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# TRACE ENRICHMENT AND DETERMINATION OF PLATINUM USING A FIA-ICP SYSTEM

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# Trace enrichment and determination of platinum using a FIA-ICP system

by

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# Trace enrichment and determination of platinum using a FIA-ICP system

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## SYNOPSIS

The platinum group of metals (PGM), in particular platinum, palladium and rhodium, have lately become indispensable to modern industry. Due to South Africa's extensive PGM-reserves, South Africa are currently the World's largest PGM-supplier. Since ICP-OES are frequently used for the determination of these elements, a procedure was developed for the determination of platinum, palladium, rhodium and nickel, the base metal normally associated with PGM deposits. The concentrations at which these elements occur in deposits and environmental samples are however generally too low for direct determination with ICP-OES. In order to improve the detection limits of the ICP-OES, the instrument was coupled to a FIA system which contained a micro-ion exchange column for the on-line

preconcentration of platinum. The performance of three different ion exchangers, namely alumina, POLYORGS IV and Dowex 1, were compared. The advantages of the preconcentration FIA-ICP systems were maximized by optimization of several of its operating parameters. These parameters included the acidity of the sample, the concentrations of the carrier and eluent streams, flow rates, preconcentration and elution times as well as, the temperature at which a system was operated.

The best preconcentration was eventually obtained with the alumina micro-column. When compared to conventional ICP-OES, this system yielded an order two magnitude improvement in the platinum detection limit. This corresponded to an enrichment factor of 25.5. The precision of the technique was better than 5% RSD at the 0.72 mg/ℓ level. Analysis of a spiked water sample further gave a 106% recovery at the mg/ℓ level. A sample rate of 5.7 samples/h was obtained with the system, which corresponded to a concentration efficiency of 2.45. Finally the consumptive index of the system was only 0.24, which indicated efficient utilization of the sample available.

# Spoor verryking en bepaling van platinum met behulp 'n VIA-IGP sisteem

deur

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## SAMEVATTING

Die platinum groep metale (PGM), spesifiek platinum, palladium en rhodium, het in die laaste jare onmisbaar vir die moderne industrie geword. Weens Suid Afrika se uitgebreide PGM reserwes, is Suid Afrika tans die wereld se grootste verskaffer van die platinum groep metale. Aangesien IGP-OES dikwels gebruik word in die bepaling van hierdie elemente is 'n prosedure ontwikkel vir die bepaling van platinum, palladium, rhodium en ook die oorgangsmetaal nikkel, wat altyd saam met die metale voorkom. Die konsentrasies van die metale in afsettings en omgewingsmonsters is oor die algemeen egter te laag om direk met IGP-OES bepaal te kan word. Ten einde die bepaalbaarheidslimiete van die IGP-OES te verbeter, is die instrument gekoppel aan 'n VIA-sisteem wat 'n mikro-ioonuitruilkolom bevat

het vir die aan-lyn prekonsentrasie van platinum. Drie verskillende ioonuitruilers, naamlik alumina, POLYORGS IV en Dowex 1, is vergelyk. Verskeie van die bedryfsparameters van die VIA-IGP sisteem is verder geoptimiseer om te verseker dat die voordele wat die sisteem bied, maksimaal benut word. Hierdie parameters het onder andere die suurgehalte van die monster, die konsentrasie van die draerstroom en elueermiddel, die vloeitempo's, die prekonsentrasie- en elueertye asook die temperatuur waarby 'n sisteem bedryf is, ingesluit.

Die beste prekonsentrasie is op die ou end met die alumina mikro-kolom verkry. Hierdie sisteem het tot 'n twee ordegroote verbetering in die deteksie limiet van die IGP-OES instrument gelei. Dit stem ooreen met 'n verrykingsfaktor van 25.5. Die presisie van die tegniek vir 'n 0.72 mg/ℓ monster was beter as 5% RSD, terwyl 'n 106% herwinning van platinum wat by die monster gevoeg is, verkry is. 'n Monsterfrekwensie van 5.7 monsters/h is verder verkry, wat beteken het dat die konsentrasie effektiwiteit maar 2.45 was. Laastens was die verbruikersindeks van die VIA-sisteem slegs 0.24, wat aandui dat die beskikbare monster effektief verbruik is.

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# CHAPTER 1

# Introduction

## 1. Economic Importance of the Platinum Group of Metals

The platinum group of metals (PGM) are widely used in a variety of industries. One of the most important applications of these metals are as catalysts in the chemical industry, with the largest single use being the production of autocatalysts. These catalysts are used in the control of automobile exhaust emissions, oxidizing the noxious carbon monoxide, hydrogen and unburnt hydrocarbon gases. Additionally, the new three-way catalysts can also reduce the oxides of nitrogen present in the exhaust emissions [1]. These three-way catalytic converters mainly employ Pt and Rh, while the initial catalysts used a combination of Pt and Pd. Additionally, the PGM's are also employed as catalysts in a variety of chemical processes, ranging from Pt catalysts for the oxidation of ammonia in the production of nitric acid to Ru catalysts in the Fischer-Tropsch process [1,2].

The PGM are further used extensively in the electrical and electronic industries. This can be attributed to the stability and inertness of these metals when they are subjected to the elevated temperatures which are typically encountered in electrical equipment. This characteristic is also exploited in the glass and fibreglass manufacturing industries, where Pt and Pd alloys are used in most glass handling equipment [1,2].

A substantial portion of the World's PGM-product are also used in the manufacture of jewellery. Here PGM alloys are currently preferred to the pure metals, due to their superior strength [1,2].

Despite the noble character of these metals, they clearly exhibit an extra-ordinary versatility with regard to their range of applications. Some of the lesser uses of the PGM include, for instance the production of chemotherapeutic agents, heart pacemakers, magnets, astronomical instruments, finger printing ink, etc. Since the successful commercial substitution of the PGM by cheaper metals are exceedingly rare, it is clear that these metals are indispensable to modern technology and industry [2].

## 2. Distribution

Although there are a considerable demand for these precious metals, they are extremely scarce. Typically the individual elements of the PGM only comprise 1-10 ng/g of the Earth's crust [1,3,4]. Furthermore, the World PGM-market are completely dominated by only two countries, namely South Africa and Russia. Together these countries produce more than 90% of the World's PGM-product. Apart from dominating the markets, South Africa also contains the World's largest and most important repository of the PGM, eg. the Bushveld Complex. Some sources have estimated that South Africa's PGM reserves represent up to 85% of that of the World's. South Africa further produces 65% of the World's Pt product, while Russia dominates the Pd-market, annually producing 61% of the World's Pd-product [1,2].

## 3. Analysis of PGM-samples

The recent growth in the economic importance of the PGM's, has stimulated the development of more sensitive and precise/effective analytical techniques for the determination of these elements. Such techniques are required, not only for exploration and resource evaluation, but also for monitoring the release of PGM's from autocatalysts into the environment [4,5,6]. The extremely low concentrations of the PGM's in these samples, do however make their accurate determination a challenge [4,5].

According to Koch *et al* [7], most analytical techniques which are used in the determination of these elements, are based on atomic absorption and/or emission spectroscopy. Using electrothermal vaporization atomic absorption spectrometry (ETV-AAS), it is possible to determine trace amounts of the PGM directly in samples. These instruments are however limited to the determination of single elements at a time. Inductively coupled plasma optical emission spectroscopy (ICP-OES), on the other hand, offers the possibility of multi-element analysis, but at the expense of sensitivity [8]. Due to its excellent sensitivity and multi-element capability, ICP-mass spectrometry (ICP-MS) is becoming increasingly popular in the determination of trace quantities of the PGM/in this application. This technique does however also suffer from distinct disadvantages, such as a lack of tolerance to samples with a high dissolved solids content. In practice, solutions containing more than 1000 $\mu$g/m$\ell$ total dissolved solid (TDS), will result in highly unstable and rapidly deteriorating performance of the instrument. In order to prevent this, samples can either be diluted or the analyte can be separated and preconcentrated [6,9]. However, in practice this means that the detection limits obtainable using ICP-MS, are often not significantly lower than those of an ICP-OES [9]. Despite the sensitive analytical techniques which are currently available, it is still necessary to separate and preconcentrate the PGM's prior to analysis [5,6].

Traditionally, the precious metals have been preconcentrated with fire assay techniques (eg. nickel sulphide fire assay). These procedures are lengthy and require special equipment as well as a thoroughly experienced assayer. Alternative preconcentration and separation techniques include ion exchange and solvent extraction [9,10]. As the PGM's form stable anionic chloride complexes in aqueous HCl, most of them are retained by anion exchange resins [11].

Anion exchange resins have been used successfully in the preconcentration and separation of the PGM. However, in the batch mode, these procedures are time consuming and require a lot of sample manipulation. These disadvantages can fortunately be overcome when the preconcentration is performed on-line, as in flow-injection analysis (FIA). Additionally, on-line preconcentration with FIA-systems will also improve the precision, while high enrichment factors can be obtained with relatively small volumes of sample [8].

## 4. Project Description

After all the above mentioned factors had been considered, it was concluded that the PGM could be determined best through the on-line preconcentration with a FIA-system which was coupled to an ICP-OES. Although the PGM actually consist of six elements, Pt, Pd and Rh are predominantly used in most of the applications mentioned. Consequently, this project initially concentrated on these three elements and Ni. Ni was included as it is always associated with these elements in natural deposits. As the ion exchange behaviour of the PGM are complicated [11], later work concentrated on the performance of Pt with ion exchange resins.

A large number of ion exchange resins are available for the preconcentration of Pt. Three of these, namely Alumina, POLYORGS IV and Dowex 1, were subsequently evaluated in the on-line preconcentration of Pt. A FIA-system was developed for each of these ion exchange resins individually. The ion exchange resins were incorporated as micro-columns.

In order to ensure optimal preconcentration, the influence of a number of parameters were investigated to determine the optimum operating conditions of the systems. Some of the factors which were investigated are the acidity of the samples, carriers and eluents, the temperature at which the system was operated as well as the flow rates of the individual streams.

The analytical performance of the most successful system was subsequently evaluated according to the detection limit, linear range, accuracy, precision and sample frequency which were obtained. Additionally, the enrichment factor, concentration efficiency and consumptive index of this system was also compared to similar systems.

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# CHAPTER 2

# Chemistry of the Platinum Group of Metals

## 1. Introduction

The platinum group of metals (PGM) consist of a family of six greyish to silver white metals, eg. platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os). These elements exhibit close physical and chemical affinities and are part of the transition elements of Group VIII, of which the ferrous metals iron, nickel and cobalt also form a part. Due to their high resistance to oxidation and corrosion, the PGM are classified as noble metals, along with gold (Au) and silver (Ag). Because of their exceeding scarcity these metals are also known as precious metals [1].

Platinum was officially discovered in 1736 in the gold mines of South America by a Spanish astronomer and naval officer, A. de Ulloa. However, long before De Ulloa's discovery of platinum, ancient Egyptian craftsmen (7th century BC) [1] as well as the Indians of Equador used impure, native platinum to make ornaments and small pieces of jewellery [2]. In fact, Spanish explorers found platinum along with gold in the rivers of Central and South America as early as the beginning of the 16th century [3]. However, thinking that the platinum was gold that had not been buried long enough to ripen, they threw it back into the rivers!

The colour, beauty and value of platinum soon earned the metal the name 'white gold' (which refers to an Au/Pd-alloy today). However this metal was much more difficult to work with than gold. This has partly been attributed to it's high melting point (1769 °C) as well as its brittle nature when impurities of Fe and Cu are present in the metal. Powder metallurgical techniques for the production of malleable platinum, were subsequently developed in Spain and London. It is interesting to note that even in these early years, great secrecy surrounded the research of these two groups. Due to its high melting point, the first platinum was only melted in 1782. Even then only small amounts could be melted at a time. It was only late in the last century that furnaces capable of sustaining sufficiently high temperatures became available, thus finally allowing the melting of Pt on a large scale.

The five remaining metals of the PGM - Pd, Rh, Ir, Ru and Os - were all discovered after the dissolution of crude Pt in aqua regia. In 1802 [1], Wollaston isolated and identified Pd in the mother liquor remaining after Pt had been precipitated as $(NH_4)_2PtCl_6$. He named this element after the newly discovered asteroid, Pallas, which in turn had been named after the Greek goddess of wisdom. Two years later Wollaston also discovered rhodium in the black residue that remained after the dissolution of Pt [1]. Because of it's rose coloured aqueous solutions, he named this element after the Greek word for rose, eg. rhodium. S.Tennant discovered both iridium and osmium in 1803 [2]. These two elements were both isolated from the residue from crude Pt-solutions. The variety of colours produced by the compound of iridium, prompted Tennant to name this metal after another Greek goddess, Iris, whose sign is the rainbow. Osmium was named after the Greek word for odour, due to the characteristic and pungent smell of its toxic, volatile oxide, $OsO_4$. The last element of the PGM, ruthenium, was only discovered in 1844. C.E. Klaus isolated it from the residues left after the dissolution of crude Pt from ores of the Urals. He consequently named this metal after *Ruthenia*, which is the latin name for Russia.

## 2. Terrestrial Abundance and Distribution

Considering the chemical and physical similarities of the six PGM's, it is perhaps not surprising that they normally occur together in global deposits. Although estimates of the abundance of these elements vary considerably, it is generally accepted that they are exceedingly rare. According to Greenwood [2] the most abundant of these elements are Pd and Pt, which respectively comprise approximately 0.015 $\mu$g/g and 0.01 $\mu$g/g of the earth's crust. After Pt, Os is the third most abundant of this group of elements, with an abundance of about 0.005 $\mu$g/g. Iridium has an estimated abundance of 0.001 $\mu$g/g, while Rh and Ru are the scarcest elements of the group with abundances estimated at only 0.0001 $\mu$g/g.

It is clear that the mining of these metals are indeed no small feat. According to Kotz *et al* [3] roughly 10 tons of ore must be mined and processed to obtain only 1 troy ounce (31.1g) of platinum! Fortunately these metals tend to occur together in deposits, thus allowing preconcentration of the whole group before attempting the separation of the individual metals. Apart from placer deposits (approximately 1%), PGM-deposits are always associated with nickel-copper sulphide ores [1]. These can be classified into PGM-dominated and Ni/Cu-dominated deposits. The most important PGM deposits include those in the Bushveld Complex in South Africa and the Great Dyke of Zimbabwe. Important deposits are also found in the USA and Canada. Ni/Cu dominated deposits are more widespread and include the Sudbury deposit of Canada, as well as those in the former Russia, Finland, China and the Duluth complex in the USA [1].

Of all these, the Bushveld Complex is the largest and most important repository of the platinum group of metals in the world. According to Odendaal [5] it contains at least 85% of the world's PGM reserves, while it supplies some 49% of the world's annual PGM-product. Vermaak [1], on the other hand, estimates South Africa's PGM resources at only 56% of the major deposits of the world (Fig. 2.1). Despite apparent discrepancies, it remains certain that South Africa has the largest PGM-reserves in the world.

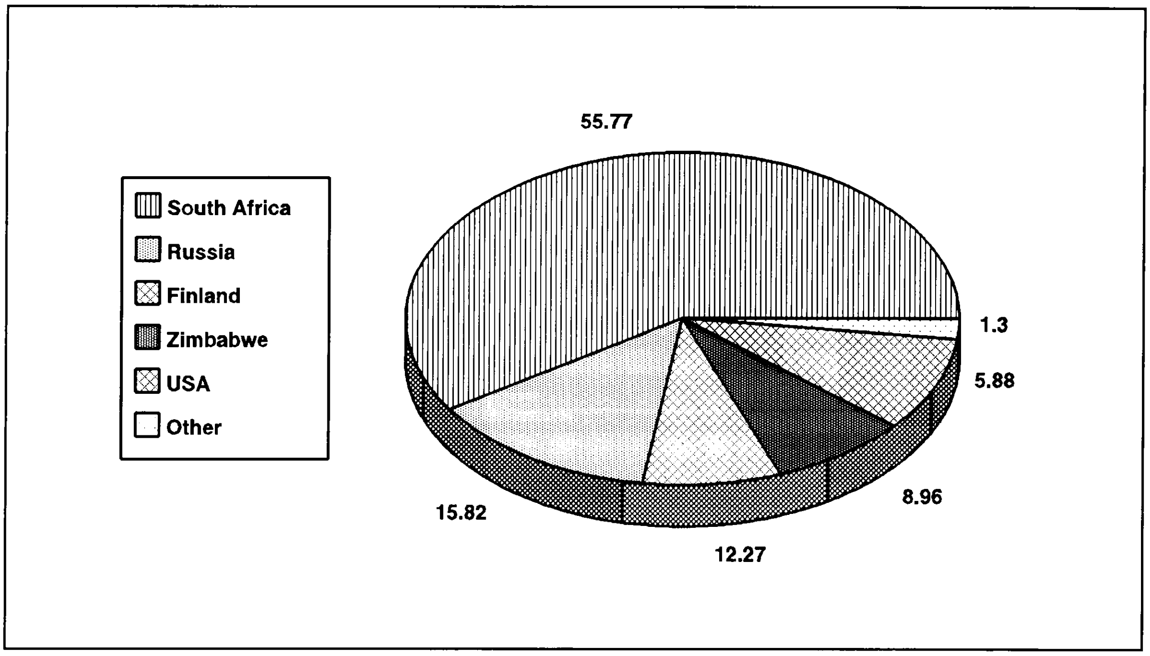

**Figure 2.1** Distribution of PGM resources among the major deposits of the world [1].

South Africa is consequently also one of the major PGM-suppliers in the world, and along with Russia these two countries dominate the world market. Russia (former USSR) supplies 42% of the world's PGM product and is also the major supplier of Pd, having supplied 61% of the world's Pd during 1990-1992 [1]. Other countries that supply significant amounts of the platinum group of metals include Canada and the USA, although their contribution cannot be compared to that of South Africa or Russia (Fig. 2.2).

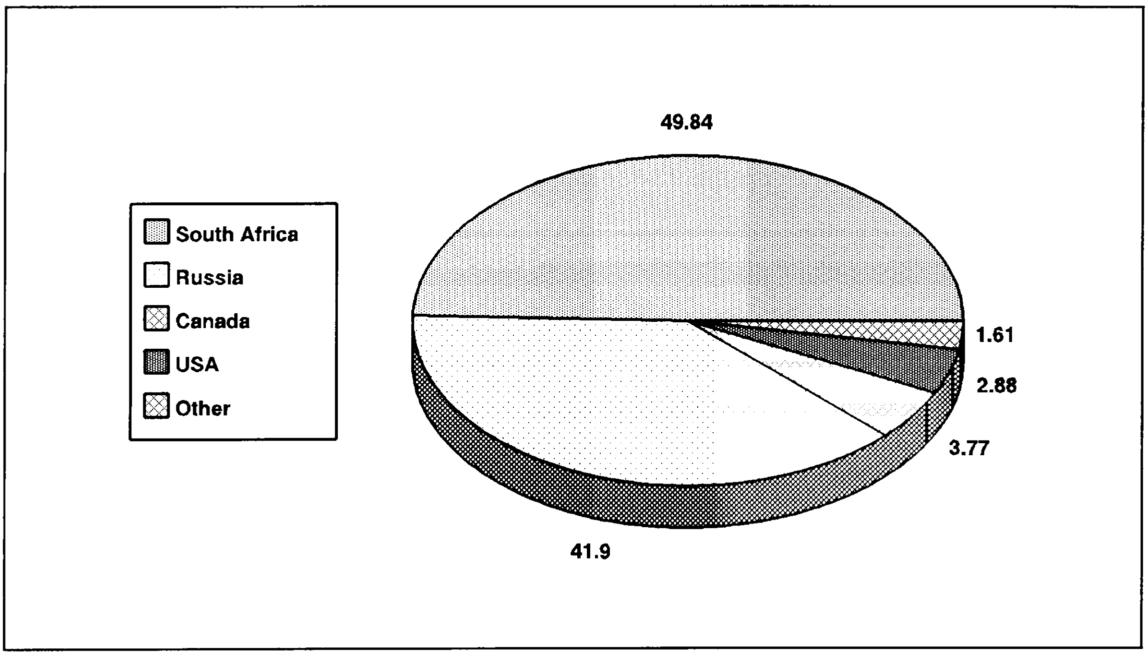

**Figure 2.2** Distribution of world PGM production by the supplying countries of the world (1990-1992) [1].

## 3. Applications

Applications of the Platinum Group of Metals cover almost every aspect of modern live, ranging from autocatalysts to jewellery and cancer chemotherapy agents. These noble metals exhibit extra-ordinary catalytic capability and their most important applications are as modern noble metal catalysts in industry [1]. There are four main applications of these elements as catalysts, the most important of these being their extensive use in environmental control. They are also used extensively in oil refining, ammonia oxidation and the production of liquid-phase chemicals. In most cases these catalysts only contain a combination of three of the six elements of the group, with platinum and palladium usually being the major constituents. The scarcer and more expensive rhodium is normally used on a smaller scale and is mostly added to enhance certain characteristics of the other elements in the catalysts [1,4].

