a 5 min count. The concentrations of Rh and Pd in the samples were calculated from the 51 keV peak of  $^{104m}\text{Rh}$  (4.4 min) and the 188 keV peak of  $^{109m}\text{Pd}$  (4.7 min).
2. A 7.5 h irradiation in an epithermal neutron flux, followed by 4 day decay and a 10 min count. The concentration of Pt was determined from the 158 keV peak of  $^{199}\text{Au}$  (3.1 days).
3. A 7.5 h irradiation in a thermal neutron flux, followed by a 10 day decay and a 1–2 h count. Osmium, Ir and Ru were determined with the 129 keV peak of  $^{191}\text{Os}$  (15.4 days), the 468 keV peak of  $^{192}\text{Ir}$  (73.8 days) and the 497 keV peak of  $^{103}\text{Ru}$  (39.4 days), respectively.

The concentrations of the PGE in the rock samples were in the ranges 24-1590 ng/g Pd, 71-3683 ng/g Pt, 11-518 ng/g Rh, 8-199 ng/g Ir, 4-109 ng/g Os and 11-453 ng/g Ru. These values represent the high concentrations found in a mineralized zone of the Bushveld complex, South Africa.

## 4. QA/QC AND REFERENCE MATERIALS

### 4.1. Reporting analytical results

Analytical values (concentrations, absolute amounts) should always be reported in combination with their uncertainty. The EURACHEM guide “*Quantifying Uncertainty in Analytical Measurement*” [65] defines the term “uncertainty” as follows: *A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand.* In practice the uncertainty on the result may arise from many possible sources, including examples such as sampling, matrix effects and interferences, environmental conditions, uncertainties of weights and volumetric equipment, reference values, etc. The reported uncertainty should include all these possible errors. It can be experimentally determined and expressed as the standard deviation of

replicate analyses (including sampling, sample pre-treatment and measurement) or it can be calculated via total combined uncertainty budget. The EURACHEM guide gives detailed instructions how to determine the total combined uncertainty for an analytical method.

#### **4.2. Selection and application of reference materials**

In this section the selection and use of matrix reference materials (RM) is discussed. Standard (reference) materials, which are used for calibration of instruments or methods, are not the topic of this Section.

Reference materials are used for:

- Method validation;
- Determining and controlling the accuracy of an analytical method;
- Verification of instrument, laboratory and analyst performance;
- Uncertainty estimation;
- Internal quality control.

Certified reference materials should not be used as primary calibrants as these materials are intended for quality control purposes and for validation of methods only.

For selecting an appropriate reference material, several points have to be taken into account:

- The matrix of the sample and the RM should be identical or similar;
- The concentrations of the certified analyte should be at the same level in sample and RM;
- The uncertainty attributed to the RM should be similar to the uncertainty of the values generated by the analytical method;
- The RM must not deteriorate by ageing (oxidation, biodegradation, sedimentation, etc.), unless this is mentioned in the certificate.

An RM is correctly used if it is treated identically to the samples. It has to be used and stored as described in the certificate. The RM must not deteriorate through use (pollution, evaporation, dilution). Once a RM has lapsed or is dubious, it cannot be recalibrated but has to be replaced by a new one. The RM is the basis of accuracy; it is unwise to alter its value to compensate for an instrumental, procedural or other error.

##### *4.2.1. List of reference materials*

For many of the materials listed in the following tables only non-certified, informational values are reported (values without uncertainty). It depends on the needs of the user if informational values are sufficient for the application. After pre-selection of matrix and concentration range, it is important to verify the quality of the material by checking the certificate and the certification procedure.

As can be seen in Tables XVII, there is a need for environmental reference materials containing certified low levels of PGE. For geological and industrial applications, which mainly involve the determination of higher PGE-contents, the situation is satisfactory.