## 3.1 PGM Catalysts

The extensive use of PGM-catalysts in environmental control are mainly due to their use in the control of exhaust emissions. The best known application of this type must definitely be the autocatalysts used in vehicles. Another important application is the reduction of air-pollution from stationary sources such as stationary engines, coal-fired electricity plants and the various industries producing vaporized organic effluents. In all these cases the use of PGM-catalysts are singularly capable of removing or converting the noxious components in these exhaust emissions [1].

PGM-catalysts also play an important role in the processing and refining of untreated crude oil. Platinum, platinum-iridium and platinum-rhenium catalysts are especially important in the reforming of petroleum nafthas to produce high-octane gasoline as well as aromatics for use in the chemical industry. Apart from reforming, PGM-catalysts are also employed to a lesser extent in hydroprocessing, hydrocracking and isomerization reactions [1,4].

In the production of nitric acid, gauzes woven from very fine platinum-rhodium wire are used for the catalytic oxidation of ammonia. These catalysts typically consist of 90% of platinum with between 5-10% of palladium and rhodium. These catalysts are of critical importance since this is the only viable method for the production of nitric acid. Nitric acid is used extensively in the production of nitrogenous fertilizers and to a lesser extent for the production of explosives and other miscellaneous applications.

PGM-catalysts are also employed in the production of a number of liquid phase chemicals. Important applications include the oil-from-coal or Fischer-Tropsch process as well as the production of sulphuric acid [1].

## 3.2 Electrical Uses

The electrical industry is probably the commercial industry that has the most numerous and diverse applications of the platinum group of metals [1]. These metals are ideally suited to these type of applications because of their inherent stability at the elevated temperatures encountered in electrical equipment. Their extreme resistance to corrosion further ensures a long life for the electrical parts manufactured from these metals.

Palladium is the PGM that is most often used in electrical equipment, although platinum and rhodium are also occasionally used [4]. In most cases these three metals are virtually interchangeable, although when operating conditions are highly corrosive platinum-rhodium alloys are preferred. Some of the most common applications of the PGM in electrical equipment include heavy duty contacts, telephone switching relays (Pd, Ru), voltage regulators (Ir), thermostats, resistors (Ru), precision potentiometers (Rh, Ru) and glow- and spark-plugs (Pt, Ir). These PGM-plugs are preferably used in jet-aircraft engines and military vehicles since they have longer life-times and ensure improved ignition [1].

In the electronics industry palladium, and to a lesser extent platinum, are very important in the manufacture of multi-layer ceramic capacitors (MLCC) as well as thick-film circuits, resistance elements and thin-film circuits. The latter are for instance employed in magnetic hard disks for computer memory systems, while multi-layer capacitors (MLCC) are important components in the production of modern electronic equipment such as lap-top computers, high resolution television screens and cellular phones.

In certain high temperature industries, eg. steel industries, thermocouples are often used to measure high temperatures. Base metal thermocouples cannot tolerate temperatures higher than a 1000 °C and thermocouples from PGM are consequently used when temperatures between 1000 and 2800 °C must be measured. Platinum-rhodium alloys are most often used in these thermocouples. Gold-palladium alloys are also used the thermal fuses employed high temperature furnaces (1063 to 1552 °C).

Certain of the PGM are also used to electrolytically, coat metals that need to be protected against corrosion. A typical example of this is the Pt and Pd coatings that are used as anodes on the submerged parts of ocean-going vessels and pipelines, thus preventing cathodic corrosion of their ferrous structures. Another interesting application is the use of iridium-coated electrodes for the electrogalvanizing of motor vehicles, in order to extend their corrosion warranties [1].

Ruthenium, one of the lesser used PGM, is very important in the production of chlorine gas and sodium hydroxide from the electrolysis of sodium chloride brine. Along with titanium dioxide, ruthenium dioxide forms an integral part of the dimensionally stabilized anode (DSA) electrolytic cell, which is currently used world-wide in these processes.

### 3.3 Jewellery

All six of the PGM are used the in the manufacture of jewellery. Of these, platinum is the most popular. Apart from being the most abundant of these elements, the pure metal is relatively malleable and ductile, making it fairly easy to work with. Furthermore platinum is durable and resistant to oxidation, eg. it does not become tarnished. Although platinum is harder and stronger than gold, it is too soft to withstand the normal strain in precious gem setting. In such cases the metal are alloyed with rhodium to produce an alloy with superior strength. Of the other metals palladium is also easily worked, but due to the high melting points of ruthenium and iridium, they can only be crafted after preliminary hot-working. Alloying these metals with each other will not only influence the metal's hardness and other mechanical properties but often also increases its resistance to corrosion. Through the formation of different alloys it is therefore possible to manipulate the physical and chemical properties of these metals to some degree. The ability of metals to form alloys, eg. their mutual solubility, are primarily determined by their crystal structures. The cubic structures of Pt, Pd, Rh and Ir indicate extensive mutual solubility, although high temperatures (eg. 1500 °C) may still be needed in certain cases. Rh and Os have hexagonal crystal structures and therefore have limited solubility with the former group [1].

Due to the superior characteristics of these PGM-alloys, they have been replacing the pure metals of the group as well as gold and silver in the manufacture of jewellery.

### 3.4 Miscellaneous Uses

Due to their high melting points, high strength when hot, low oxidation rate and their resistance to corrosion and erosion, the PGM also play an important role in the glass and fibreglass manufacturing industries. Here, platinum is used predominantly, either as the pure metal or as an alloy with rhodium, gold or iridium. The unique low thermal expansion and wetting properties of these alloys make them ideally suited for use in a wide variety of glass handling, stirring and forming equipment [1,4].

The PGM also have a wide range of applications in the medical field, the best known being the use of *cisplatin* as a chemotherapeutic agent [3]. Apart from this and other anti-cancer drugs, platinum has also been used in antiviral, antiparasitic and anti-inflammatory drugs. Bioelectrodes also commonly employ PGM (platinum) since it is biocompatible and provides long-life mechanical stability. An excellent example is the 90Pt/10Ir-alloy that is used as a heart-pacemaker. Pt-alloys with either ruthenium or iridium also provide some of the sharpest and most durable cutting edges that are used in surgical instruments [1]. Palladium-alloys are also popular in the dental field, being used in the crowning of teeth as well as a bonding agent during the capping of teeth with porcelain [4].

Other lesser uses of the PGM include the production of some of the most powerful magnets in the world. These magnets are produced from a platinum-cobalt alloy and are most often used in miniaturized instruments. The metals are also popular in the construction of astronomical and other fine instruments. With these applications palladium is normally preferred, since it much lighter than for instance platinum. On being cooled from red heat, palladium also has the unique property of being able to absorb up to 935 times its own volume of hydrogen gas (this approaches the concentration of hydrogen in liquid hydrogen!). Upon heating, $H_2$ is given off again, thus providing means of purifying and possibly, in future, storing hydrogen [1,2]. Certain organic rhodium and ruthenium complexes also have the ability to separate water into hydrogen and oxygen by a solar- and photo-induced electron-transfer mechanism [1]. In the chemical laboratory, platinum and platinum-rhodium crucibles are essential when certain materials have to be fused at high temperatures. Other interesting applications that deserves mentioning is the use of iridium-phosphorus alloys in the production of durable tips for gold fountain pen nibs as well as the use of osmium in finger printing ink.

## 4. Chemical Properties of the Platinum Group of Metals

As mentioned earlier, the platinum group of metals (PGM) are also classified as noble metals. This is an indication of the exceptional inertness which is characteristic of these metals. Dissolution of the PGM is consequently no small feat, especially since no single acid is capable of dissolving all six elements [6].

Osmium and ruthenium are for instance barely affected by hydrochloric acid, sulphuric acid, oxidizing acids as well as aqua regia. They will however, dissolve in molten alkalis and oxidizing fluxes such as $KClO_3$ or NaOH and $Na_2O_2$ [4,6]. Rhodium and iridium are both extremely inert to acids, also being unaffected by even aqua regia. Finely divided rhodium may however be dissolved in aqua regia or hot sulphuric acid. The best method for rhodium dissolution are nevertheless fusion with sodium or potassium bisulphate. Iridium is even more inert and requires a two-step dissolution procedure. In the first step, it reacts with molten alkalis such as $Na_2O_2$ or KOH and $KNO_3$ to produce $IrO_2$, which can then be dissolved in aqua regia. Alternatively, Ir and Rh may both be dissolved by heating them with concentrated HCl and $NaClO_3$ in a sealed tube at 125-150 °C [6]. Of the six PGM's, platinum and palladium are the most reactive towards acid attack. Palladium will for instance dissolve in hot concentrated nitric and sulphuric acid. The presence of oxygen and the oxides of nitrogen, will further accelerate this reaction. Platinum is less reactive than palladium and is barely affected by mineral acids, although it will dissolve in aqua regia [6]. Both platinum and palladium may also be dissolved in fused alkali metal oxides and peroxides [4].

All six the PGM's are attacked by fluorine and chlorine. The conditions under which the attack occurs will however vary considerably between the elements. Osmium will for instance be attacked at 100 °C, while ruthenium will only react at about 300 °C. Iridium is not attacked below red heat, while rhodium is extremely resistant to halogen attack. Once again platinum and palladium are the most reactive elements in the group. Palladium will react with moist halogens at room temperature, while platinum will also react slowly under these conditions [4].

The aqueous chemistry of the noble metals is almost exclusively based on the elements' ability to form a wide range of complexes. Although aqueous ions of $Ru^{+2}$, $Ru^{+3}$, $Rh^{+3}$, $Ir^{+3}$, $Pd^{+2}$ and $Pt^{+2}$ exist in solution they will react readily with most anions to form complexes. Apart from the large number of ligands available, these elements can also occur in a number of oxidation states. Osmium can for instance occur in oxidation states ranging from +1 to +8. However, complexes with the PGM in oxidation states higher than +6 are generally not stable. The most stable oxidation states for the various PGM are respectively $Ru^{+3}$, $Os^{+4}$, $Rh^{+3}$, $Ir^{+3}$, $Pd^{+2}$ and $Pt^{+4}$ as well as $Pt^{+2}$ [2].

Most of these PGM-ions exhibit an affinity for certain ligands. According to these preferences it is possible to classify each of the PGM-ions either as class-a (hard) or class-b (soft) acceptors.

Generally, class-a acceptors are the most electropositive elements which will form the most stable complexes with ligands favouring electrostatic bonding, eg. $F^-$, $O^{2-}$ and $OH^-$. The $Pt^{+4}$-ion closely approaches a class-a character and will form thermodynamically stable and kinetically inert complexes with halides, pseudo-halides (eg. $CN^-$, $SCN^-$ and $SeCN^-$), N-donor ligands (eg. $NH_3$, amines) as well as O-donor ligands (eg. $OH^-$).

The $Os^{+4}$- and $Ru^{+3}$-ions exhibit a combination of class-a and class-b characteristics and are therefore classified as borderline acceptors. Osmium complexes of the type $[OsX_6]^{2-}$ are well-known and will form with $F^-$, $Cl^-$, $Br^-$ and $I^-$. A number of complexes with mixed halide and Group V-donor atoms are also formed. $Ru^{+3}$ also forms an extensive series of halide complexes, although iodo-complexes are not formed. $Ru^{+3}$ will further also coordinate with N-donor ligands and amines.

Class-b acceptors are less electropositive and have relatively full d-orbitals. They will therefore form the most stable complexes with ligands which do not only possess lone-pairs of electrons, but also have empty $\pi$-orbitals available. The latter orbitals stabilize the formed complex by accommodating some charge from the d-orbitals of the metal ion. The $Rh^{+3}$, $Ir^{+3}$, $Pd^{+2}$ and $Pt^{+2}$-ions all exhibit class-b characteristics. $Ir^{+3}$ and $Rh^{+3}$ will therefore coordinate readily with P-, As- and S-donor ligands, while they also have an affinity for ammonia and amine ligands. With $Pd^{+2}$ and $Pt^{+2}$ -ions, complexes of the type $[MX_4]^{2-}$ are easily obtained with $Cl^-$, $Br^-$, $I^-$, $CN^-$ and $SCN^-$. In the case of the thiocyanate ligand ($SCN^-$), bonding will take place through the $\pi$-acceptor end, eg. the S-atom. Furthermore, only a few complexes with O-donor ligands are formed, while a number of complexes will also be formed with ammonia and amine ligands. In the presence of class-b ligands such as S- and Se-donor ligands and especially P- and As-donor ligands, $Pt^{+4}$ will be reduced to $Pt^{+2}$ [2,7].

## 5. Analysis of PGM-samples

During the last few decades the relative importance of the PGM have increased significantly. This has high-lighted the need for effective analytical procedures for the determination of these elements in a variety of samples, ranging from geological samples and airborne dust to biological samples [8,9]. The PGM-levels in most of these samples are generally extremely low and the analysis thereof thus represents a formidable challenge for the analytical chemist. Furthermore, certain sample types (eg. geological samples) may create additional challenges due to the difficulties associated with decomposition of the samples. Almost two decades ago Beamish stated that "...despite more than a century of analytical effort, no procedure has been recorded that can be used with confidence for the direct determination of each of the noble metals in primary deposits." [10]. Unfortunately this still appears to be true since most recently developed methods, are still characterized by low recoveries.

The determination of PGM in geological samples can be divided into 3 important steps [8,9]. Firstly, since these elements are commonly very inhomogeneously distributed in rocks, it is essential that large, representative samples are taken. Samples should subsequently be decomposed to allow further separation and quantitative analysis of the PGM. The following methods represent those that are most often used the determination of the PGM in geological samples:

### 5.1 Nickel sulphide fire assay

This is considered to be the most successful method for the simultaneous decomposition and concentration of geological PGM-samples [8,9,11]. The PGM is selectively concentrated in a metal-collector which is formed during fusion. Although lead can be used as the metal-collector, it cannot collect Ir, Ru and Os quantitatively. NiS is therefore preferred as the metal collector in fire assay procedures.

One of the biggest advantages of fire assay is its ability to accept large samples (10-100 g) [12,13]. Samples are heated with a mixture of appropriate fluxes (eg. sodium carbonate, sodium tetraborate) to temperatures of up to 1000 °C. A homogeneous melt is subsequently formed, which separates into a glassy slag and the metal collector (NiS) upon cooling. During fusion the major elements are partitioned into the glassy slag while the PGM are collected in the NiS-layer. After separation, the NiS-button is usually dissolved in acid to remove the Ni and S matrix [11,12]. A black precipitate (PGM-sulphides) remains after dissolution and can either be analyzed directly by neutron activation analysis (NAA) or be dissolved for analysis by atomic absorption spectroscopy (AAS), graphite furnace AAS (GFAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP-mass spectrometry (ICP-MS) [9]. With the development of laser ablation-ICP-MS it has also become possible to analyze the NiS-button directly [13].

Although this method is widely accepted as the most reliable for the preparation of geological samples, it does suffer from some serious limitations. Firstly, the quality of the results obtained depend on the experience of the analyst and the composition of the flux selected for a particular sample type. Furthermore, large quantities of reagents are used and may contribute to high blank values if they are not of very high purity [8]. PGM-recoveries with NiS fire assay may not always be quantitative since element losses may occur during fusion [8,11]. It is also likely that losses will occur during the crushing and dissolution of the NiS-button [8,11,13].

### 5.2 Alkali Fusion

This is also considered an effective procedure of sample dissolution, although it is limited to much smaller samples (0.5-1.0 g) than fire assay techniques [8]. Decomposition of the sample is obtained by heating it with an alkaline flux or flux mixture. Although a variety of fluxes are available, $Na_2O_2$ are generally favoured [9,11,12]. Sodium peroxide fusion ensures the effective attack of sulphide and refractory minerals [8], while the released PGM are also uniformly converted to their highest oxidation state [11]. After fusion the resulting cake is dissolved in a mixture of de-ionized water and 6 mol/l HCl. This solution can then be analyzed directly. When an ICP-MS system is used as detector, it may be necessary to dilute the solution before analysis since the level of total dissolved solids (TDS) are often higher than what the instrument can tolerate ($< 0.2\%$). In certain cases this dilution of the sample may lead to concentrations which are lower than the detection limit of the instrument [12].

Alternatively, the PGM in the solution may be collected through Te-coprecipitation. After precipitation, the precipitate is collected and dissolved with concentrated $HNO_3$. This solution is subsequently evaporated to dryness and then redissolved with a small volume of aqua regia [8], which can be analyzed. This procedure also acts as a concentration step, which may improve the detection limits of the procedure.

Since this method is only applicable to relatively small samples, it is often used to dissolve the insoluble residue obtained after procedures such as acid dissolution or microwave digestion. The two solutions obtained are then combined before analysis and good agreement with reference values have been obtained in this way [12].

### 5.3 Microwave Digestion

The use of microwave digestion to dissolve refractory samples offer a number of distinct advantages, such as reduced heating times. When closed vessels are employed even higher temperatures and pressures can be obtained, while trace element losses due to the formation of volatile molecular species (eg. $OsO_4$) are also reduced [14]. Microwave digestion has consequently also been used for the dissolution of PGM-containing ores, although success has been limited. Once again, this can probably be attributed directly to the general resistance of the PGM towards acid attack.

In one such an application 10 g samples were dissolved in 30 ml aqua regia at pressures of up to 160 psi. Poor recoveries were however reported and ranged from just 30% for ruthenium to 90% for rhodium [14].

Totland *et al* [12] obtained better recoveries in a study where different acid mixtures were evaluated. They concluded that it was essential to include a oxidizing acid in the original acid mixture. Although perchloric acid initially gave the best results, it could not be used safely when a higher pressure system was used. Aqua regia was consequently used in combination with hydrofluoric acid. In this system pressures of up to 200 psi were obtained, but not even at these extreme conditions were complete dissolution obtained. The insoluble residue was subsequently dissolved by $Na_2O_2$-fusion. The final results obtained compared relatively well with reference values, although sample dilution was one again necessary since an ICP-MS were used as detector. This meant that the quantitation limits of the procedure were only between 0.2 and 1.0 $\mu$g/g.

It is therefore clear that microwave digestion alone is not suitable for the dissolution of geological samples.

### 5.4 Dry Chlorination

Dry chlorination has been employed for the determination of very low levels of PGM present as native metals, natural alloys and sulphides in geological material [9]. In this method the PGM are converted to their sodium salts by heating samples at 580°C in the presence of chlorine gas and sodium chloride. The salts formed are subsequently dissolved in dilute HCl, filtered and analyzed. It has been found that this method yielded results which were comparable or better than those obtained by fire assay. Advantages of this procedure include the use of large samples (up to 250g) as well as extremely low blank values.

### 5.5 Acid Dissolution

As stated earlier, acid dissolution of PGM-containing geological samples are generally not quantitative. The best results are obtained when a mixture of acids are used (eg. aqua regia and HF). Any insoluble residues should then be fused with a flux such as $Na_2O_2$ and added to the acid solution. This solution can then be analyzed directly or Te-coprecipitation may be performed prior to the final analysis. This procedure has been used successfully and yielded results that agreed well with certified values [9].

Once PGM-samples have been dissolved a separation and/or preconcentration step are normally required before analysis [11]. In certain cases, eg. fire assay, this is performed simultaneously with sample dissolution, however when this is not the case, solvent extraction and ion-exchange procedures may be employed for the separation and concentration of the PGM. With ion-exchange either a cation-exchanger can be used to separate the PGM form the matrix, or otherwise an anion-exchanger may be used to simultaneously separate and preconcentrate the PGM. This will however be discussed in detail in Chapter 5.

A wide variety of instruments are used in the determination of the PGM in samples. Some of these include spectrophotometry, ICP-OES, GFAAS as well as ICP-MS. Of these systems, ICP-MS has lately been the most popular. This can be attributed to the excellent sensitivity of the technique as well as its multi-element capability. Unfortunately these instruments require very low TDS-levels. Due to the subsequent dilution of samples, the detection limits of most of these procedures are not substantially better than those obtained with ICP-OES for instance [12].

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# CHAPTER 3

# Flow Injection Analysis

## 1. Introduction

In the last few decades tremendous changes have taken place in the Analytical Laboratory [1]. With the development of sophisticated analytical instrumentation such as the ICP-OES, ICP-MS, etc. it has become possible to achieve very accurate, precise and sensitive results. In the true spirit of the computer age most of these instruments can today be operated directly from the keyboard of a computer. The computer is also used for data accumulation and manipulation, often giving you results within seconds of the analysis [2].

Unfortunately the development of basic analytical techniques in the laboratory could not keep up with the instrumentation being made available, thus leading to the sample preparation step becoming the proverbial 'Achilles heel' of most analytical procedures [1]. Traditional batch processes often involve several time-consuming sample manipulation steps such as pipetting, extraction, precipitating, etc. Even in the hands of an experienced analyst the high degree of sample handling, seriously increases the risk of sample contamination leading to poor precision and accuracy [3].

In order to ensure more efficient and reliable sample preparation, chemists started to look at various ways to automize these processes. At first manual batch operations were mechanized. However these systems frequently proved too expensive with only limited use (eg. one specific application) [1]. Furthermore these devices are known to cause errors due to a lack of precision in measuring volumes, cross-contamination between samples as well as problems associated with control of the identity of a series of samples [3]. Although most of these problems can and have been circumvented, the systems tend to become large and complex, involving a range of discrete vessels having to be manipulated [3].

An important development in the automatization of sample treatment came with the introduction of continuous flow analysis by Skeggs in 1957 [4]. His system, which became known as the "AutoAnalyzer"$^{TD}$ was the first to incorporate conduits instead of the discrete vessels for the manipulation of samples [1]. The principle of air-segmented continuous flow lay the stage for the later development of the non-segmented flow analysis systems by Růžička and Hansen [5,6]. These FIA-systems abandoned the principle of steady state read-out by introducing accurately timed measurements at non-equilibrium conditions.

Since FIA is based on a combination of sample injection, controlled dispersion and exact timing [6] the importance of the computer to coordinate the various manipulations and measurements are self-evident. With the development of FIA it has thus became possible to match laboratory techniques available for solution manipulation with the characteristic efficiency of the computer age [1].

## 2. What is FIA?

According to Růžička and Hansen - who coined the name Flow Injection Analysis (FIA) - this is a technique based on a combination of sample injection, controlled dispersion and exact timing. They formally defined FIA as: "Information-gathering from a concentration gradient formed from an injected, well-defined zone of a fluid, dispersed into a continuous unsegmented stream of a carrier" [5]. Since then FIA has developed extensively to cover a broad field of applied analytical chemistry. However with these developments some of the classical distinctions of FIA disappeared eg. the introduction of segmented flow in hydride generation systems. According to Fang [1] the essential features of FIA that still remain are:

- Reproducible manipulation of sample and reagent zones through precise timing.
- Quantitative evaluation of analyte concentration under thermodynamically non-equilibrated conditions.

Considering that FIA is a field that is still rapidly developing, one can assume that the controversy surrounding the precise definition of FIA will still continue for some years.

## 3. Controlled Dispersion as a Foundation of FIA

Dispersion is defined as the dilution a sample undergoes when it is injected into a flowing stream, eg. carrier stream [3]. Due to the nature of FIA, mixing (dispersion) is highly reproducible and also time-dependant. The degree of dispersion is thus controllable, giving rise to a time-dependant concentration gradient of the sample in the carrier stream. This is critical, since FIA is based on accurately timed measurements of a reaction which is not at equilibrium [1].

In FIA the extent of dispersion is determined by a number of mechanisms. Initially, after the injection of the sample, *convective transport* will occur under the typical laminar flow conditions prevailing with FIA. This will yield a parabolic velocity profile, eg. with the highest dispersion at the centre of the tube. The resulting concentration gradients give rise to *axial* and *radial diffusion*. The latter type makes a significant contribution to the overall dispersion and ensures that the sample integrity is maintained [3].

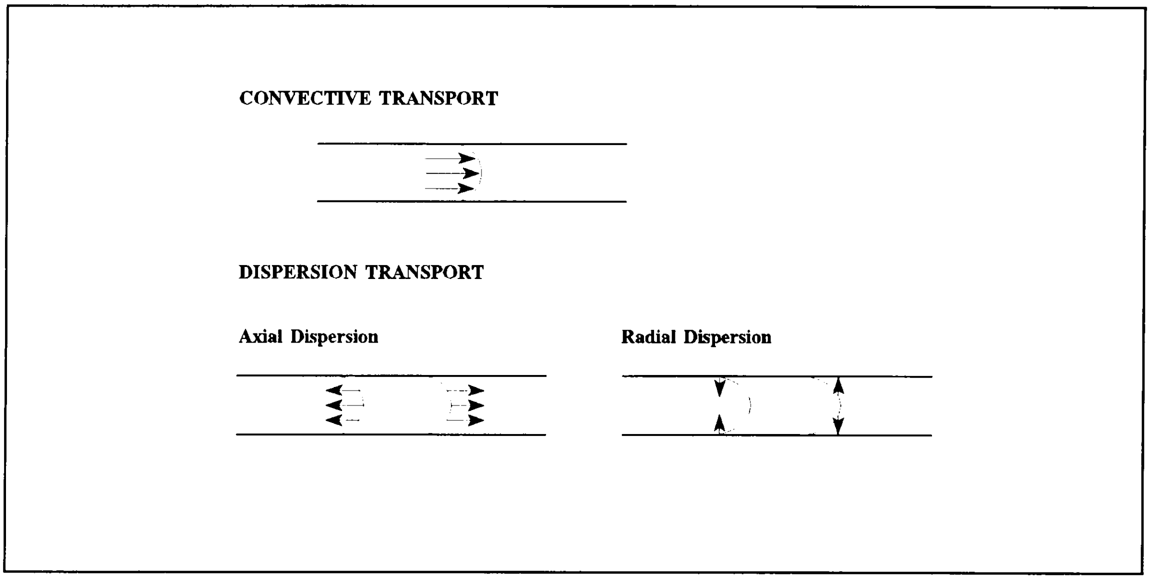

**Figure 3.1** Dispersion in a Tube.

As mentioned before, the degree of dispersion obtained in FIA may be controlled. Some of the most important parameters influencing the sample dispersion are the sample volume, the carrier flow-rate, the flow-rate ratio between the sample carrier and the merging reagent as well as the geometrical dimensions and configurations of manifold components. Depending on the analytical objectives it is therefore possible to design a system according to the degree of dispersion required. In order to evaluate the dispersion, Růžička and Hansen [5,6], have defined the dispersion coefficient, D. This is merely the ratio of the analyte concentration before ($C^0$) and after dispersion. In most cases the dispersion at peak maximum is considered, eg.

$$D = \frac{C^0}{C_{\max}} \qquad \textbf{(1)}$$

where $C_{max}$ is the analyte concentration at peak maximum.

The value of D is greater than unity and reflects the dilution factor of the analyte under investigation. Depending on the degree of dispersion obtained, FIA systems may be classified as high, medium or low dispersion systems.

Systems with high dispersion, eg. $D > 10$, are normally used where samples are too concentrated for the detector. In these cases components such as mixing chambers may be required to achieve the high degree of dilution [1,2]. According to Fang [1], systems with a dispersion coefficient between 2 and 10 are classified as medium dispersion systems. These systems are popular when a chemical reaction should occur between the injected sample and a reagent [2]. Finally systems with dispersion coefficients below 2 are classified as low dispersion systems and limits unnecessary dispersion of the original sample. These systems are most important as preconcentration systems, where the highest possible sensitivity enhancement effects are desired [1].

## 4. Basic components of a FIA-system

Despite all the changes that have been introduced, the basic components of a FIA-system remained the same, namely the pump, sample injection system, the reactor (eg. a mixing coil or a column) as well as the detector.

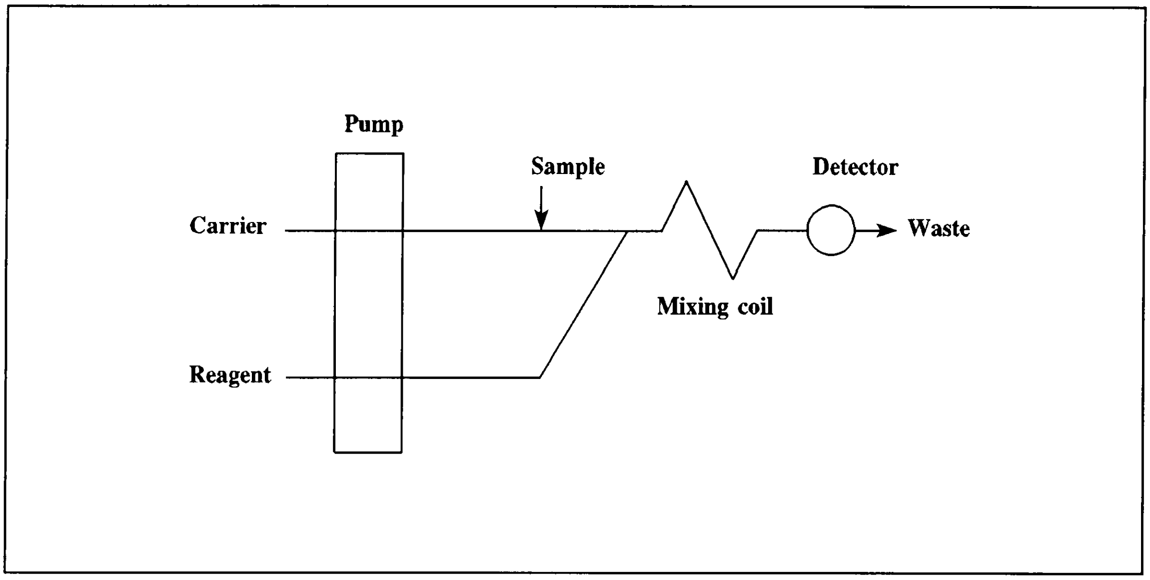

**Figure 3.2** Schematic representation of a basic FIA-system.

### 4.1. Liquid propulsion devices

These devices, or pumps as they are commonly known, produce the flow in the FIA-system. Due to the highly reproducible timing inherent to this technique, the propulsion system chosen should comply with certain important criteria. Ideally flow rates must be reproducible on the short and long term, providing a pulse-free fluid delivery. Multi-channel capability of pump should be combined with readily adjustable flow rates. The pump must also be resistant to strong reagents and solvents. Finally the initial investment and running costs should be as low as possible [1].

A number of liquid delivery devices are currently available. Of these, peristaltic pumps are definitely the most popular in FIA. Although they do not meet all the requirements for an ideal propulsion device, most of the drawbacks associated with these pumps can usually be overcome. In cases where organic solvents and strong reagents are used, Tygon pump tubes cannot be used for extended periods. However special solvent resistant tubes are available in such cases. Alternatively a cheap solution would be to use a solvent displacement bottle if the organic solvent is immiscible with water [1]. In the case of on-line separation/preconcentration systems, where the flow impedances are often significantly higher than normal, it is especially important to ensure that these pumps are operated properly. If not, a stable, reproducible flow may not be obtained with a subsequent deterioration in the precision.

Other delivery devices that are also used are reciprocating piston pumps, syringe pumps and gas-pressure systems, while gravitation has also been used. Although these systems individually have features that may, in certain cases, make them more desirable than the peristaltic pumps, they are not generally used.

### 4.2. Sample injection system

A large number of valve designs performing sample injection and/or other flow functions, are available. With FIA it is important that the injection system should be able to provide reproducible insertion or introduction of an accurately measured sample volume into the flow without stopping it. Compared to valves used in other techniques such as HPLC, FIA-valves should be more versatile and also be able to provide a larger number of leak-proof operations using a wide range of solvents [1].

Valves that are frequently used in FIA are the 6- or 10-port rotary valves as well as the 8-channel 16-port multifunctional valve. The operation principle of most of these valves are basically the same, with the versatility of the valve generally increasing with the number of ports available. Only a brief description of the 10-port valve will therefore be given.

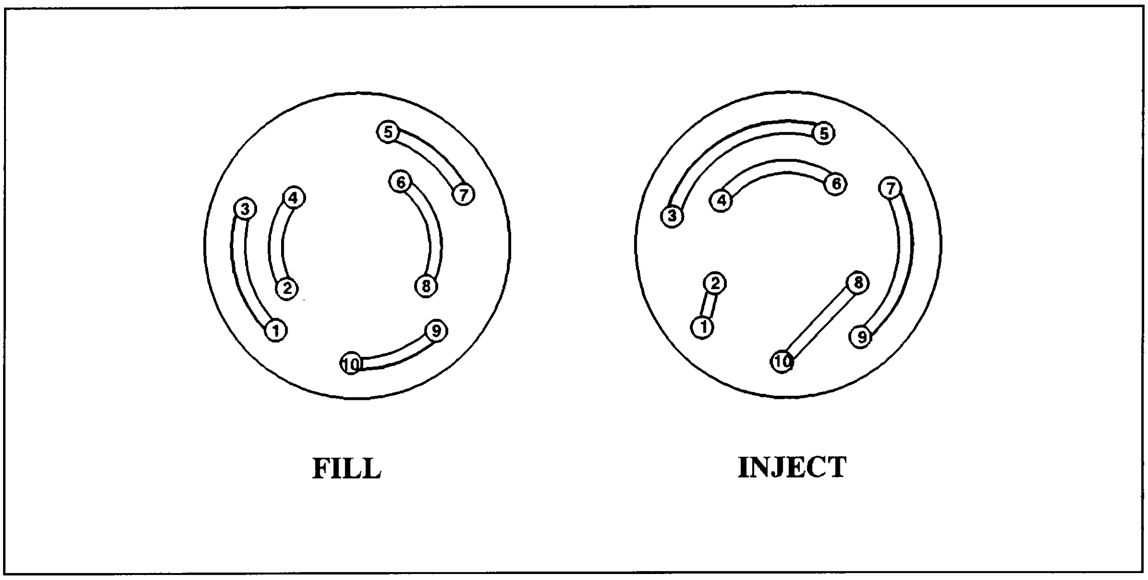

**Figure 3.3** Schematic representation of a 10-port valve.

This valve has 5 channels engraved on the contact surface of the rotor and 10 ports on the stator, or *vice versa*. Rotation of the valve between the two available positions (Fill and Inject) will cause each channel to connect a different set of ports, thus making manipulations such as sample loading and -dilution possible.

## 4.3 Reactors

According to Varcárcel and Castro [3], "Reactors are units of the transport system acting on the residence time and the sample plug and endowing the latter with the required characteristics for measurement by the detection unit." A wide variety of reactors are available and are greatly responsible for the extreme versatility of the FIA technique. A number of these reactors are:

### 4.3.1 Open tubes

A variable length of open tubing between the injector and detector mainly promotes axial dispersion. The degree of dispersion will also depend on the inner diameter of the tube.

### 4.3.2 Coiled and knotted reactors

A variable length of open tubing which has been helically wound around a cylinder with a specific diameter is known as a coiled reactor. A knotted or 3-dimensional reactor can be formed by making a number of sequential knots in a piece of tubing. By changing the flow direction these reactors produce a secondary flow in the radial plane, which in turn promotes radial mixing while decreasing the axial dispersion of the injected sample. The knotted reactor's superior capability to limit dispersion can be attributed to the fact that it changes the flow direction three-dimensionally as opposed to the two-dimensional change with coiled reactor.

### 4.3.3 Packed reactors

These reactors are made by filling a length of tubing with chemically inert or active material [3]. Chemically active material that are commonly used are ion-exchange resins, oxidants, reductants and even enzymes. These reactors normally require FIA-systems which can cope with higher internal pressures, but nevertheless form a very important application within FIA.

### 4.3.4 Single bead string reactor (SBSR)

In this case a variable length of tubing is packed with chemically inert beads (glass or polymer) with diameters 60 - 80% of that of the tubing [3]. The reactor basically acts as an effective mixing reactor, offering greater residence time and lower dispersion [3]. They are however more difficult to produce and less flexible when compared to knotted reactors and may therefore not be as popular[1].

## 4.4 Detectors

Although any detection system which can be adapted for flow-through detection may, in principle, be used as a detector in FIA, certain detectors are inherently more suitable than others [1]. Some of the common requirements for a flow injection detector are small volume, low noise level, fast and linear response over a wide concentration range and high sensitivity. The detection limit and the detector contribution to the peak width are also important features [3]. The following detectors are most frequently used:

### 4.4.1 Spectrophotometers

Due to the large number of species that may be monitored - either because of their intrinsic optical properties or because of selective colour forming reactions - visible and UV spectrophotometers are by far the most frequently used type of detectors in FIA [1,3]. These detectors do not require large capital investment while a conventional batch spectrophotometer can easily be converted into a flow-through detector by simply substituting the conventional cuvette with a flow-through cell. Although a number of cells are available the Hellma U-shaped cells are definitely the most popular. The Z-shaped cell is used less frequently, due to the difficulty associated with its adaption to ordinary photometers. Depending on the spectral region covered, the cells are furnished with either glass or quarts windows. Major limiting factors associated with these detectors are noise and light-source instability as well as the generation of spurious peaks. The latter can be attributed to differences in refractive properties of the sample and the carrier/reagent.

### 4.4.2 Spectrometers

Atomic Absorption (AAS) and Inductively Coupled Plasma (ICP) Emission Spectrometers are inherently flow-through detectors and the FIA-system can therefore be coupled directly to the nebulizer-system of these spectrometers.

A number of the advantages associated with the use of spectrometers with FIA are:

- Decrease in sample volumes used (typically $\mu\ell$'s).
- Strong tolerance to high concentrations of dissolved solids in the sample, since the sample is only present as a plug in the continuous feed of carrier to the

nebulizer. (Up to 40% m/v can be tolerated [2])

- The use of a pump in FIA ensures minimal matrix effects due to differences in viscosity.
- Interference effects may be minimized through careful manipulation of operating conditions of detector. A separation technique may also be incorporated when serious interferences are present.
- A higher sample throughput can be obtained than with conventional sample introduction. The coupling with separation or preconcentration techniques will however lead to a decrease in sample frequency.
- Most spectrometers currently have the capability to monitor and record the characteristic transient signals of FIA, thus ensuring easy automatization.
- Multi-element capability of certain ICP-spectrometers [1].

A disadvantage of most spectrometers are the relatively large volume of the spray chamber (*ca* 100 m$\ell$) when compared to the volume of sample used ($\mu\ell$-range). However, with AAS it has been shown that the detector's contribution to the dispersion of the injected sample is comparable to that of other FIA-components [1]. In the case of ICP, a number of techniques have been developed to enable the direct introduction of the sample into the torch [1,2].

Problems with sample introduction rates may also occur when spectrometers are coupled to FIA systems. Typically the aspiration rates for flame-AAS are much higher than the flow-rates of FIA systems. In the case of ICP-spectrometers optimum uptake rates are however much lower than for AAS and the former may therefore be coupled easier to FIA systems with their typically lower flow rates.

### 4.4.3 Electrochemical Detectors

A large variety of these detectors have been used in combination with FIA. A few of these include those based on potentiometry, amperometry, conductimetry and voltammetry, with the ion-selective electrode having the most widespread application [1]. Two of the most common designs for these electrodes are the tubular flow-through liquid membrane and the solid membrane flow-through ion-selective electrodes.

On-line ion-selective electrodes offer a number of additional advantages when compared to the conventional ion-selective electrodes, eg.

- Improved precision of measurements.
- Selectivity of electrodes can be improved through kinetic discrimination.
- The short exposure time of the FIA mode of operation prolongs the lifetime of electrodes and decreases the risk of damaging sensing surfaces by hazardous materials in real samples [1].

Other detectors which are used less frequently include chemiluminescence, bioluminescence and fluorimetric detectors.

## 4.5. Transport conduits

Transport conduits are used to provide connections between the different components in a

FIA-system. Tygon and PTFE tubing are most frequently used and depending on the application, tubes with different inner diameters (i.d.) can be used. Tubes with small i.d.'s will ensure low dispersion of the injected sample, while tubes with inner diameters of 1 mm or above are used with higher flow rates as well as to decrease flow-impedance in gas-segmented flows. These tubes may be connected to the different components of the FIA system by means of push-fit connections or threaded fitting connectors. The former type are the most convenient to use, although they are not considered reliable where high internal pressures are expected. In such cases threaded fitting connectors or push-fit connectors with a slip-proof design should be used.

## 5. Advantages of FIA

One of the most important features of FIA must be the extreme versatility of the technique. This can be attributed to its modular nature, allowing adaption to a variety of applications in analytical chemistry. It is for instance fairly easy to change one or two of the components/reagents in an existing system with any other of the wide range that is available, to obtain an entirely different system. This is also an indication of the great simplicity which is another great advantage of the technique. Furthermore the manifolds used to construct a FIA system are usually relatively inexpensive and easy to obtain, while the reagent consumption of a FIA system are typically 20 - 100 times lower than that of manual techniques. Another outstanding feature of FIA is the speed of analysis, with sample frequencies which are much higher than those obtained with traditional manual methods. According to Varcărcel and Castro [3] up to 54% of FIA methods in the literature up to 1987, had a sample frequency between 50 - 120 samples per hour. Despite the rapidity of the technique and the fact that quantitative analysis are performed under thermodynamically non-equilibrated conditions, the precision obtained with FIA is often less than 1% [3].

In general FIA methods have a higher tolerance level for interference than conventional methods. The higher selectivity can in part be ascribed to the kinetic aspect of the methods, eg. unwanted reactions do not develop to a significant extent in the short measurement period characteristic to FIA. It is also possible to reduce any interference to a minimum by using carefully optimized manifolds [3].

## 6. Limitations of FIA

Generally basic FIA methods are considered to be less sensitive than their manual and SFA counterparts. This is due to the fact that equilibrium is not attained before measurements are made, as well as the physical dispersion or dilution of the sample in the carrier. The presence of interfering elements in samples may, in certain cases, also lead to a decrease in the sensitivity of the method.