TABLE XVII. LIST OF AVAILABLE RM WITH CERTIFIED OR INFORMATION VALUES FOR PGE

*Platinum*

Name	Code	Pt-value	Uncert. [%]	Unit
Platiniferous black sand	CANMET-PTA-1	3.05	5	µg/g
Noble metals-bearing sulphide concentrate	CANMET-PTC-1	3		µg/g
Noble metals-bearing sulphide concentrate	CANMET-PTC-1a	2.72	4	µg/g
Noble metals bearing nickel-copper matte	CANMET-PTM-1	5.8		µg/g
Noble metals-bearing nickel-copper matte	CANMET-PTM-1a	7.31	3	µg/g
Sulphide ore mill tailings	CANMET-RTS-1	< 0.07		µg/g
Sulphide ore mill tailings	CANMET-RTS-2	0.217	9	µg/g
Sulphide ore mill tailings	CANMET-RTS-3	< 0.07		µg/g
Sulphide ore mill tailings	CANMET-RTS-4	0.055	65	µg/g
Nickel ore	CANMET-SU-1A	0.41		µg/g
Diabase rock	CANMET-TDB-1	0.0058	19	µg/g
Ultramafic ore tailings	CANMET-UMT-1	0.1283	8	µg/g
Gabbro rock	CANMET-WGB-1	0.0061	26	µg/g
Mineralized gabbro	CANMET-WMG-1	0.731	5	µg/g
Massive sulphide	CANMET-WMS-1	1.741	8	µg/g
Altered peridotite	CANMET-WPR-1	0.285	4	µg/g
Tunnel dust	Electrofilter, Austria	13		ng/g
Andesite	GSJ-JA-1	0.12		ng/g
Andesite	GSJ-JA-2	0.0013		µg/g
Andesite	GSJ-JA-3	0.0017		µg/g
Basalt	GSJ-JB-1	6.7		ng/g
Basalt	GSJ-JB-2	< 200		ng/g
Basalt	GSJ-JB-2	0.004		µg/g
Basalt	GSJ-JB-3	0.0043		µg/g
Dolomite	GSJ-JDo-1	< 0.0005		µg/g
Feldspar	GSJ-JF-1	< 0.0005		µg/g
Feldspar	GSJ-JF-2	< 0.0005		µg/g
Granodiorite	GSJ-JG-1	4.8		ng/g
Granodiorite	GSJ-JG-1a	< 0.0005		µg/g
Granite	GSJ-JG-2	< 0.0005		µg/g
Granodiorite	GSJ-JG-3	< 0.0005		µg/g
Gabbro	GSJ-JGb-1	< 0.0005		µg/g
Lake sediment	GSJ-JLK-1	0.0014		µg/g
Limestone	GSJ-JLs-1	< 0.0005		µg/g
Peridotite	GSJ-JP-1	0.0049		µg/g
Rhyolite	GSJ-JR-1	< 0.0005		µg/g
Rhyolite	GSJ-JR-2	< 0.0005		µg/g
Stream sediment	GSJ-JSd-1	< 0.0005		µg/g
Stream sediment	GSJ-JSd-2	0.0167		µg/g
Stream sediment	GSJ-JSd-3	0.0013		µg/g
Slate	GSJ-JSI-1	0.0013		µg/g
Slate	GSJ-JSI-2	0.0015		µg/g
Platinum ore	NIM, SARM-7	3.74		µg/g
Used catalyst	NIST-SRM 2556	697		µg/g
Used catalyst	NIST-SRM 2557	1131		µg/g
Toxic metals in urine (normal)	NIST-SRM 2670-1	0.000008		mg/L
Toxic metals in urine (elevated)	NIST-SRM 2670-2	0.12		mg/L
Ocean sediment environmental radioactivity standard	NIST-SRM 4357	< 2.2		µg/g
Urine, trace elements level I	RECIPE-8847	0.038	39	mg/L

Name	Code	Pt-value	Uncert. [%]	Unit
Urine, trace elements level II	RECIPE-8848	0.121	30	mg/L
Trace elements in lyophilized plasma (level I)	RECIPE-8883	60	32	µg/L
Trace elements in lyophilized plasma (level II)	RECIPE-8884	222	27	µg/L
Platinum ore	SABS-SARM-7	3.74	1	µg/g
Cordierite	Tübingen Univ., Germany	50		ng/g
Corn leaves	Univ. Of Munich, Germany	585		ng/g
Oregon basalt	USGS-BCR-1	2		ng/g
Iceland basalt	USGS-BIR-1	2.8		ng/g
North Carolina dolerite	USGS-DNC-1	36		ng/g
Washington dunite	USGS-DTS-1	5.7		ng/g
Rhode Island granite	USGS-G-1	8.2		ng/g
Rhode Island granite	USGS-G-2	5.9		ng/g
Colorado granodiorite	USGS-GSP-1	< 5		ng/g
Jasperoide	USGS-GXR-1	300		ng/g
Jasperoide	USGS-GXR-2	100		ng/g
Jasperoide	USGS-GXR-4	100		ng/g
Jasperoide	USGS-GXR-5	50		ng/g
Jasperoide	USGS-GXR-6	100		ng/g
Peridotite	USGS-PCC-1	10		ng/g
Virginia diabase	USGS-W-1	14		ng/g