However a number of ways are available to overcome these limitations. The incorporation of a preconcentration and/or separation manifold in a FIA system is one of the most effective ways used to improve the sensitivity of a method. Apart from the effective concentration of an analyte on a solid phase or in an organic phase, interfering elements may also be removed on a suppressor column before analysis. In these cases the traditional use of ion-exchange columns are far too time consuming and the possibility of sample contamination is also greatly increased. Furthermore, a substantial improvement in the detection limits of an instrument are usually obtained in this way.

## 7. Important criteria for the evaluation of a FIA preconcentration system

In order to be able to compare the performance of different preconcentration systems in literature, it is necessary to define certain criteria. According to Fang [1] the following criteria should be considered:

### 7.1 Enrichment factor (EF)

In practice this factor is used most frequently during the evaluation of preconcentration systems [7]. By definition, the enrichment factor (EF) describes the ratio between the analyte concentration in the concentrate, $C_e$, and the original sample, $C_s$:

$$EF = \frac{C_e}{C_s} \tag{2}$$

The value of this factor is often approximated by the ratio of the slopes of the linear section of the calibration curves before and after preconcentration. Despite the fact that this evaluation is based on response enhancement and not only on the increase in concentration, the EF-value obtained in this way is acceptable in most cases.

### 7.2 Enhancement factor (N)

In Flow-Injection preconcentration systems the analyte signals are sometimes enhanced through mechanisms other than the increase in the concentration of the analyte. A classic example is the signal enhancement in flame AAS when the analyte is introduced in an organic solvent. In order to obtain a valid evaluation of the preconcentration performance of a FIA system, it is therefore necessary to differentiate between these additional factors ($N_i$) and the true enrichment effects. This can be obtained by the determination of the true enhancement factor under operational conditions excluding the preconcentration step. The total enhancement factor ($N_t$) will then be the product of the individual enrichment factors, $N_1$ - $N_n$, and the enrichment factor (EF).

$$N_t = N_1 \times N_2 \times \ldots \times N_n \times EF \qquad \textbf{(3)}$$

### 7.3 Concentration Efficiency (CE)

According to Fang [1], the enrichment factor does not provide adequate information when the efficiency of a preconcentration system is evaluated, since high enrichment factors may be obtained at the expense of sample frequency. He consequently defined the concentration efficiency (CE) as the product of the enrichment factor and the sampling frequency.

$$CE = EF \times \frac{f}{60} \qquad \textbf{(4)}$$

where f is samples analyzed per hour.

The value of this parameter therefore dictates the factor of enrichment of an analyte achieved by the preconcentration system in one minute. It is subsequently possible to compare the preconcentration efficiency of various procedures - including those based on different separation mechanisms - by simply using this value.

### 7.4 Consumptive Index (CI)

This criterion gives an indication of the efficiency of sample utilization in a preconcentration system. Fang [1] defined this factor as the volume of sample ($V_s$) in millilitres, consumed to achieve unit EF, eg.

$$CI = \frac{V_s}{EF} \qquad \textbf{(5)}$$

The consumptive index is a very important parameter when only a limited amount of sample is available, such as in the case of clinical samples.

### 7.5 Phase Transfer Factor (P)

Due to the non-equilibrium nature of FIA methods, the analyte in a sample may often not be completely transferred into the concentrate. This may in certain cases also be ascribed to the inadequate capacity of the collection medium. Although this does not necessary lead to the deterioration of the precision and enrichment factor, these conditions will make the preconcentration system more vulnerable to matrix effects and interferences from competing species. The completeness of analyte transfer from the sample phase into the concentrate phase are consequently an important aspect to consider when evaluating Flow-Injection preconcentration systems. The phase transfer factor (P) is subsequently defined as the ratio between the analyte mass in the original sample ($m_s$) and that in the final concentrate ($m_e$).

$$P = \frac{m_e}{m_s} \qquad \textbf{(6)}$$

In column preconcentration systems P is often referred to as the retention efficiency (%E) of a specific column [15].

## 8. Classification

Apart from simply removing interferents, most separation systems may also be employed for the preconcentration of analytes. The principle difference being that the final volume in which the sample is contained should be less than the original volume of the sample. The classification of these techniques are consequently similar, and can be represented as follows:

- Liquid - liquid interface
    - Solvent extraction
- Liquid - solid interface
    - Ion - exchange
    - Adsorption
    - Sorbent extraction
    - Precipitation

These techniques may further be classified according to the medium in which the preconcentration takes place. Solvent extraction will, for example most often employ membrane techniques while columns are predominantly used with ion-exchange and sorbent extraction.

## 8.1 Liquid - liquid extraction

Liquid-liquid extraction with FIA was first introduced in 1978 [8,9]. Since then the popularity of the technique has grown to such an extent that it is presently considered to be the most frequently used separation technique in FIA [1].

Apart from introducing high sensitivity and selectivity levels, this technique also eliminates some of the unpleasant features associated with manual operations. It is for instance a well known fact that traditional liquid-liquid extraction is a tedious operation with a high risk of introducing contaminations. Apart from eliminating these problems, on-line extraction also limits physical manipulation of organic solvents which are often toxic and have annoying odours.

Flow-Injection liquid-liquid extraction systems typically consist of a phase segmentor, extraction coil and a phase separator [1,3]. The phase segmentor acts as a merging or mixing point for the immiscible organic and aqueous phases. Its main purpose is to let regular, alternate segments of both phases enter the extraction coil in a defined ratio. In the case of preconcentration, the segment of the extractor phase will consequently be smaller than that of the sample phase. In the extraction coil the two phase are brought into extensive contact with each other thus enabling effective mass transfer between the phases. Finally the phase separator are responsible for the physical separation of the continuous, heterogeneous stream into two separate streams. Here, it is critical that the stream containing the analyte do not contain any trace impurities of the other phase. The following detectors are those that are most frequently used with FI liquid-liquid extraction systems.

Of the available detectors the spectrophotometer is once again the most frequently used. This can possibly attributed to the large number of reagents which form extractable species with the analyte while simultaneously acting as chromogenic reagents. Furthermore the spectrophotometric flow-cell (glass or quarts) is resistant to organic solvents and does not pose any limitations on the flow-rate and flow direction through the cell. However any contamination by accidental entrained aqueous phase in the flow-cell will cause an interruption in the procedure since the cell can only be cleaned through rinsing with a water miscible solvent such as acetone.

Another detector which may be used in conjunction with FI liquid-liquid extraction is flame AAS. A special feature of this combination is that the occasional entrainment of traces of the aqueous phase into the detector will usually not produce noticeable effects. The introduction of the analyte in an organic solvent extract, instead of the aqueous phase, may further create an additional two to three fold sensitivity enhancement. As could be expected from FIA-AAS, the flow-rate of the separated concentrate normally needs to be to be adapted to match the optimum of the spectrometer's nebulizing system. According to Fang [1], the flow-rate of the nebulizing system are normally about an order of magnitude higher than that of the FIA system. It is possible to create starvation conditions in the nebulizer, although this could lead to a deterioration in the sensitivity and precision of measurements.

ICP-emission spectrometry (ICP-OES) has also been coupled to FI liquid-liquid extraction, although the number of applications are unexpectedly few [1]. Normally FIA systems can be coupled fairly easy with ICP-OES, since the normal uptake rates of ICP nebulizers do not differ a lot from the optimal flow-rates of FIA systems. A definite disadvantage of this detector, possibly explaining the lack of applications in this field, is the sensitivity of the plasma to changes in solvent conditions. The introduction of organic solvents usually requires higher power levels, while the accidental entrainment of traces of water into the plasma can cause severe noise.

Finally FI liquid-liquid systems has also been coupled successfully to liquid and gas chromatography systems.

### 8.2 Column Preconcentration

In 1980, Bergamin *et al* [10], made the first attempt to incorporate an ion-exchange micro-column in a FIA system, determining ammonia. Burguera *et al* [11] soon followed suit, using an ion-exchange column for the successive elution of Zn and Cd in a sample. However it was only after Olsen *et al* [12] coupled FI column preconcentration to flame-AAS in 1983, that these systems really started to attract attention. Since then the use of FIA for on-line separation and preconcentration by sorption has developed to become one of the most active research fields in automated solution analysis [1].

The use of FI sorption column techniques offer several advantages when compared to other separation and preconcentration methods; both off- and on-line. Firstly the technique is easier to operate since no careful sample manipulation is required as for instance in liquid-

liquid extraction, while the equipment are generally more robust. Furthermore this technique is also extremely versatile, with a wide range of different sorbents, complexing systems and eluents being available.

### 8.2.1 The micro-column

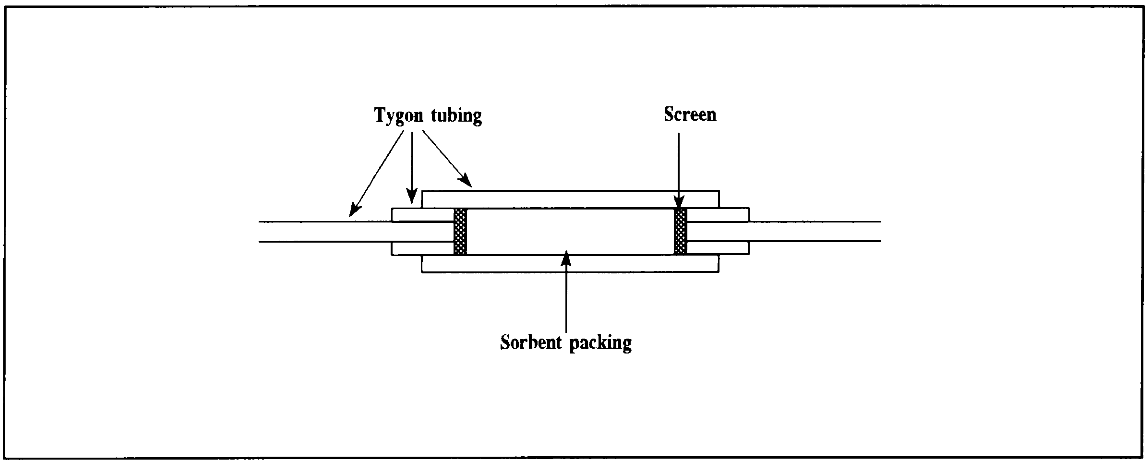

**Figure 3.4** Design of an uniform-bored column with push-fit connections.

The design of the micro-columns used in FIA are characterized by its simplicity and can easily be constructed from tubing etc. that is readily available in a FIA laboratory. The design chosen will however have a strong influence on the performance of the preconcentration system and the following guidelines should be considered [1,14]:

- Higher enrichment factors (EF) and stronger tolerance to interferences are obtained with columns which have large aspect ratios. The aspect ratio has been defined as the ratio between the length, L, and the diameter, d, of a column, eg. L/d [13]. In practical terms this would mean the longest and thinnest columns possible. Unfortunately the enrichment that may be obtained with columns with large aspect ratios are limited by the extensive back-pressure generated at high sample loading rates.

- Columns with larger column capacities exhibit stronger tolerance to interferences, but this also causes a decrease in the EF-value. Small columns of approximately 100 $\mu\ell$ and with aspect ratios between 10 - 15 are recommended [14] to obtain acceptable recoveries and sensitivity with both flame-AAS and ICP-spectrometry.
- Improved breakthrough capacities and sharper elution peaks may be obtained by using column packing with a finer particle size. However, increased back-pressure will once again limit the sample flow-rates and a compromise should be found to ensure optimum enrichment of the analyte.

Despite the wide range of sorbents available from batch column preconcentration procedures, only a portion of these are suitable for FIA systems. Apart from being able to concentrate the analyte, sorbents that can be used in FIA must meet certain additional requirements. Generally these sorbents must show negligible swelling and shrinking when solvent conditions are changed. It is also essential that these sorbents are strong enough to maintain long column life times and withstand high linear flow-rates. Finally the kinetic properties should ensure sufficient retaining as well as easy elution of the analyte. The following types of sorbents are most frequently used in FIA micro-columns [1]:

- Chelating Ion-Exchangers, eg. Chelex-100
- $C_{18}$ Bonded Silica Gel
- Polymer Sorbents, eg. XAD-4
- Strongly Basic Anion Exchangers, eg. Dowex 1-X8
- Strongly Acidic Cation Exchangers, eg. BioRad AG50W-X8
- Activated Alumina

### 8.2.2 General Procedure

With FIA column preconcentration procedures it is usually possible to distinguish three definite steps, namely sample loading, elution and detection.

### (i) Sample Loading

Samples can be loaded onto a packed column either directly, by *time-based sampling* or indirectly, through *volume-based sampling*. In time-based sampling the sample is pumped through the column for a fixed period of time, whereas in volume-based sampling the carrier stream is used to displace the sample from a fixed volume loop. The former system is usually preferred as it is more straightforward to operate and also generally more efficient. However this system is strongly dependant an the flow stability of the pump used. The pump should therefore be able to handle the large flow impedances created by packed columns. Volume-based sampling is less dependant on flow stability, but the effect of sample dispersion creates additional problems. This can be ascribed to the large sample loops that are used to obtain the high enrichment factors required for on-line preconcentration systems. Since no sample loop are used in time-based sampling, sample dispersion are negligible. With both these techniques additional dispersion occur when the sorbed analyte band is acted upon by the large volume of the sample solvent. The degree of dispersion will primarily be determined by the distribution coefficient of the analyte between the sorbent (stationary phase) and the solvent (mobile phase). However according to a mathematical model developed by Li and Tsalev [1], the final profile will nevertheless be independent of the distribution of the analyte on the column.

To ensure high EF and CE values, high loading rates are desirable during column loading. The kinetic features of the sorptive packing material, as well as the back-pressure created, will however limit the optimum flow-rate obtainable. At higher flow-rates incomplete retention of the analyte would lead to a subsequent decrease in the phase transfer factor (P).

### (ii) Elution

Traditionally, procedures for column preconcentration required two column washing steps before and after sample loading. The purpose of these washing steps were firstly to equilibrate the column with a buffer solution for optimum preconcentration and secondly to remove residual sample before elution. According to Fang [16] the inclusion of these washing and/or equilibration procedures in on-line preconcentration systems showed no additional improvement in the sensitivity and precision of a determination. However, if the sample matrix interfere during the final determination (eg. spectrophotometry), it would be wise to include a washing step before elution.

Another important difference between batch and FIA column preconcentration systems is the capability of the latter system to monitor the elution peak directly. In FIA it is therefore possible to measure the peak-height at the maximum concentration instead of using the average concentration. The peak profile and dispersion characteristics of the eluent now also becomes important. In order to produce sharp elution peaks and obtain high enrichment factors it is consequently important to limit dispersion. Since the concentrated sample is usually located as a thin band at the end of the column were the sample is introduced, reversed flow elution is frequently used to minimize the dispersion of the concentrate during elution. It is therefore also essential to use the shortest and thinnest possible conduits between the column and the detector.

The properties of the eluent used, also have a significant influence on the enrichment factors and the concentration efficiencies that can be obtained. Firstly the eluent must have the ability to achieve fast and complete elution, without destroying the column. Another important feature is the compatibility of the eluent with the detector. In spectrometry the eluent should for instance not block the nebulizer, while with spectrophotometry the refractive index of the eluent should preferably closely match that of the interfacing sample/carrier. In AAS the use of organic solvents may create additional enhancement effects and this should be considered when an eluent is chosen.

The speed of elution is another crucial factor for the efficiency of on-line preconcentration systems and will, amongst other factors depend on how strongly the analyte is retained on the sorbent as well as the releasing strength of the eluent.

### (iii) Detection

Although a lot of different detectors have been used in combination with column preconcentration systems, flame-AAS remain the most popular. ICP-OES offer the same advantages as the AAS and are therefore becoming increasingly popular. The performance of these systems are generally superior to those using other detectors. As mentioned previously, the selection of the optimum introduction flow-rates may present some minor difficulties. This is especially true with flame-AAS, where the optimum introduction flow-rate are often significantly higher than the optimum elution flow-rate. With ICP-OES this is normally not a problem.

Apart from spectrometry, spectrophotometers are also used in combination with FIA column preconcentration systems, although there are fewer applications. This may be attributed to interferences arising from variations in the refractive index between the sample/carrier and the eluent (Schlieren effects). Dilution effects, due to post-column reactions required by spectrophotometric determinations, are also not ideal in a preconcentration system. Although it is possible to compensate for these effects - at least in part - these difficulties are not experienced with flame-AAS or ICP-OES.

Other detectors that are used less frequently include graphite furnace AAS, ion-selective electrodes, chemiluminescence determinations and lately also solid phase optosensing.

## 8.3 Precipitation

Traditionally precipitation is a time consuming separation technique which requires a large degree of sample manipulation. The special features of FIA would therefore appear to be the ideal alternative for classical precipitation-dissolution batch procedures. However the on-line continuous manipulation of a heterogeneous solution could obviously create serious blockage problems in FIA. The first application [17] in this field was therefore only published in 1986.

The most important component in any on-line precipitation system is the *precipitate collector*. The design and geometric design of this component is critical since it will influence the performance of the entire system. Some of the designs which are currently available include:

- Stainless steel filters: These are used most frequently, although high dispersion may be a drawback.
- Disposable membrane filters: They are characterized by poor precision and sensitivity.
- Packed bed filters: These filters are made from standard tubing and are filled with polystyrene granules, cotton or filter pulp. The capacity of these filters are rather low.
- Knotted reactors : These are the cheapest and also represent the simplest design. It offers a relatively large capacity for precipitate collection with low back pressure, negligible dispersion and are made from inert material with a long life time.

The FIA manifolds which are typically used with on-line precipitation-dissolution procedures can be characterized as follows. Firstly on-line systems, incorporating filter collectors, may be used with/without precipitate dissolution. The latter system requires a periodical interruption of the sequence in order to wash the filter, thus limiting the possible applications. Systems used with precipitate dissolution are consequently more versatile and best suited for precipitation applications. In filterless systems a suspension is usually introduced directly into the detector. These systems are not very popular, while preconcentration is also not possible since the precipitate cannot be collected. Finally a filterless system, with precipitate dissolution may be used. Characteristic of such systems are the use of a knotted reactor as the precipitate collector. These systems utilise the favourable characteristics of these reactors mentioned previously and are also suitable for preconcentration.

Although precipitation preconcentration has been combined successfully with FIA, possible applications are limited by the number of selective reactions which produce precipitates with sufficiently low solubility products.

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# CHAPTER 4

# ICP-OES

## 1. Introduction

The first inductively coupled plasma (ICP) was generated by Hittorf more than a century ago (1884) [1]. In 1941, Babat conducted an investigation to determine the ability of the inductively coupled plasma to act as a vaporization, atomization and excitation cell. He was the first person able to sustain a RF-ICP at atmospheric pressures. In 1961 Reed extended this to ICP's in open vessels (torches) and used the plasma to grow crystals of refractory compounds [2]. This prompted researchers in Britain (Greenfield *et al*) and the USA (Wend and Fassel) to independently develop ICP systems for spectrochemical analysis [1,3]. The former group used a high power argon/nitrogen Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) and designed a torch which allowed the direct introduction of samples into the hot core of the plasma. This resulted in superior analytical performance and this design was soon adopted universally. Fassel's group developed a more economical, low-power all-argon ICP-OES. These instruments were the first to become commercially available (1974), and are still the most popular.

## 2. Advantages of ICP-OES

The popularity of ICP-OES, as an analytical instrument in a variety of application-fields can be attributed to the following attractive features of the technique [1,3,6]:

- Rapid and simultaneous multi-element analysis is possible with polichromators.
- Owing to its high temperature, the ICP is relatively free from matrix interferences.
- Large linear dynamic ranges with linearity typically up to concentrations of $10^4$ - $10^5$ times the detection limit can be obtained [1]. According to the observations of Thompson and Walsh [6] the upper limit is normally not higher than 1000 mg/g, after which non-linear response becomes a problem. Nevertheless, this important feature makes the simultaneous determination of major, minor and trace elements in a single sample possible (eg. without sample dilution steps).
- Outstanding detection limits can be achieved for a wide range of elements, typically between 1 to 100 ng/g.
- Very good precision and accuracy are obtainable for the analysis of most trace and major elements. Precision are generally about 1% RSD.
- Up to 72 elements can be determined with ICP-OES.

The ICP-OES clearly is a convenient, powerful and versatile multi-element analytical instrument which is particularly suitable for large routine laboratories [1].

# 3. Instrumentation

Typically an ICP-OES system consist of the following components:

## 3.1 Nebulizer:

Normally a plasma can only tolerate the introduction of an aerosol, since the direct introduction of a solution will lead to the extinction of the plasma. Nebulizers are therefore used to fulfil the important function of converting the sample solution to an aerosol.

Two main types of nebulizers are most frequently used with ICP-OES. The *pneumatic nebulizer* is the most popular and creates an aerosol by introducing a fast stream of argon to the sample solution. The most common designs for pneumatic nebulizers include the concentric and cross-flow nebulizers, with the former offering greater mechanical stability. Cross-flow nebulizers are however known to be more tolerant of solutions with a high salt content. Nevertheless tip blockage, due to salting out, do occur with both types.

With an *ultrasonic nebulizer* the sensitivity of an ordinary ICP-OES instrument can be increased with more than an order of magnitude when compared to instruments using pneumatic nebulizers. This can be ascribed to the increased nebulization efficiency obtained with these nebulizers. With these nebulizers the sample is pumped onto a vibrating crystal transducer which then create a larger portion of small aerosol droplets (less than 10 $\mu$m). In order to reduce the subsequent water loading in the aerosol, it is usually necessary to incorporate a desolvation step in these systems. This may however lead to poor long term stability.

Occasionally, a third type of nebulizer - the *Babington type* - are used when solutions with a high salt content (10% or more) as well as slurries must be analysed. In these nebulizers, the sample solution trickles along a 'V'-shaped groove. Nebulization is subsequently affected with a gas jet which is introduced from a capillary hole situated in the middle of this groove. The design of these nebulizers ensure that they are virtually unblockable in routine analytical work [1].

### 3.2 Spray chamber

When pneumatic nebulizers are used, a spray chamber should be introduced before the aerosol reaches the plasma, to remove unfavourably large droplets from the aerosol. Although the purpose of the spray chamber is to reduce signal instability [1], fluctuations of the pressure inside the spray chamber can in fact introduce further fluctuation of emission signals [5,6]. Drainage arrangements should therefore be carefully designed to avoid any pressure fluctuations. Another problem generally associated with the use of spray chambers is their poor transport efficiency (less than 3%). This results in a significant reduction in the sensitivity which may be obtained with an instrument.

Since the spray chamber is only used to remove larger droplets from the aerosol, it need not be used when a direct-injection/micro-nebulizer for micro-samples are used. With ultrasonic nebulizers the spray chamber are also unnecessary, but needs to be replaced with a desolvation unit.

## 3.3 Plasma torch

The modern plasma is formed in a fused silica or quartz torch. This is one of the most critical components in the ICP assembly and consist of three concentric tubes. The plasma gas (usually argon) is introduced tangentially between the intermediate and outer tubes. The vortex flow subsequently created, both stabilize and thermally isolates the plasma, thus preventing the torch from overheating [1,2,3]. Under normal circumstances the second flow of gas, eg. the intermediate gas flow between the injector tube and the intermediate tube, is not essential. However, when organic solvents are introduced into the plasma this gas flow plays an important role in stabilizing the plasma. Finally, the aerosol carrier gas are introduced into the base of the plasma via the inner injector tube, thus creating the distinctive axial channel through the middle of the plasma. This method of introducing the sample was first used by Greenfield *et al* [1] and ensures that the analyte species are subjected to a relatively long residence time in a very hot inert atmosphere. The introduced sample consequently undergoes complete dissociation and atomization, while ionization is also almost complete. This feature accounts for the relative freedom of matrix interference typically associated with ICP-OES.

Both types of torches, which are used today, are based on the first torch designed by Reed in 1961. The *Greenfield-torch* is the larger of two designs and was designed for high-power nitrogen-cooled ICP's. The smaller *Fassel-type* torch are normally used with low-power argon ICP's and uses lower gas flow-rates than the Greenfield torch. However the latter can tolerate larger quantities of air or hydrogen injected into the plasma during applications such as hydride-generation techniques [1].

## 3.4 Radio-frequency supply

This very important component of the ICP-OES system supplies the power needed to generate and sustain the plasma. All radio-frequency (RF) generators consist of a capacitor and inductor which is tuned to resonate at the operating frequency [2]. Two types of oscillators are generally employed in the RF-generator. In *free-running* oscillators, the actual frequency of oscillation varies to accommodate changes in the plasma frequency. This prevents the loss of plasma power. Alternatively, *crystal controlled* oscillators are used to maintain a fixed operating frequency. Since the piezoelectric crystals used cannot carry large currents, additional amplification is required to obtain the kilowatt output range required for the ICP. In modern ICP-OES instruments, automatic power stabilization is also provided with this type of RF-generator.

## 3.5 Optical Spectrometer

The optical spectrometer of an ICP-OES instrument normally consists of focusing optics, a diffraction grating and one or more detectors. Mirrors or lenses are used to collect the emitted light from the plasma and focus it onto the entrance slit of the spectrometer. The diffraction grating then produces a spectrum of light, which can consequently be measured at precisely defined wavelengths. Depending on the type of spectrometer used a number of wavelengths can be measured either simultaneously (polychromator) or sequentially (monochromator). Simultaneous instruments are very fast and can cope with a large number of samples. However, since the wavelengths are fixed these instruments are less versatile. Sequential instruments, on the other hand, are slower since they can only analyze one element at a time. These instruments may nevertheless be preferred since they offer complete freedom of choice with regard to the selection of analytical wavelengths and are usually smaller and less expensive.

At this stage photomultiplier tubes are widely used as photometric detectors in both polychromators and monochromators. These tubes are ideal due to their extremely high photometric sensitivity as well as very low dark current.

### 3.6 Computers

In order to comply with the requirements of the modern analytical laboratory, most modern ICP-OES instruments make extensive use of dedicated microprocessors. These computers are not only used for rapid data collection and analysis of data, but also enables more *user friendly* instrument control.

## 4. Principles governing ICP-generation and analyte emission in ICP-OES

Most of the excellent features of ICP-OES mentioned previously, can be attributed directly to the unique properties of the inductively coupled plasma. According to Selby *et al* [2] "A plasma is simply a gas whose properties are influenced by the presence of a significant, if often rather small, concentration of ions and electrons. These exist in approximately equal numbers over the volume of the plasma, so overall electrical neutrality is maintained."

Since gas is a poor conductor, the plasma can only be initiated once a Tesla coil has supplied a sufficient number of energetic electrons to ionize the Ar-gas in the RF-field. In principle the mode of energy transfer to the plasma is the same as that in a transformer. In this case the changing current in the induction coil (primary coil) electromagnetically induces an electromotive force in the ionized Ar (secondary circuit). The accelerated, charged particles in the plasma collide with other gas atoms, transferring their energy to the latter. Due to the high rate of collisions at atmospheric pressure, a high degree of excitation and ionization is obtained, resulting in a highly ionized, high temperature plasma.

Once the sample solution is introduced into the plasma, it is converted into free emitting atoms and ions, which may be measured qualitatively and quantitatively. Figure 2 represents the sequence of events following the introduction of a sample into the plasma:

During nebulization, the sample solution is converted into a fine aerosol. After separation in the spray chamber, only the smallest droplets (0.1-5 $\mu$m) are introduced into the plasma. To ensure complete desolvation of these droplets a long enough residence time (few milliseconds) in a plasma with sufficient power is required. The resulting dry solute are subsequently vaporized into gaseous molecules or atoms. The efficiency of this process is once again determined by the sample's residence time as well as the size and temperature of the plasma. Although some compounds vaporize more slowly than others, such interferences are minimized at the high temperatures of the ICP. The molecules produced during vaporization are subsequently dissociated to produce free atoms, which may then be ionized. Through high energy collisions, both these final species (atoms and ions) can acquire enough energy to reach an excited energy state. When these excited species return to their lowest

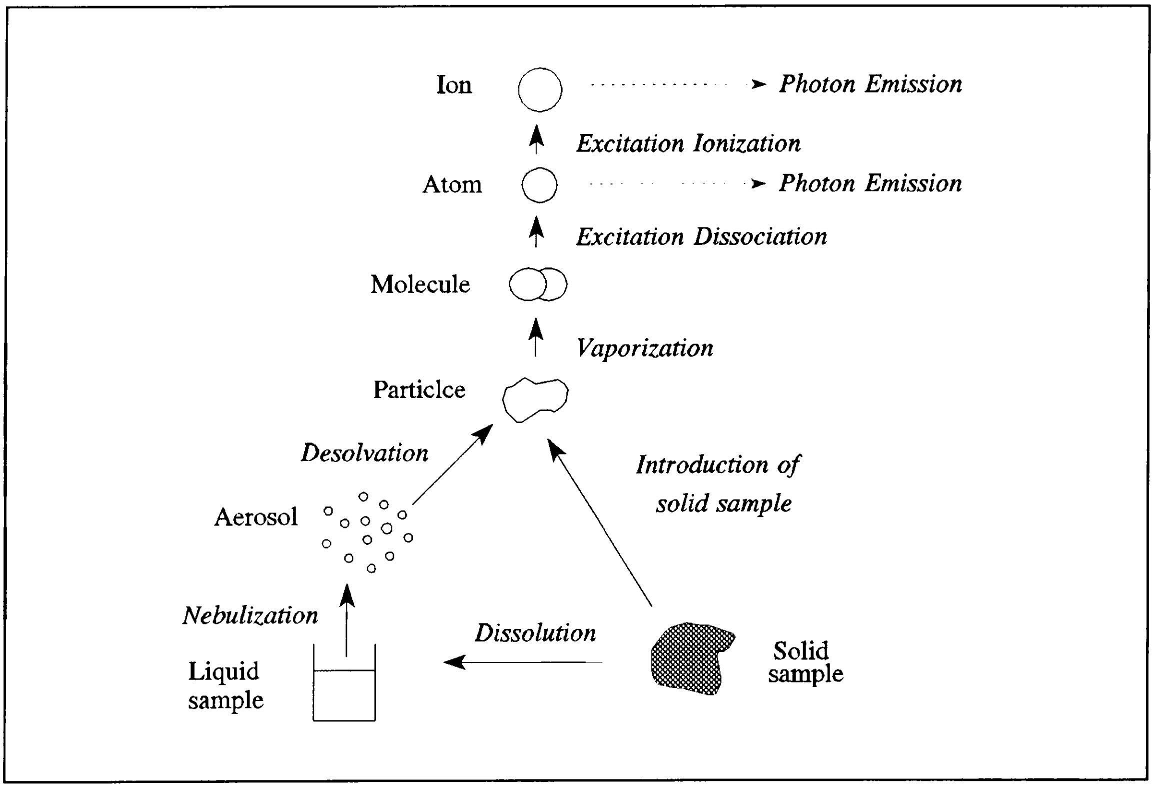

**Figure 4.1** Analyte Emission in ICP-OES [1,2].

energy state, the analyte releases a photon of radiation which results in line emission, specific to the analyte.

## 5. Zones in the ICP

A number of distinct zones can be observed in the ICP and can be attributed to the various processes occurring in the plasma. In the intensely luminous *induction zone*, energy from the induction coil is transferred to the plasma. The temperature in this zone may reach 10 000 K. This causes high background values which are not desirable for sensitive analytical work. The aerosol injector gas passes axially through the induction zone and is visible as a darker, central channel. At the bottom of this channel - in the *pre-heating zone (PHZ)* - desolvation, evaporation and dissociation processes occur. The *initial radiation zone*

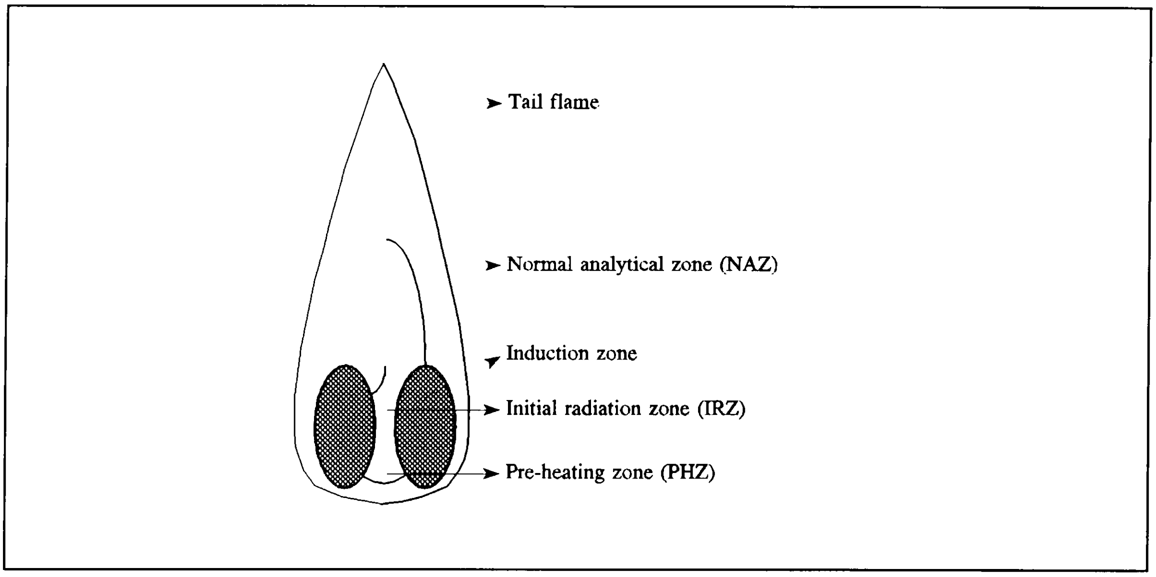

**Figure 4.2** Zones in the ICP [1].

*(IRZ)* is positioned in the middle section of the central channel. In this region excited atoms will start emitting at distinct wavelengths. Continuous emission from the surrounding induction zone will however lead to the high background values mentioned previously. In the region above the IRZ and induction zone, ionization is almost complete. The emission of most species is consequently most intense in this region, which is suitably named the *normal analytical zone (NAZ)*. Finally, the *tailflame* of the plasma extends several centimetres above the induction zone. This region of the plasma is cooler and recombination of species are occurring. The tailflame is therefore not considered to be suitable for analytical work.

## 6. Interferences in ICP-OES

Contrary to initial claims of being interference free, the presence of spectral and matrix interferences in ICP cannot be debated today. However, at the same time it should be stated that the ICP-OES is less susceptible to interferences than most other spectrometric techniques. Furthermore, interferences that do occur can in most cases be overcome to obtain satisfactory results [1,6].

## 6.1 Spectral Interferences

Due to the ICP's superior excitation capability, more than 100 000 wavelength lines have been recorded in the 200-1000 nm range. The possibility of spectral overlap can therefore be considered as one of the greatest limitations in ICP-OES and is an aspect that must receive serious attention during line selection [1]. It is possible to distinguish between three basic types of spectral overlap:

### 6.1.1 Direct spectral overlap

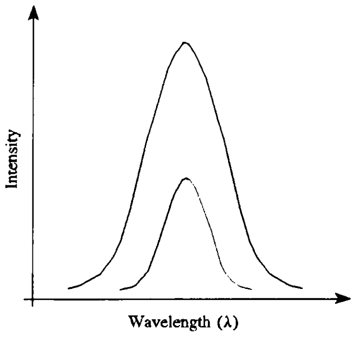

**Figure 4.3** Direct Spectral overlap [1,6].

In this case increased resolution of the spectrometer will not reduce the interference and another line should preferably be selected. If this is not possible the interference can be minimized by applying a mathematical inter element correction factor.

However this is only applicable when the interference is less than 10% [7,6].

### 6.1.2 Wing Overlap

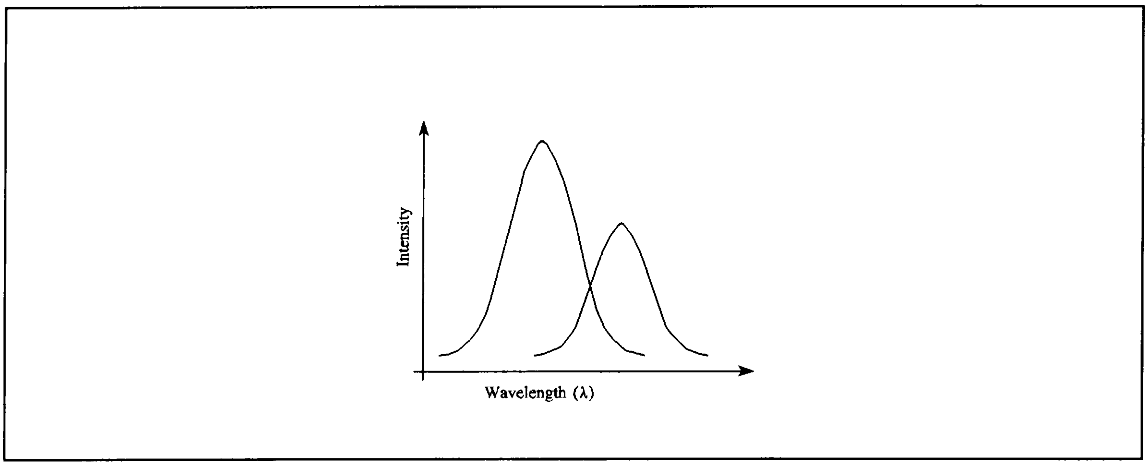

**Figure 4.4** Wing overlap [1,6].

Although the degree of interference is smaller, this kind of overlap creates greater problems. Once again another suitable line should first be looked for. When another suitable line is not available and if the interfering line cannot be resolved from that of the analyte, an interelement correction factor may also be used. This is not recommended since small changes in the profile setting of the spectrometer may significantly alter the degree of overlap. In such cases the calculated correction factor would be incorrect and lead to poor accuracy. Fortunately the excellent temperature stabilization in modern ICP spectrometers largely eliminates the possibility of changes in excitation and hence the amount of spectral overlap of the interfering lines [6].

### 6.1.3 Background continuum overlap

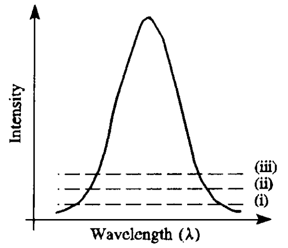

**Figure 4.5** Background continuum overlap [1,6]. Three different levels of background overlap (i), (ii) and (iii) are indicated.

The continuous background present in ICP-OES can be attributed to detector dark current as well as any spectral continuum emitted by the ICP. The level of continuum background emission varies considerably with changes in wavelength, plasma power and viewing height. The aspiration of different solutions can also result in background changes, eg. in the presence of a sloping background resulting from an intense concominant line changes in the concentration of the concominant will lead to varying degrees of interference. Ion-electron recombinations and molecular band spectra will also contribute to the background, with the latter especially difficult to correct since it is often highly structured.

Stray light arising from light reflections or scatter from within the spectrometer may also contribute to spectral interferences. The improved designs and increased incorporation of holographic gratings in modern spectrometers have however effectively minimized these problems. In cases where stray light still causes interference, normal interference correction procedures may be used once the interfering elements have been identified [1].

## 6.2 Matrix Interferences

Another main source of interferences in ICP-OES is due to matrix effects. Generally these interferences constitutes as nebulization, transport, volatilization, chemical and excitation interferences.

Physical properties such as the viscosity, density and surface tension of solutions play a critical role in nebulization and transport efficiency. Whenever one of these properties changes significantly between samples and calibration standards, the rate of generation and transport of appropriately sized aerosol droplets to the plasma, will change accordingly. This type of interference can however be overcome by matrix matching, standard addition or by internal standardization.

Due to the high temperatures maintained in an ICP, the influence of solute volatilization interferences are less prominent than in other spectrometric methods, eg. flame AAS [3]. In practice, these interferences can usually be reduced to negligible levels through careful optimization of the plasma power, nebulizer gas flow rate and the viewing height. By optimizing these parameters it is possible to ensure that enough power is available to volatilize a particle during its residence time in the plasma. Additional interferences can be overcome by matrix matching of the calibration standards with the samples [1].

Chemical interferences occur when an interfering element causes a reduction in the population of free atoms reaching the plasma. Once again the high temperatures maintained in the plasma limits the extent to which these interferences manifest [1].

The presence of relatively high concentrations of certain substances in a sample, may alter the excitation conditions in the plasma. This will affect ionization equilibria and therefore also the intensity of the analyte emission. Generally, excitation interferences will cause the intensity of atomic lines to increase, while the intensity of ionic lines will decrease [1,3]. Substances that have been reported to cause these interferences include the salts of alkali metals, calcium, magnesium, mineral and organic acids as well as organic solvents [7]. Optimization of plasma conditions and the observation height may, in certain cases reduce these interferences appreciably. Matrix matching or standard addition methods can once again be applied to ensure complete elimination of any remaining excitation interferences.

Despite the number of possible interferences mentioned above, it is generally agreed that ICP-OES is relatively free from matrix interferences. Furthermore any interferences that do occur, can normally be reduced to acceptable levels by optimization and matrix matching.

## 7. Organic Solvents with ICP-OES

Although ICP-OES can be used in the analysis of a wide range of sample matrices, the majority of these samples are aqueous, acidic solutions [8]. The introduction of organic solvents are normally avoided, since it is known to create a number of serious problems. However, under certain circumstances it may offer distinct advantages. An important example is solvent extraction, which may be employed to remove the analyte from an interfering matrix or to preconcentrate it [8].