### *Palladium*

Name	Code	Pd-value	Uncert. [%]	Unit
Montreal gabbro	CANMET-MRG-1	21		ng/g
Noble Metals-Bearing Sulfide Concentrate	CANMET-PTC-1	12.7		µg/g
Noble Metals-Bearing Sulphide Concentrate	CANMET-PTC-1a	4.48	3	µg/g
Noble Metals-Bearing Nickel-Copper Matte	CANMET-PTM-1	8.1		µg/g
Noble Metals-Bearing Nickel-Copper Matte	CANMET-PTM-1a	10.01	4	µg/g
Sulphide Ore Mill Tailings	CANMET-RTS-1	< 0.02		µg/g
Sulphide Ore Mill Tailings	CANMET-RTS-2	0.136	12	µg/g
Sulphide Ore Mill Tailings	CANMET-RTS-3	< 0.02		µg/g
Sulphide Ore Mill Tailings	CANMET-RTS-4	0.015		µg/g
Nickel Ore	CANMET-SU-1A	0.027		µg/g
Nickel-Copper-Cobalt Ore	CANMET-SU-1A	0.37		µg/g
Syenite	CANMET-SY-1	3		ng/g
Syenite	CANMET-SY-2	1.5		ng/g
Diabase Rock	CANMET-TDB-1	0.0224	6	µg/g
Ultramafic Ore Tailings	CANMET-UMT-1	0.1042	6	µg/g
Gabbro Rock	CANMET-WGB-1	0.0139	15	µg/g
Mineralized Gabbro	CANMET-WMG-1	0.382	3	µg/g
Massive Sulphide	CANMET-WMS-1	1.185	4	µg/g
Altered Peridotite	CANMET-WPR-1	0.235	4	µg/g
Andesite	GSJ-JA-3	0.001		µg/g
Basalt	GSJ-JB-2	0.0063		µg/g
Basalt	GSJ-JB-3	0.0032		µg/g
Dolomite	GSJ-JDo-1	< 0.0005		µg/g
Feldspar	GSJ-JF-1	< 0.0005		µg/g
Feldspar	GSJ-JF-2	< 0.0005		µg/g
Granodiorite	GSJ-JG-1a	< 0.0005		µg/g

Name	Code	Pd-value	Uncert. [%]	Unit
Granite	GSJ-JG-2	< 0.0005		µg/g
Granodiorite	GSJ-JG-3	< 0.0005		µg/g
Gabbro	GSJ-JGb-1	0.00018		µg/g
Lake Sediment	GSJ-JLK-1	0.003		µg/g
Limestone	GSJ-JLs-1	< 0.0005		µg/g
Peridotite	GSJ-JP-1	1.3		µg/g
Rhyolite	GSJ-JR-1	< 0.0005		µg/g
Rhyolite	GSJ-JR-2	< 0.0005		µg/g
Stream Sediment	GSJ-JSd-1	< 0.0005		µg/g
Stream Sediment	GSJ-JSd-2	0.0212		µg/g
Stream Sediment	GSJ-JSd-3	0.0032		µg/g
Slate	GSJ-JSI-1	0.0008		µg/g
Slate	GSJ-JSI-2	0.0013		µg/g
Platinum Ore	NIM, SARM-7	1.53		µg/g
Ocean Sediment Environmental Radioactivity Standard	NIST-SRM 4357	< 1		µg/g
Platinum Ore	SABS-SARM-7	1.53	2	µg/g
Oregon Basalt	USGS-BCR-1	10		ng/g
Hawaii Basalt	USGS-BHVO-1	3.5		ng/g
Iceland Basalt	USGS-BIR-1	5.6		ng/g
North Carolina Dolerite	USGS-DNC-1	16		ng/g
Washington Dunite	USGS-DTS-1	3		ng/g
Rhode Island Granite	USGS-G-1	1.9		ng/g
Peridotite	USGS-PCC-1	6.2		ng/g
Virginia Diabase	USGS-W-1	14		ng/g
Virginia Diabase	USGS-W-2	11		ng/g