It has been known for some time that volatile, organic solvents cause instability of the plasma. This can be attributed to their characteristic high transport efficiency, which causes excessive solvent loading of the plasma [9,11]. In certain cases the associated changes in the thermal and electrical properties of the plasma may even lead to the extinction of the plasma [7].

A number of measures can however be taken to counteract the cooling effect of organic solvents on the plasma. The first step normally being to increase the forward RF-power, thus enabling the plasma to break down the pyrolysis products of the organic solvents completely [1,8]. Since most of the problems experienced can be attributed to excessive solvent loading of the plasma, it is also advisable to take steps to reduce this. The most straight-forward way is normally to simply reduce the sample aspiration rate of the more volatile solvents. In certain cases, eg. with the most volatile solvents such as benzene and acetone, the maximum aspiration rate obtainable with an analytically useful plasma are as low as 0.1 or 0.2 mℓ/min [8,9]. Apart from decreasing the solvent load, this also ensures smaller primary droplets, thus increasing the evaporation efficiency [8]. In conjunction with this the nebulizer pressure may also be reduced.

A very effective way of decreasing the solvent load to the plasma, is the introduction of a water-cooled spray chamber [8,11,13,14] or a condenser between the spray chamber and the torch [12]. These condense the solvent vapour before it reaches the plasma, thus improving the plasma stability as well as its tolerance to organic solvents. A low gas flow torch has also been described [15], which makes it possible to aspirate xylene at input powers of as low as 0.3 kW.

To further ensure stable excitation conditions in the plasma the outer and intermediate gas flows should preferably be increased [7]. Oxygen may also be added to the intermediate gas, thus further aiding the decomposition of the solvent. Deposition of carbon in the tip of the injector tube as well as around the intermediate tube of the torch are subsequently prevented.

The introduction of organic solvents to the plasma will also lead to the formation of additional molecular band spectra, eg. CN, $C_2$, and CS. Fortunately serious interferences are normally encountered in the region of the spectrum above 300 nm, whereas the most intense analytical lines in the ICP are in the spectral region below 300 nm. Interferences arising from $C_2$ and CN-species are usually the most intense and are present with all organic solvents. Fortunately their potential interferences are with the less commonly determined elements such as the lanthanides. Solvent spectral interferences will therefore not usually be a limiting consideration for determinations in organic solvents [8]. Molecular emission from these organic species may also be reduced by the addition of oxygen to the intermediate gas [7,8].

Despite the problems associated with the use of organic solvents with the ICP-OES, it is clear that measures can and have been taken to overcome them. It is however important to select an appropriate solvent, since a significant reduction in matrix interference can be obtained by simply using another solvent [11].

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# CHAPTER 5

# Ion Exchange

## 1. Introduction

Although ion exchange is a natural process, scientists have only recently became aware of this phenomenon. In fact, scientific publications on ion exchange indicate that active research on this subject has only became prominent in the last 50 years [1].

The first person to notice ion exchange was probably Aristotle, who noted that sea water loses part of its salt content when it is filtered through certain types of sands [1,2]. However after this discovery it took a couple of centuries, before Thompson and Way rediscovered ion exchange in soils. The next important discovery only came more than 50 years later when Horm and Rümpler prepared the first synthetic, industrial ion exchanger for the softening of hard water [1]. The most important development in ion exchange only came after 1935, when Adams and Holmes were able to synthesize the first organic ion exchange resins [1]. These ion exchange resins had much better properties than the inorganic ion exchangers which had been used until that stage. This consequently stimulated research into the development of even better resins which had superior chemical stability at both low and high pH-values [1,2].

In principle, ion exchange is simply the reversible exchange of ions between a solid matrix, the ion exchanger, and a solution. Ion exchangers are therefore insoluble, solid materials which contain certain fixed charges, which is also known as ionogenic groups. Depending on the charge of the ionogenic groups, either cations or anions can then be bonded to them. In the presence of an electrolyte solution, these counter ions can then be exchanged for a stoichiometrically equivalent amount of ions with the same charge [1,3].

During the last half century ion exchange has developed to become a well established technique and although its main industrial application is still the purification and demineralization of water, it is also used extensively in other industrial processes. These applications range from the recovery of metals from industrial wastes, the separation of rare earths as well as the catalysis of organic reactions [1]. In the chemical laboratory ion exchangers are also used in a variety of sample preparation and manipulation procedures. These include removing interferences from samples, separation of equivalent species from samples as well as the preconcentration of trace amounts of such species.

## 2. Ion Exchange Resins

As mentioned earlier, ion exchange resins are insoluble material which contain ionogenic groups to which counter ions are reversibly bonded. Although quite a number of substances have the ability to behave as ion exchangers, synthetic organic ion exchange resins are definitely the most important type [1,3]. These resins consist of a 3-dimensional network of organic polymers, eg. styrene-divinylbenzene, to which ionic groups, such as $-SO_3^-$ and $-NR_3^+$ groups are chemically bonded. These ionogenic groups give the polymers a hydrophillic character and the resins could therefore be dissolved in aqueous solutions. A crosslinking compound, typically divinylbenzene, is therefore introduced during polymerization of the resins to interconnect the hydrocarbon chains. The subsequent increase in the polymer's molecular weight dramatically decreases its solubility and additionally also increases its mechanical stability. Apart from mechanical stability, a high degree of crosslinking will also ensure that the resin do not swell extensively in solutions. This will however also inhibit the mobility of the counter ions, thus leading to slower exchange rates. The degree of crosslinking of a resin is often indicated in its name, eg. a Dowex 1X8 resin will contain 8% divinylbenzene [1,3,4].

The ion exchange behaviour of a resin is primarily determined by the number and nature of the fixed ionogenic groups. The number of groups determine the capacity of the resin, whereas the nature of the groups will influence the ion exchange equilibria. Since these groups are usually acidic or basic functional groups, the pH at which the resin is operated can be critical. Depending on the acid or base strength of the ionogenic groups (eg. $pK_a$-values), they will only be ionized at certain pH-values. When the pH is lower than the $pK_a$ of an acid functional group (or higher than the $pK_b$ of a base functional group), the ionogenic groups will not be ionized and no ion exchange will be possible. Careful attention should therefore always be given to the pH of the resin to ensure that the ionogenic groups are ionized at the conditions used [1].

A number of ionogenic groups are typically used in ion exchangers. According to these, it is possible to divide ion exchange resins into 3 classes [2,3]:

## 2.1 Anion Exchange Resins

In anion exchange resins the fixed ionogenic groups have positive charges, eg. basic groups, while the exchangeable counter ions are negatively charged. The most important types of anion exchange resins contain quaternary ammonium functional groups as the ionogenic groups [3]. The degree of substitution of these terminal amine groups will determine the ionizability ($pK_b$) of the resin and it is therefore possible to distinguish between strong, medium and weak base anion exchange resins.

*Strong base anion exchange resins* normally contain highly substituted ionogenic groups, eg. trimethylamine, which will be ionized at pH-values ranging from 1 to 15 [2]. These resins are stable in all common solvents as well as certain oxidizing agents and will only start to deteriorate at temperatures higher than 60°C [3]. As the name imply, the characteristics of *medium base anion exchangers* will be a compromise between those of strong and weak anion exchangers. These resins typically contain both strong and weak base functional groups and can therefore not be used at high pH-values. *Weak base anion exchange resins* typically contain lower substituted amines or ammonia (eg. $-NH_2R^+$ and $-NH_3^+$) ionogenic groups which will only be ionized (protonated) at pH-values lower than 9. The ability of these resins to function as ion exchangers are therefore highly dependant on the pH of the resin [2].

## 2.2 Cation Exchange Resins

In cation exchange resins cationic counter ions are reversibly bonded to the negatively charged ionogenic groups of the resin matrix. In this case the ionogenic groups are acidic functional groups of varying strengths. Cation exchangers can also be classified as strong, medium and weak acid cation exchangers, depending on the relative strength ($pK_a$-values) of the individual acid ionogenic groups [3].

The most common *strong acid cation exchange resins* contain sulphonic functional groups ($-SO_3^-$) which are typically bonded to the benzene rings of a organic polymer matrix. Since the $pK_a$ of these acid groups are approximately equal to 1 [2], these groups will be ionized in highly acidic and basic solutions. *Medium acid cation exchangers* generally contain weaker acid groups such as $-PO(OH)_2$ or $-OPO(OH)_2$. These groups are not dissociated at low pH-values and these resins can therefore only be used with solutions with pH-values of greater than 5. Similar to weak base anion exchangers, the ion exchange ability of *weak acid cation exchange resins* will be highly dependant on the pH at which the resin is operated. Most of these resins contain weak carboxylic acid functional groups which will only be ionized at high pH-values and these resins can therefore only be used at pH-values of between 6 and 14 [2].

## 2.3 Chelating Ion Exchange Resins

These resins contain chelating functional groups which will form complexes with a limited number of selected metal ions [3]. The functional group used in a particular resin will determine the resin's affinity for certain metal ions, while the size, charge and other physical characteristics of the resin and metal ions will only be of secondary importance. The selectivity of chelating ion exchange resins will therefore be superior to that obtained with the other resins and may be even further improved through pH-control. Since metals are chemically bonded in these resins, ions will be retained more efficiently and these resins will therefore be ideally suited for the concentration of trace elements or for the separation of a selected group of elements. The kinetics of the exchange reactions of these ion exchangers are however unfavourable, since the exchange rates are often determined by either secondary chemical reactions or particle diffusion [2]. When a suitable chelating functional group is selected, the one offering favourable kinetics should be preferred [3].

## 3. Capacity

The capacity of a resin can be defined as the number of ionogenic groups contained in 1 g of the dry resin [1,3,4]. A resin with a high capacity will therefore be able to accommodate more ions, although elution will be more difficult. In such cases complete elution may be affected by using higher eluent concentrations. Resins with low capacities are generally preferred for use in ion chromatography, where separation of ions should be achieved quickly, without having to use eluents with high concentrations.

## 4. Selectivity

### 4.1 Selectivity Coefficient

Since ion exchange reactions are reversible they can be represented in terms of a general equilibrium reaction:

$$a\,A_s + b\,B_r \rightleftharpoons a\,A_r + b\,B_s \tag{1}$$

In this reaction a and b refer to the molar quantities of the exchanged ions A and B respectively. The subscripts r and s indicate whether the ions are in the resin or solution phases. The equilibrium constant of this reaction is represented as:

$$K_B^A = \frac{[A_r]^a \times [B_s]^b}{[A_s]^a \times [B_r]^b} \tag{2}$$

In this equation $[A_r]$ and $[B_s]$ refers to the concentrations of ions A and B in the resin and solution phases respectively. When a and b are not equal, these concentrations should be expressed in mmol/ℓ for solutions and mmol/g for the resin, otherwise it is only necessary to use the same concentration units throughout [2,5]. Since ion exchangers usually have a preference for certain species, the equilibrium constant will not be equal to one. This constant gives an indication of the affinity of a particular resin for an ion and is also referred to as the selectivity coefficient. A selectivity coefficient, $K_B^A$, of greater than one would therefore indicate that the resin has a higher affinity for ion A than for ion B. The value of the selectivity coefficient can also be used to estimate the efficiency of different ions which may be used as eluents, eg. ions (A) with high $K_B^A$-values are usually good eluents [3].

## 4.2 Factors influencing selectivity

The selectivity of a resin is determined by a number of factors, including the type and concentration of the ions in solution and the nature of the resin. The exchange of ions on a resin often involve the formation of chemical bonds between ions in the solution and the ionogenic groups of the resin. When such bonds are formed, the resin will have a higher affinity for the ions which interact more strongly with the fixed ionic groups or the matrix.

Instead of chemical bond formation, ion exchange may also be due to purely electrostatic interactions. In this case ions will merely be localized in the neighbourhood of the fixed ionic groups. Since electrostatic interactions are proportional to the charge and inversely proportional to the distance between the charges, ion exchange resins will also have a preference for ions of higher valencies. Ions with smaller, solvated, equivalent volumes and a greater polarizability will consequently also be preferred.

Secondary reactions of exchanged ions with species in the external solution, eg. complex formation, will generally cause a decrease in the ion exchanger's selectivity towards such ions. However, when cations form anionic complexes with ligands in the solution, anion exchangers will prefer the cation which forms the stronger complex or the complex with the greater average ligand number [2,3].

The selectivity of a particular resin may be enhanced by increasing the degree of crosslinking as well as decreasing the solution concentration (eg. dilution) and temperature [1].

## 5. Distribution Coefficient

Like $K_B^A$, this coefficient is a measure of the affinity of a resin for a particular solute ion A and is defined as follows:

$$D_g = \frac{[A_r]}{[A_s]} \qquad (3)$$

As previously, $[A_r]$ and $[A_s]$ represent the concentration of the exchanged ion A in the resin (mmol/g) and solution (mmol/mℓ) respectively. A large distribution coefficient would therefore indicate a greater affinity of the ion for the resin than for the solution. The value of $D_g$ will however be specific for the ion exchange resin and the eluent conditions used and generally increases with increasing atomic weight [3].

## 6. Kinetics of Ion Exchange

The rate at which ion exchange reactions occur will often determine whether a specific ion exchange resin can be used successfully for either separation or concentration processes. The ion exchange process is in principle a diffusion process and can be represented by the following simple reaction:

$$A_s + B_r \rightleftharpoons A_r + B_s \qquad (4)$$

Despite its straightforward appearance, this reaction actually consist of 5 individual reactions which occur simultaneously. According to the electroneutrality principle, which require that the flux of ions A and B are equal, these reactions can be further divided into the following 3 steps [2,5]:

(i) Diffusion of ion A from the solution to the surface of the resin particle while ion B diffuses from the resin surface into the external solution.

(ii) Diffusion of ion A from the resin surface to the ion exchange position in the particle while ion B diffuses from the ion exchange position to the surface of the resin particle.

(iii) Exchange of ion B with ion A at the exchange position.

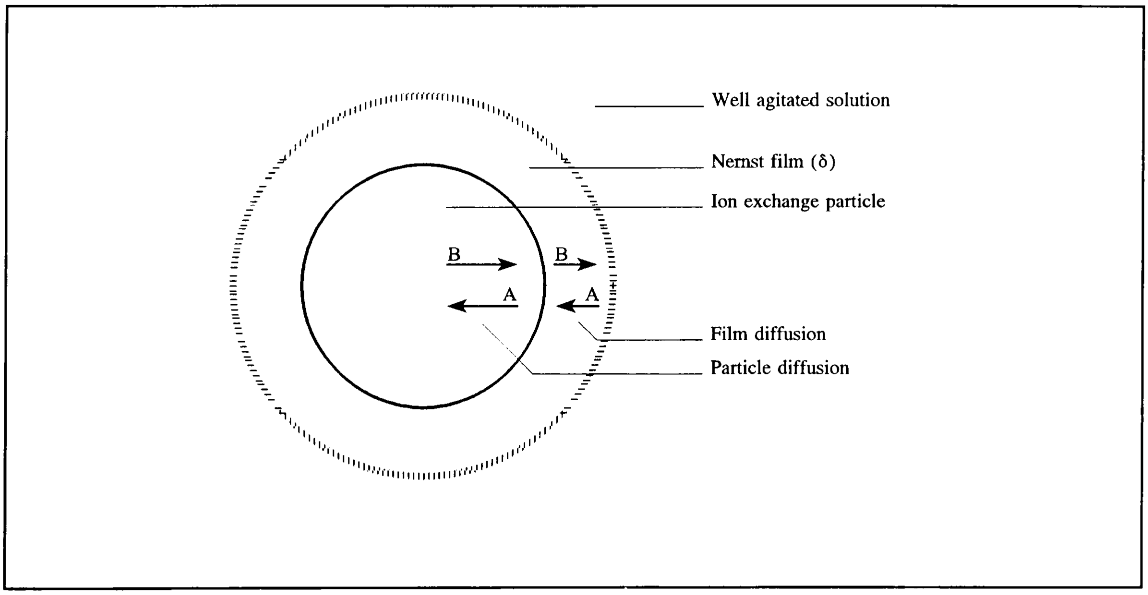

**Figure 5.1** Schematic representation of the diffusion processes during ion exchange.

The overall ion exchange rate can subsequently be determined by any of these reactions [1,2,5]. However, reaction (iii) is generally not considered to be the rate-determining reaction since reactions of free dissociated ions in aqueous solutions are normally very fast [2,5]. Chelating ion exchange resins may be an exception, as complexing reactions can be very slow [1]. In these cases the chemical exchange of the ions will then constitute the rate-determining reaction.

In most cases the ion exchange reaction rate will be determined by either reaction (i) or (ii), eg. one of the diffusion processes [1,2,5]. In reaction (i) the diffusion rate of ions A and B will primarily be determined by the degree to which the solution is agitated. Normally the bulk of the solution will be well agitated with both batch and column processes. However, due to hydrodynamic factors a thin film of solution directly surrounding the resin particle will be static, eg. no agitation will occur in this film. The concept of this film has first been introduced by Nernst and is consequently referred to as the Nernst film or the Nernst diffusion layer ($\delta$). Since the bulk of solution is well mixed, the diffusion rate of ions A and B will depend mainly on the rate at which they diffuse through this thin film. This process is known as *film diffusion* [1,2].

Film diffusion will normally be the rate-determining step when ion exchange resins consisting of small particle sizes and a low degree of crosslinking are used. Ion exchange with dilute solutions which are not sufficiently mixed will also favour film diffusion as the rate-determining step. If film diffusion is rate-determining the overall reaction rate may be increased as follows [2,5]:

- Decreased thickness of the Nernst film($\delta$) by increased agitation of the solution in batch processes, or by increased flow rate (column processes).
- Increased concentration of the exchangeable species.
- Increased surface area of the ion exchange resin through the use of smaller particles.
- Increased temperature.

Alternatively, reaction (ii) may be rate-determining. This process involves the diffusion of the ions within the particle and is referred to as *particle diffusion*. Particle diffusion will often be the rate-determining step when the overall reaction rate is slow [5], which is normally the case when resins have a high degree of crosslinking and large resin particles are used. The following steps can be taken to increase the particle diffusion rate [2,5]:

- Increase the porosity of the resin particles through the use of a resin with a lower degree of crosslinking.
- Use smaller resin particles.
- Increase the reaction temperature.
- Use a resin with a higher capacity [1].

It has been found that film diffusion is normally the rate determining reaction in solutions with concentrations of 0.001 mol/ℓ and lower. At concentrations of 0.01 mol/ℓ particle diffusion will also start to become important [2], while at concentrations of 0.1 mol/ℓ and higher, particle diffusion will be the rate-determining step [2].

Since increasing the reaction temperature and using smaller particles will increase the reaction rates of both film and particle diffusion, it is possible to increase the overall ion exchange reaction rate irrespective of which of these processes are rate-determining.

## 7. Ion Exchange of the Platinum Group of Metals

The concentration of the platinum group of metals (PGM) in geological, industrial, environmental and biological samples are generally extremely low, typically ranging from the ng/g to the sub-ng/g level. It is therefore necessary to separate and preconcentrate the PGM's from the sample matrix before analysis with even the most sensitive analytical techniques is possible [6]. Ion exchange resins are therefore ideally suited for the preparation of PGM samples.

Due to the easy formation of stable anionic PGM complexes, anion exchange of the PGM in hydrochloric acid systems are the most effective to separate them from practically all matrix elements. The only matrix elements which may co-adsorb from 0.5 mol/ℓ HCl solutions are Au(III), Ag, Cu(I), Re(VII), Tc(VII), Zn, Cd, Hg, Tl(III), Sn, Pb, Sb(III), Bi, Te(IV) and Cr(IV) [6,7]. Fortunately most of these elements will normally not be present in PGM samples, while it is also possible to reduce certain of these species to lower oxidation states which are not retained by anion exchangers [6]. Using anion exchangers it is also possible to separate the individual PGM from one another, while concentration of the retained species on the resin is also possible [7].

Cation exchangers are in most cases only used to isolate the PGM from its sample matrix in dilute HCl solutions. In these systems the matrix elements are retained by the resin, while the anionic chloride complexes are eluted directly. In media containing complexing agents such as thiourea the PGM may be converted to cationic complexes, which can be retained by cation exchange resins [7]. Separations with anion exchangers are however much more straightforward than these cation exchange procedures.

Unfortunately, great difficulties are often associated with the separation and concentration of these elements by ion exchange [7]. This has partly been ascribed to their characteristic tendency to form complexes of varying composition with inorganic acids (eg. HCl), which will invariably influence their behaviour during ion exchange procedures. Furthermore, the method of converting the individual elements into solution will determine the predominant species in solution and may seriously affect the extent to which these elements undergo ion exchange. Aging of the PGM solutions may also result in partial hydrolysis of the chloro complexes, especially those of Rh and Ir [7,8].

## 7.1 Anion Exchange

Since most of the PGM are present as stable anionic chloro complexes in HCl systems, they are strongly retained by strong base anion exchange resins. In fact, these chloro complexes form such stable ion pairs with the quaternary ammonium groups of the resins that they are generally quite difficult to elute. Furthermore when the ions are in contact with the resin they can be reduced to ions of lower oxidation states or to the metal, which will further hamper the complete elution of the adsorbed species [7,8].