### *Rhodium*

Name	Code	Rh-value	Uncert. [%]	Unit
Noble Metals-Bearing Sulphide Concentrate	CANMET-PTC-1	0.62		µg/g
Noble Metals-Bearing Sulphide Concentrate	CANMET-PTC-1a	0.33	18	µg/g
Noble Metals-Bearing Nickel-Copper Matte	CANMET-PTM-1	0.92		µg/g
Noble Metals-Bearing Nickel-Copper Matte	CANMET-PTM-1a	0.92		µg/g
Diabase Rock	CANMET-TDB-1	0.0007		µg/g
Ultramafic Ore Tailings	CANMET-UMT-1	0.0098	30	µg/g
Mineralized Gabbro	CANMET-WMG-1	0.026	8	µg/g
Massive Sulphide	CANMET-WMS-1	0.225	7	µg/g
Altered Peridotite	CANMET-WPR-1	0.0134	7	µg/g
Platinum Ore	NIM, SARM-7	0.24		µg/g
Ocean Sediment Environmental Radioactivity Standard	NIST-SRM 4357	< 2.2		µg/g
Platinum Ore	SABS-SARM-7	0.24	5	µg/g
Oregon Andesite	USGS-AGV-1	< 5		ng/g
Oregon Basalt	USGS-BCR-1	0.2		ng/g
Iceland Basalt	USGS-BIR-1	0.35		ng/g
North Carolina Dolerite	USGS-DNC-1	0.35		ng/g
Peridotite	USGS-PCC-1	1		ng/g

## *Ruthenium*

Name	Code	Ru-value	Uncert. [%]	Unit
Noble Metals-Bearing Sulphide Concentrate	CANMET-PTC-1a	0.21		µg/g
Noble Metals-Bearing Nickel-Copper Matte	CANMET-PTM-1a	0.7		µg/g
Diabase Rock	CANMET-TDB-1	0.0003		µg/g
Mineralized Gabbro	CANMET-WMG-1	0.035	14	µg/g
Massive Sulphide	CANMET-WMS-1	0.099	16	µg/g
Altered Peridotite	CANMET-WPR-1	0.022	18	µg/g
Peridotite	GSJ-JP-1	0.0065		µg/g
River Clay Sediment	LGC-6139	108	7	µg/g
Sargasso Seaweed	NIES-CRM-09	24	8	µg/g
Platinum Ore	NIM, SARM-7	0.43		µg/g
Spinach Leaves	NIST-SRM 1570a	12.7	13	µg/g
Trace Elements in Natural Water	NIST-SRM 1640	0.002	1	µg/g
Trace Elements in Water	NIST-SRM 1643d	0.13		µg/g
Indoor Dust (nominal 1 % Pb)	NIST-SRM 2584	33		µg/g
Mussel Tissue (Trace Elements and Methylmercury)	NIST-SRM 2976	4.14		µg/g
Mussel Tissue	NIST-SRM 2977	6.7		µg/g
Ocean Sediment Environmental Radioactivity Standard	NIST-SRM 4357	< 2.2		µg/g
Humber River Sediment	NWRI-HR-1	80.2		µg/g
Sudbury Sediment	NWRI-SUD-1	77.1		µg/g
Great Lakes Sediment	NWRI-TH-2	94		µg/g
Lake Ontario Sediment	NWRI-WQB-1	152		µg/g
Great Lakes Sediment	NWRI-WQB-3	91.4		µg/g
Platinum Ore	SABS-SARM-7	0.43	13	µg/g
Oregon Andesite	USGS-AGV-1	< 4000		ng/g
Oregon Basalt	USGS-BCR-1	1		ng/g
Washington Dunite	USGS-DTS-1	2.5		ng/g
Peridotite	USGS-PCC-1	10		ng/g
Virginia Diabase	USGS-W-1	< 400		ng/g