Despite these problems, anion exchange of the PGM are nevertheless popular as it offers excellent distribution coefficients. Values for these distribution coefficients on a strong base anion exchange resin such as Dowex 1X8, range from $10^2$ for Ru(IV) to $10^4$ for Pt(IV) and Os(III) in dilute HCl solutions [7]. Adsorption of the PGM will however decrease with increasing HCl concentrations, but Pt(IV), Ir(IV) and Os(III) will still be strongly retained from 12 mol/l HCl solutions. Rh(IV) is also strongly retained over the range of HCl concentrations [7].

**Platinum:** In hydrochloric acid solutions of 0.1 to 12 mol/$\ell$ HCl, Pt(IV) will be present as the $PtCl_6^{2-}$ complex [5,7]. During adsorption, this complex will exchange two of its own chloride ligands to bond with those on the resin. This reaction can be represented as follows [9]:

$$PtCl_6^{2-} + 2\ \overline{Cl^-} \rightleftharpoons \overline{PtCl_6^{2-}} + 2\ Cl^-$$

Although Pt is retained strongly under these conditions most of the other PGM (excluding Ir(III) and Rh(III)) are also retained [7]. Separation of the individual elements will therefore only be possible when suitable eluents are available. The strong adsorption of the group may be advantageous when group separation of the PGM is required.

As mentioned, elution of adsorbed Pt can be extremely difficult. Two modes of elution, eg. reductive and nonreductive elution, are commonly used for the elution of Pt. With reductive elution, thiourea is often used to reduce Pt(IV) to Pt(II) and to subsequently form the cationic Pt(II)-thiourea complex. The resulting complex has a much lower distribution coefficient and can consequently be eluted much easier. Unfortunately the reduction and subsequent complexation of Pt are slow and elevated temperatures are usually required to ensure complete elution of the adsorbed Pt. High temperatures are also important to prevent precipitation of the Pt-thiourea complexes on the resin. It is further possible to use mixed organic/aqueous solvents (eg. acetone in HCl) as eluents to prevent precipitation. Unfortunately thiourea is not selective for Pt, and Pd(II) is subsequently coeluted. The situation is further complicated since the reaction of Pd with thiourea is faster than the reaction with Pt [7].

Among the nonreductive eluents for Pt, the perchlorate ion is considered to be the most important. These systems utilise the fact that Pt(IV) forms stable cationic complexes with perchlorate which can subsequently be eluted from anion exchange resins. The elution of Pt is further aided by the high affinity of strong base anion exchange resins for the perchlorate ion. However this do not only favour the elution of Pt, but also all other adsorbed anions. Pd will consequently be co-eluted with Pt. Nitric acid and ammonia solutions may also be used as nonreductive eluting agents for Pt. However, with nitric acid large volumes are typically required for complete elution, while Pd will also be eluted with ammonia.

Due to the difficulties associated with the elution of Pt, procedures have also been developed in which Pt may be determined without having to elute it from the resin. Some of these methods include the ignition of the resin, radiometric measurements following neutron activation of the resin as well as the injection of the resin as a slurry into an ICP-source [7].

**Palladium:** The behaviour of Pd on anion exchange resins is generally identical to that of Pt, with Pd only being retained less strongly than Pt. Similar to Pt(IV), Pd(II) is also adsorbed from HCl-solutions with concentrations ranging from ~0.1 to 12 mol/ℓ HCl. Furthermore, evidence suggest that Pd is also retained as the hexachloride complex on the resin (eg. $PdCl_6^{4-}$) [9]. In solution the $PdCl_6^{4-}$ complex will be predominant in 2 to 12 mol/ℓ HCl solutions, while $PdCl_4^{2-}$ will be the major complex in 0.5 to 2 mol/ℓ HCl solutions. Although it is possible to adsorb Pd from 9 to 12 mol/ℓ HCl solutions this is normally not done, since distribution coefficients at these concentrations indicate poor adsorption on anion exchangers. In fact, 12 mol/l HCl solutions have been used to elute Pd selectively from an anion exchanger which contained Pt as well.

As with Pt, the adsorbed $PdCl_6^{4-}$ complex can also be eluted with reductive and nonreductive eluents. Thiourea, ammonia, perchloric acid and nitric acid solutions are consequently used for the elution of Pd as well. Elution of Pd is also easier than the elution of Pt and it is for instance possible to selectively elute Pd with a 0.2 mol/ℓ perchloric acid solution. In order to avoid the problems associated with the elution of the PGM's it is also possible to perform direct determinations of Pd on the resin [7].

**Iridium:** Anion exchange resins can adsorb Ir from hydrochloric solutions as either Ir(III) or Ir(IV) ions. Ir(III) will only be retained from dilute HCl solutions in which it occurs as either $IrCl_4^-$ (0.1 to 0.5 mol/ℓ HCl) or as $IrCl_5^{2-}$ (0.5 to 2 mol/ℓ HCl). Both of these complexes will be adsorbed as $IrCl_4^-$. Ir(IV), on the other hand, is strongly adsorbed from 0.1 to 12 mol/ℓ HCl solutions where Ir(IV) will be present as the $IrCl_6^{2-}$ complex [7,9]. The behaviour of Ir(IV) with anion exchange resins is once again similar to that of Pt(IV). As is the case with the other PGM's, the distribution coefficients of Ir(IV) decrease with increasing HCl concentrations from which Ir(IV) will be adsorbed as $IrCl_6^{2-}$. The actual adsorption of Ir(IV) on the resin, will occur in a similar as for Pt(IV), eg. two chloride ligands will be exchanged for two chloride counter ions, upon bonding with the resin. This exchange can consequently represented as [9]:

$$IrCl_6^{2-} + 2\,\overline{Cl^-} \rightleftharpoons \overline{IrCl_6^{2-}} + 2\,Cl^-$$

An important difference between the behaviour of Ir(IV) and Pt(IV) is the tendency of the Ir(IV) ions to be reduced to Ir(III) when in contact with the resin. Whenever this happens, Ir(III), which is less strongly retained than Ir(IV), will be co-eluted with other PGM species. In the presence of oxidizing agents such as Ce(IV), Cl, Br and $H_2O_2$, this is prevented.

Additional care should be taken when Ce(IV) is used as the holding oxidant since it will be reduced when HCl concentrations are higher than 1 mol/ℓ [7].

Elution of Ir(IV) from strong base anion exchangers is very difficult and it is often necessary to reduce the Ir(IV) to Ir(III), which is less strongly retained by these resins and can be eluted with only HCl. Reducing agents which are typically used include thiourea, sulphurous acid, hydroxylamine and Fe(II) solutions. Care should however be taken to avoid possible reduction of Pt(IV), which would subsequently co-elute. Nitric acid, hydrochloric acid and sodium hydroxide are often used as non-reductive eluents for Ir(IV) [7].

**Rhodium:** In 0.1 to 0.5 mol/ℓ HCl solutions, $RhCl_2^+$ will be the predominant Rh(III) species. Despite being cationic, this complex are retained slightly by strongly basic resins. This can be ascribed to the formation of polymeric forms of this ion. Alternatively the anionic $RhCl_6^{3-}$ complex may be obtained by boiling a Rh solution with 6 mol/ℓ HCl for at least one hour, but this complex is also not retained strongly by anion exchangers. These systems are therefore mostly used to separate Rh from the other PGM's. Direct determination of Rh on a resin is normally not necessary, although in the presence of stannous chloride Rh will be adsorbed irreversibly and radiometric measurements should then be performed [7].

**Osmium:** Os(III) is strongly retained from HCl solutions of 0.5 to 12 mol/ℓ HCl,in which the pentachloride complex ($OsCl_5^{2-}$) will predominate. The behaviour of Os(III) is comparable to that of Pt(IV) and Ir(IV), while its distribution coefficients also decreases with increasing HCl concentrations [7]. Applications of the anion exchange of Os are however relatively few, since Os is most often separated from the other PGM by distillation of its volatile tetroxide.

**Ruthenium:** As with Os, Ru is usually separated from the other PGM through the distillation of its volatile tetroxide. In certain cases, anion exchange of Ru may however still be performed. In dilute HCl solutions (0.1 to 0.5 mol/ℓ HCl), Ru(III) and Ru(IV) are present as $RuCl_2^+$ and $Ru(OH)_2Cl_2$ respectively. Ru(III) will consequently not be adsorbed by anion exchangers, while Ru(IV) are retained from dilute HCl solutions, possibly as $RuCl_6^{2-}$. As with the other PGM the adsorption of Ru(IV) on strongly basic anion exchangers, also decreases with increasing HCl concentration. Ru can consequently be separated from Pt by elution with 11 to 12 mol/ℓ HCl [7].

Finally, hydrochloric acid eluents containing organic solvents may also be used for the elution of the PGM from anion exchangers [7]. These conditions will improve the ability of the PGM ions to form complexes with halide and pseudo-halide anions [3]. With certain organic solvents it would therefore be possible to obtain conditions which will ensure complete elution of the retained species. This principle is most often employed during cation exchange of the PGM's.

Although HCl media are mostly used with anion exchange of the PGM's, other media such as HBr, $HNO_3$ and HF, nitrite and acetic acid systems can also be in special cases [7].

## 7.2 Cation Exchange

In HCl solutions at concentrations higher than 3 mol/ℓ HCl, the PGM are essentially non-adsorbable on strongly acidic cation exchangers. The PGM complexes will however show negligible adsorption in dilute HCl solutions of 0.1 to 3 mol/ℓ HCl. A notable exception is Rh(III) which occur as $Rh(H_2O)_6^{3+}$ in 0.1 to 0.2 mol/ℓ HCl solutions and as $RhCl^{2+}$ and $RhCl_2^{+}$ in 0.1 to 0.5 mol/ℓ HCl solutions, which can be retained by cation exchange resins. Ir(III) may also be adsorbed, but this interaction is very weak. The adsorption of the PGM chloro complexes from dilute HCl solutions on strongly acidic cation exchange resins will generally decrease in the order:

$$\mathrm{Rh(III)} > \mathrm{Pd(II)} > \mathrm{Ir(IV)} \sim \mathrm{Pt(IV)}$$

The PGM's may also be converted to cationic complexes, which can subsequently be separated successfully with cation exchangers. As mentioned previously, thiourea will react with all the PGM's to form stable cationic complexes. Thiourea also acts as a reducing agent and will reduce metal ions to lower oxidation states, eg. Pt(IV) to Pt(II). However, complications often arise since the rate of the reduction and complex formation reactions for the individual complexes may vary considerably. Generally these reactions are slow, while those of Rh(III) and Ir(IV) are extremely slow. Consequently, cation exchange of the PGM-thiourea complexes have limited applications. As with anion exchange of the PGM, adsorption of the PGM thiourea complexes decrease with increasing HCl concentrations. This has been attributed to increased anionic chloro complex formation. Adsorption may further be increased by increasing the temperature. Alternatively, with ammoniacal solutions of the PGM-chlorides, Pd may be separated as $Pd(NH_3)_4^{2+}$ from the Ir, Rh and Pt chloro complexes.

The PGM can also be separated from other solutions such as HBr and perchloric acid solutions. With HBr solutions the PGM's will behave similar to when HCl-solutions are used. However in perchloric acid solutions the PGM's will form cationic complexes which are adsorbed strongly by cation exchange resins [7].

## 7.3 Chelating Ion Exchange

When chelating resins are used, the selectivity of the resin for the PGM are generally superior to that obtained with other ion exchange resins. Typically these chelating ion exchange resins contain one or more N-atoms which will stabilize the $d^8$-electronic configuration of the PGM ions upon bonding with the resin. A good example of a chelating ion exchange resin specific for the PGM's is the Srafion$^R$ NMRR-resin. This resin contains a guanidine group and is represented in Figure 5.2.

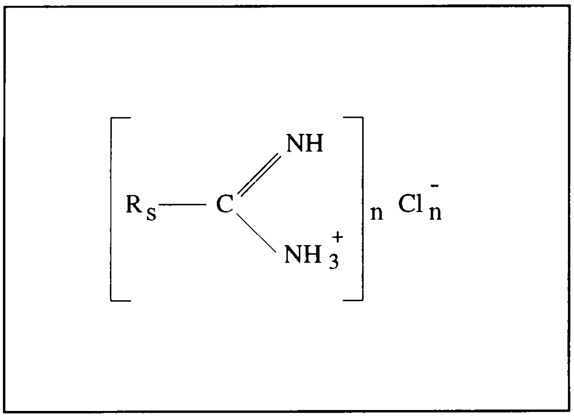

**Figure 5.2** Structure of the Srafion NMRR-resin.

The double bonds contained in this resin reduce ions such Pt(IV) and Ir(IV), before bonding them as Pt(II) and Ir(I) square planar complexes. Elution can subsequently be performed with a 5% solution of thiourea in 0.05 mol/ℓ HCl [7]. Elution with other types of chelating ion exchange resins are however generally more difficult. When resins with an isothorium functional group are for instance used, recovery of the PGM are only possible after the resin has been destroyed [3].

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# CHAPTER 6

# Optimization of the ICP-OES system

## 1. Introduction

ICP-OES is a versatile technique which literally offers thousands of wavelengths for the analysis of elements [1]. Of these only a limited number is however of practical importance, the most sensitive lines generally being preferred for analysis. In certain cases, eg. when the analyte concentration is very high or when serious spectral interferences exist, the less sensitive lines will however be preferred. The selection of sufficiently sensitive, interference-free lines is particularly important in trace analysis [1] and consequently received a lot of attention during the development of an analytical procedure for the analysis of trace quantities of Pt, Pd, Rh and Ni.

Apart from the analytical lines chosen, the performance of an ICP-OES system is also affected by a number of adjustable parameters. These include the RF power, observation height, sample introduction rate and the aerosol carrier-, plasma- and intermediate gas flow rates [3]. The influence of the plasma (outer) gas flow on the analyte emission are normally small and are mostly determined by economical factors [2]. The flow rates chosen will therefore generally not be too far above the lower limit beyond which the torch will be damaged or the plasma extinguished. The intermediate gas flow are also not very important and with the exception of organic solvents, it may even be omitted. Sample introduction rates are not considered to be critical, but may have a deterious effect on results if very low or high flow rates are used. This can be ascribed to the fact that at normal flow rates of higher than *ca* 1.0 mℓ/min, the nebulization efficiency will mainly be determined by the aerosol flow rate [3]. In fact, along with the power and observation height, these three parameters generally have the most significant effect on the analytical performance of an ICP-OES instrument [2]. When the best detection limits are required, these parameters should be optimized according to their signal-to-background ratios (SBR's). In order to ensure good precision it is further necessary to consider the relative standard deviation (RSD)-values obtained [2,3]. In this study the input power, observation height and sample introduction rate were optimized.

The analytical performance of an optimized ICP-OES systems can be evaluated according to the detection limits, accuracy and precision obtained with the system. These factors, as well as the analytical ranges obtained, were calculated to evaluate the performance of the final optimized system.

## 2. Experimental

### 2.1 Instruments

A Varian Liberty 220 ICP Emission Spectrometer was used as detector. This instrument is fitted with a monochromator and a standard glass pneumatic nebulizer.

## 2.2 Reagents

1 mg/ℓ Pd, Rh, Ni- and 2 mg/ℓ Pt-standard solutions were prepared from 1000 mg/ℓ Pd, Rh, Ni- and 2000 mg/ℓ Pt-standard stock solutions (Merck). Dilutions were performed with deionized water. Solutions were prepared daily and used for the optimization of the ICP-OES instrument. During the investigation of interference effects, these solutions were additionally spiked with standard solutions of the interfering elements. 500 mg/ℓ Ir, Ru, 1000 mg/ℓ Pd, Rh, Ni, Co, Cr, Cu and 2000 mg/ℓ Pt standard solutions were used for this purpose. The final concentration of these spiked elements typically ranged between 7 and 13 mg/ℓ. For the evaluation of the optimized system, standard solutions were prepared having final concentrations ranging from 0.2 to 400 mg/ℓ.

## 2.3 Procedures

### 2.3.1. Line Selection

According to Moore [1] the selection of analytical lines is governed by considering both the sensitivity of the lines and the likelihood of spectral interference. During the selection of analytical lines for Pt, Pd, Rh and Ni, preference was given to the lines with the highest sensitivity (eg. SBR), but which did not suffer from any known interferences. Since complete reliance can however not be placed in wavelength and line coincidence tables, the absence of interferences were also confirmed experimentally. Wavelength scans of solutions containing the element and possible interfering species were subsequently analyzed to identify interferences (eg. line overlap). In each case a t-test was also performed to determine whether the average SBR-values obtained from these solutions were different. It was therefore possible to conclude unambiguously whether significant interferences existed. This procedure was repeated until a sensitive, interference-free line had been identified for each element.

### 2.3.2 Optimization of the ICP-OES system

To ensure the lowest detection limits possible for trace analysis, the operating conditions of the ICP-OES were optimized to obtain the highest possible SBR-values corresponding to the lowest possible background RSD [2,3].

Optimization was performed in a univariate fashion, eg. only one parameter were changed at a time while the others remained constant. Of the selected parameters the sample introduction rate was analyzed first, followed by the power and finally the observation height. The observation height was determined with an automatic viewing height package available with the software of the specific instrument. These parameters were further optimized for each element individually.

### 2.3.3 Evaluation of optimized ICP-OES system

#### (i) Detection Limits

According to IUPAC the instrumental detection limit is defined as the concentration that produces a nett line intensity equivalent to three times the standard deviation of the background signal [2]. Since this definition does not include the value measured for the background intensity, the values obtained are generally unrealistically low [2]. The detection limits ($C_L$) will consequently be determined as the concentration corresponding to a signal three times the standard deviation *above* the background signal, eg.

$$C_L = S(\overline{x_{bl}} + 3\sigma_{bl}) \tag{1}$$

where S is the sensitivity (slope) of the calibration curve

$\overline{x}_{bl}$ is the average background signal and

$\sigma_{bl}$ is the standard deviation of the background signal.

These values were determined following 14 consecutive integrations of the background signal during the continuous nebulization of a blank solution (deionized water).

### (ii) Dynamic Range

The dynamic range refers to the concentration interval over which a calibration curve is linear. With ICP-OES instruments, large dynamic ranges typically ranging over 5 orders of magnitude, are normally obtained [3]. This is one of the outstanding characteristics of the technique and permits the simultaneous determination of major and trace element concentrations in a single sample. Practically, the dynamic range can be determined as the concentration interval within which the RSD-values do not exceed a predefined value. The maximum RSD selected will depend on the precision required for a particular system.

The dynamic ranges were determined by analysing standard solutions with concentrations ranging from 0.2 to 400 mg/ℓ for each element. 14 Repetitions were performed for each sample analyzed and the RSD-values were determined as follows:

$$\%RSD = \frac{s}{\bar{x}} \times 100 \qquad \textbf{(2)}$$

where s is the standard deviation of a specific concentration and

$\bar{x}$ is the mean signal intensity of the concentration.

These results were represented graphically and the analytical range were taken as the concentration range with RSD-values lower than 1%.

## 3. Results and Discussion

### 3.1 Line Selection

Since the presence of an interfering element may lead to either spectral or chemical interferences, the analyte signal may either be enhanced or suppressed in the presence of an interfering element [4]. A two-sided t-test was consequently conducted to identify possible interferences.

For each analyte-interferent pair, the null hypothesis stated that the mean SBR of the analyte and that of the analyte and interferent are the same. Since the tests were performed at a 5% probability level with 10 degrees of freedom, the calculated t-values were compared to the tabulated t-value of 2.23. The null hypothesis was rejected when the absolute value of the calculated t-value was greater than 2.23. At a 5% probability level this would then mean that a significant interfence could be predicted with a 95% certainty [5]. The calculated t-values of some of the analytical line interferences considered are given in Table 6.1.

**Table 6.1** : Calculated t-values for selected element-interferent pairs.

| Analyte | Interferent | $t_{calculated}$ | Hypothesis test |
|---|---|---|---|
| Pt 214.423 nm | Ir | -2.45 | $\|t\| > 2.23$ |
| Pt 265.945 nm | Rh | -1.37 | $\|t\| < 2.23$ |
| Pt 265.945 nm | Ru | -0.272 | $\|t\| < 2.23$ |
| Pt 265.945 nm | Pd | 0.303 | $\|t\| < 2.23$ |
| Pd 340.458 nm | Co | 0.614 | $\|t\| < 2.23$ |
| Rh 343.489 nm | Ni | -7.38 | $\|t\| > 2.23$ |
| Rh 339.682 nm | Ar | -- | * |
| Ni 221.647 nm | Ir | -5.34 | $\|t\| > 2.23$ |
| Ni 221.647 nm | Co | -2.65 | $\|t\| > 2.23$ |
| Ni 221.647 nm | Cr | -2.78 | $\|t\| > 2.23$ |
| Ni 221.647 nm | Cu | 0.457 | $\|t\| < 2.23$ |

* No interfering Ar could be identified in the wavelength scan.