## *Osmium*

Name	Code	Os- value	Uncert. [%]	Unit
Mineralized Gabbro	CANMET-WMG-1	0.024		µg/g
Massive Sulphide	CANMET-WMS-1	0.119		µg/g
Altered Peridotite	CANMET-WPR-1	0.013		µg/g
Andesite	GSJ-JA-1	< 5		ng/g
Basalt	GSJ-JB-1	1.9		ng/g
Basalt	GSJ-JB-2	< 5		ng/g
Granodiorite	GSJ-JG-1	2.7		ng/g
Peridotite	GSJ-JP-1	0.0079		µg/g
Platinum Ore	NIM, SARM-7	0.0635		µg/g
Ocean Sediment Environmental Radioactivity Standard	NIST-SRM 4357	< 15		µg/g
Platinum Ore	SABS-SARM-7	0.063	11	µg/g
Oregon Andesite	USGS-AGV-1	< 0.02		ng/g
Oregon Basalt	USGS-BCR-1	6.01		ng/g
Washington Dunite	USGS-DTS-1	0.99		ng/g
Rhode Island Granite	USGS-G-1	0.11		ng/g
Peridotite	USGS-PCC-1	8		ng/g
Virginia Diabase	USGS-W-1	600		ng/g

## *Iridium*

Name	Code	Ir-value	Uncert. [%]	Unit
Noble Metals-Bearing Sulphide Concentrate	CANMET-PTC-1a	1100		µg/g
Noble Metals-Bearing Nickel-Copper Matte	CANMET-PTM-1a	0.35		µg/g
Diabase Rock	CANMET-TDB-1	0.00015		µg/g
Ultramafic Ore Tailings	CANMET-UMT-1	0.00873	4	µg/g
Mineralized Gabbro	CANMET-WMG-1	0.046	9	µg/g
Massive Sulphide	CANMET-WMS-1	0.235	11	µg/g
Altered Peridotite	CANMET-WPR-1	0.0135	13	µg/g
Granodiorite	GSJ JG-1	< 0.01		ng/g
Andesite	GSJ-JA-1	< 0.01		ng/g
Andesite	GSJ-JA-2	0.000013		µg/g
Andesite	GSJ-JA-3	0.000014		µg/g
Basalt	GSJ-JB-1	< 0.02		ng/g
Basalt	GSJ-JB-2	< 0.05		ng/g
Basalt	GSJ-JB-3	0.000037		µg/g
Granite	GSJ-JG-2	0.000004		µg/g
Granodiorite	GSJ-JG-3	1.6E-06		µg/g
Peridotite	GSJ-JP-1	0.002		µg/g
Rhyolite	GSJ-JR-2	2.2E-06		µg/g
Platinum Ore	NIM, SARM-7	0.074		µg/g
Ocean Sediment Environmental Radioactivity Standard	NIST-SRM 4357	< 15		µg/g
Platinum Ore	SABS-SARM-7	0.074	16	µg/g
Hawaii Basalt	USGS BHVO-1	0.44		ng/g
Iceland Basalt	USGS BIR-1	0.15		ng/g
North Carolina Dolerite	USGS DNC-1	0.52		ng/g
Washington Dunite	USGS DTS-1	0.67		ng/g
Peridotite	USGS PCC-1	4.8		ng/g
Virginia Diabase	USGS W-1	0.28		ng/g

### **4.3. Other tools for testing the accuracy of analytical results**

#### *4.3.1. Inter-method comparison*

The comparison of results obtained by two independent analytical methods is a very suitable QA-tool. The checks should be performed over the whole working range of a method. The values obtained for the two methods are evaluated by linear correlation. After an appropriate period of observation, the correlation coefficient including upper and lower threshold values is assessed. Action should be taken, if the threshold values have been exceeded. The checks should be performed in suitable intervals. Documentation of the obtained values is important.

#### *4.3.2. Proficiency testing (PT)*

Proficiency testing is a QA-tool for controlling the accuracy of the results of an analytical laboratory. It is complementary to other QA-tools for laboratories as it monitors a laboratory's outputs. Proficiency tests are usually conducted by means of interlaboratory comparisons, where similar samples are sent to all participating laboratories. PT enables laboratories to monitor their measurement capability both by comparison to peer laboratories, and over time within their own laboratory. Laboratories are recommended to take action when

they obtain unsatisfactory performance in a PT scheme. This will usually involve investigating the cause of the poor result(s), and then taking corrective action, where appropriate.

As a service to help laboratories with their quality, a laboratory should take advantage of PT as often as possible.



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