With Ni, an interference-free line with sufficient sensitivity could not be identified. The sensitive Ni 221.647 nm line was subsequently selected. However, this line suffers from Ir, Co and Cr interferences. The influence of these interferences were quantified by analysing 1 mg/ℓ Ni standard solutions with increasing concentrations of the interfering elements (Fig. 6.1). Of these interferences, Cr caused the greatest enhancement of the Ni-signal. The intensity of the Ni-line increased sharply with increasing Cr-concentrations of up to 2 mg/ℓ, after which the effect was smaller. The same type of interference was observed for Ir, although the Ni-signal did not increase as much as with the Cr-interference. Co caused the smallest enhancement of the Ni signal at low concentrations, although the signal enhancement did not reach a maximum up to concentrations of 10 times that of the Ni-concentration.

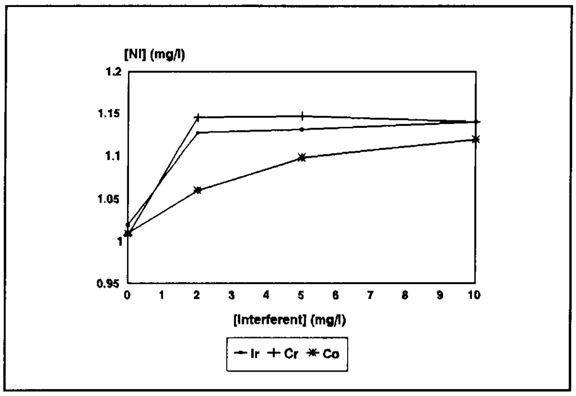


**Figure 6.1** Influence of increasing interferent concentrations on the Ni concentration determined.

Since these interferences will clearly influence the accuracy of analysis, interference correction factors were determined for each of the elements. Interference correction factors indicate the analyte intensity enhancement corresponding to a specific interferent concentration. When the interferent concentration is subsequently determined, the apparent analyte concentration caused by the specific interferent concentration can then be substracted from the measured concentration. In this case the correction factors were calculated automatically by the instrument after the analysis of a 1 mg/ℓ Ni solution and 5 mg/ℓ solutions of the interferents. During the determination of Ni, the instrument would therefore perform the interference correction itself.

For the final selection of analytical lines for the individual elements, a compromise had to be found between the optimum sensitivity that could be obtained and the interferences that existed.

In the case of Pt, the less sensitive 265.945 nm line was selected as the 221.423 nm line suffered from a Ir-interference. With the Pd 340.458 nm line, no interferences could however be identified. As with Pt, a less sensitive line had to be selected as the 343.389 nm line suffered from a Ni-interference. As mentioned previously, all the sensitive Ni-lines suffered from interferences. The 221.647 nm line was therefore selected as it would yield the required sensitivity, without too serious interferences. Interference corrections were consequently determined to correct for any Ir, Cr and Co-interferences during subsequent Ni-determinations. The analytical lines which were finally selected are:

| | |
|---|---|
| Pt (I) | 265.945 nm |
| Pd (I) | 340.458 nm |
| Rh (I) | 339.682 nm |
| Ni (II) | 221.647 nm |

## 3.2 Optimization of the ICP-OES

### (i) Sample introduction rate

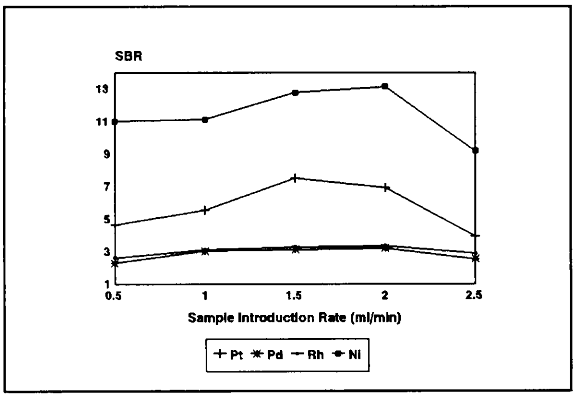


**Figure 6.2** Optimum sample introduction rate.

As expected, changes in the sample introduction rate did not have a significant influence on the SBR of the analyte lines (Fig 6.2), except when very low or high flow rates are used. Optimum flow rates varied between 1.5 and 2.0 mℓ/min for the individual elements and a 1.5 mℓ/min flow rate was selected as optimum for all the elements.

### (ii) Power Input

When the SBR-values of the individual elements at various power levels are compared, the lines of the noble metals reach their optimum at lower values than the Ni-line. This can be expected since the selected Pt, Pd and Rh lines are all atomic lines. Atomic species generally require less energy to be excited, and will therefore give maximum responses at lower power values [3]. As the chosen Ni-line is an ionic line it was expected to have a maximum intensity at higher power levels. The optimum power of 0.8 kW is however not as high as would be expected.

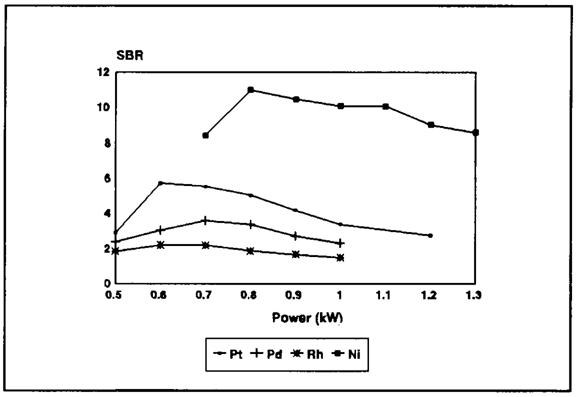


**Figure 6.3** Optimum input power.

**Table 6.2** : %RSD-values of selected power levels.

| P(kW) | %RSD(Pt) | %RSD(Pd) | %RSD(Rh) | %RSD(Ni) |
|---|---|---|---|---|
| 0.5 | 1.76 | -- | 3.88 | -- |
| 0.6 | 2.62 | 1.91 | 1.41 | -- |
| 0.7 | 4.70 | 1.75 | 2.19 | 3.34 |
| 0.8 | 2.78 | 0.52 | 1.54 | 5.22 |
| 0.9 | -- | -- | -- | 6.28 |

The RSD-values obtained were generally high and showed some instability. The SBR-values were consequently considered to be the more important parameter during the selection of the optimum power levels. The optimum values which were finally selected are:

| | |
|---|---|
| Pt 265.945 nm | 0.6 kW |
| Pd 340.458 nm | 0.7 kW |
| Rh 339.682 nm | 0.6 kW |
| Ni 221.647 nm | 0.8 kW |

### (iii) Observation Height

The optimum observation height was determined employing an automatic viewing height program available with software of the instrument. The optimum heights, corresponding to the maximum SBR-values, were:

| | |
|---|---|
| Pt 265.945 nm | 5 mm |
| Pd 340.458 nm | 7 mm |
| Rh 229.682 nm | 6 mm |
| Ni 221.647 nm | 8 mm |

Once again a distinction can be made between the atomic and ionic lines. According to Boumans [3] two vertically distinctive zones can be identified in the central channel of the argon ICP. In the first *thermal zone*, which is closest to the induction coil, the atomic lines will show the highest intensities, as they require less energy to become excited. The second *non-thermal zone* is located higher up in the plasma and in this region the ionic lines will exhibit maximum emission. This can be explained by the fact that the emitting species must first be ionized before emission can take place. This tendency is also reflected in the behaviour of the elements under investigation, eg. the atomic lines of Pt, Pd and Rh had low observation heights while the Ni line reached an optimum at a higher value.

## 3.3 Evaluation of the optimized ICP-OES system

### (i) Detection Limits

The calculated detection limits for each of the analytes are summarised below:

**Table 6.3** : Detection Limits for the analyte elements.

| Element | Wavelength (nm) | Detection Limit ($C_L$) ($\mu g/\ell$) |
|---|---|---|
| Pt | 265.945 | 123 |
| Pd | 340.458 | 7.63 |
| Rh | 339.682 | 78.8 |
| Ni | 221.647 | 119 |

## (ii) Dynamic Range

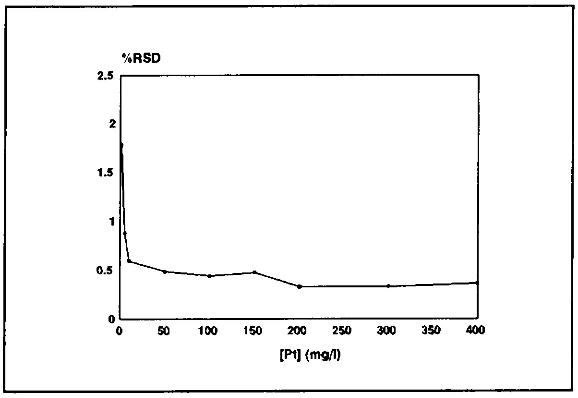


**Figure 6.4** Dynamic range of Pt.

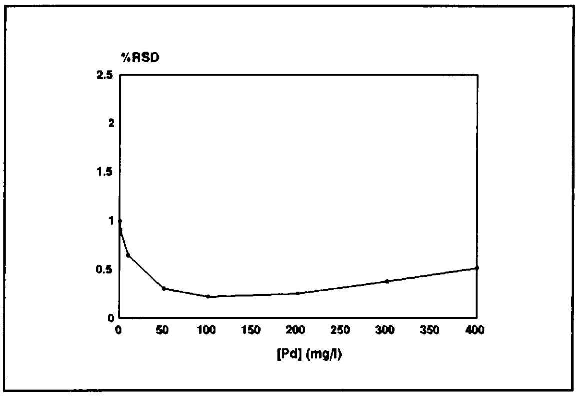


**Figure 6.5** Dynamic range of Pd.

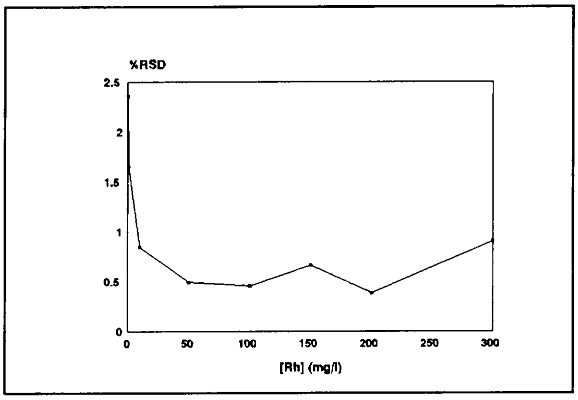


**Figure 6.6** Dynamic range of Rh.

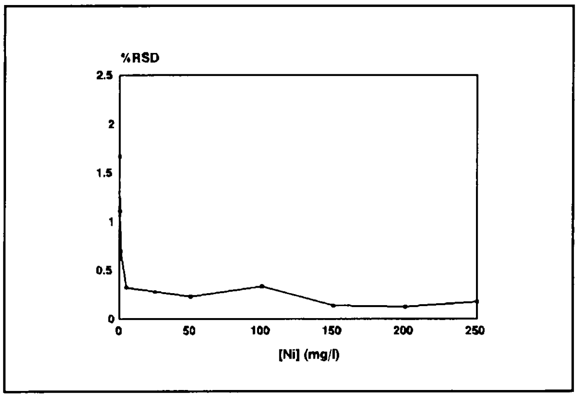


**Figure 6.7** Dynamic range of Ni.

The dynamic range of the individual elements were derived from the graphical representation of the RSD-values against the concentration of the elements (Fig. 6.4 to 6.7). Although it is clear that the analytical ranges extend beyond the 250 to 400 mg/ℓ concentrations analyzed, higher concentrations were not included. This has not been done since the ultimate aim of this investigation was to perform trace analysis. It was therefore anticipated that, even with the preconcentration of samples, the range covered was sufficient to ensure accurate analysis. The dynamic ranges are subsequently summarised below. The linearity of the resulting calibration curves are indicated by the corresponding regression coefficients ($r^2$).

**Table 6.4** : Dynamic Ranges obtained for the analyte elements

| Element | Dynamic Range (mg/ℓ) | Linearity ($r^2$) |
|---|---|---|
| Pt | 4 - 400 | 0.9884 |
| Pd | 0.5 - 400 | 0.9996 |
| Rh | 9 - 300 | 0.9821 |
| Ni | 1 - 250 | 0.9986 |

## 4. Identification of an interfering $N_2$ 265.93 nm line

During the optimization, a *"Pt peak"* was observed high in the plasma when deionized water was aspirated. Additionally, two other peaks appeared adjacent to the *"Pt peak"*, thus indicating that this is probably due to some kind of molecular spectra (Fig. 6.8). Since these bands are also observed in a dry plasma it can be concluded that the molecular species do not originate from the solvent but rather from ambient air (Fig. 6.9).

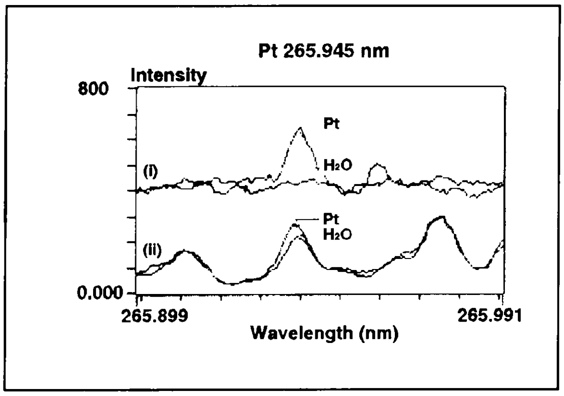


**Figure 6.8** 1 mg/ℓ Pt and deionized water analyzed at observation heights of (i) 8 mm and (ii) 25 mm.

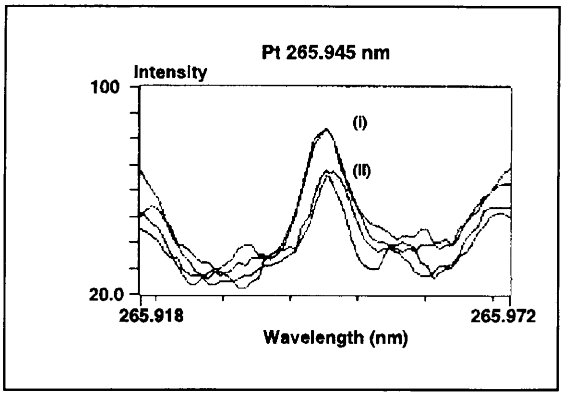


**Figure 6.9** Interferent peak at 22 mm with a (i) dry plasma and (ii) wet plasma.

A literature survey was consequently conducted to identify all molecular species emitting at this position. Of all the possible interferences, $N_2$ (comprising 78.1% of the atmosphere [6]), seemed the most likely interference. According to Pearse and Gaydon [7], the fourth positive system of $N_2$ has a band head at 265.93 nm, which is probably the observed *"Pt peak"*. In order to confirm that this spectra is indeed due to the fourth positive system of $N_2$, wavelength scans were performed at the positions of the other band heads of the system. In each case, band spectra corresponding to those indicated for the fourth positive system of $N_2$ were identified.

The notion that this peak may be attributed to the entrainment of atmospheric $N_2$ are further supported when some of the operating conditions of the ICP are changed. At higher observation heights the intensity of the band spectra did, for instance increase (Fig. 6.10-6.12). This corresponds to the results obtained by Northway *et al* [8] who found that the amount of $N_2$ present in the plasma rapidly increases with increasing height above the top of the torch. Since the amount of $N_2$ present inside the torch was almost negligible, the $N_2$ in the plasma has been attributed to the entrainment of atmospheric $N_2$. It was furthermore also possible to suppress the intensity of this band by increasing the plasma gas flow rate. The increased flow rate effectively shielded the plasma from the entrainment of ambient air [2], resulting in less $N_2$ reaching the plasma (Fig. 6.13). Alternatively the entrainment of air into the plasma may also be prevented by using a long (extended) torch [9]. At higher input powers the intensity of the band spectra also increased as increased excitation occurred at the subsequent higher temperatures of the plasma.

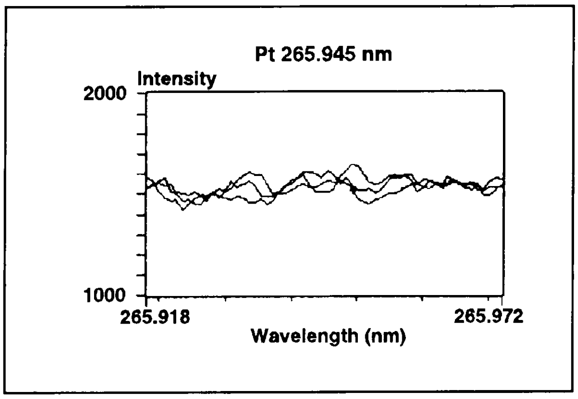


**Figure 6.10** Interferent peak at 15 mm.

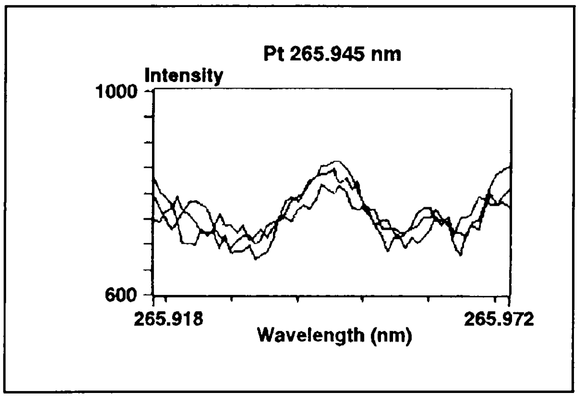


**Figure 6.11** Interferent peak at 20 mm.

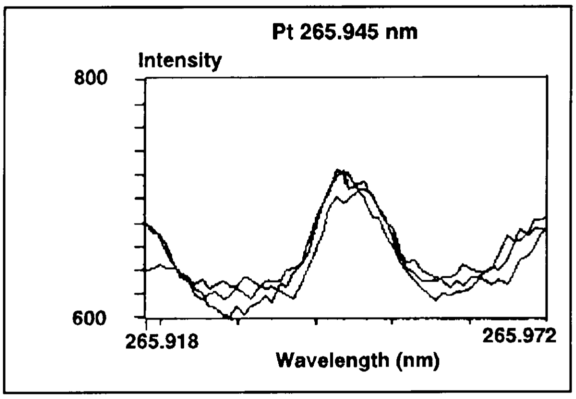
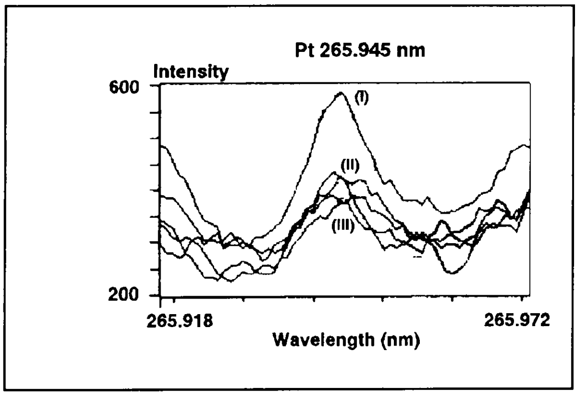


**Figure 6.12** Interferent peak at 25 mm.



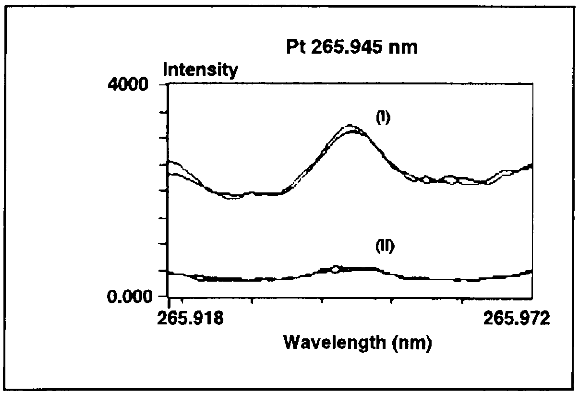


**Figure 6.13** Interferent peak at 25 mm with the plasma gas flow rate at (i) 15.0 ℓ/min, (ii) 19.5 ℓ/min and (iii) 22 ℓ/min.

**Figure 6.14** Interferent peak at power levels of (i) 1.5 kW and (ii) 1.0 kW.

Since this interference is however only present high in the plasma it should generally not interfere with the atomic Pt 265.945 nm line. At low power levels possible interferences will further be limited as these band spectra are less pronounced at lower power levels. In conclusion it is clear that this interference can be completely avoided if the ICP-OES has been properly optimized. It may however be anticipated that the fourth positive system of $N_2$ would be more pronounced when mixed Ar-$N_2$ ICP's are used and it is possible that the determination of Pt may subsequently be affected.

## 5. Conclusions

During the selection of analytical wavelengths for Pt, Pd, Rh and Ni, care has been taken to avoid any possible spectral interferences. The selected lines are indicated below. For Ni no interference-free, sensitive line could be identified. The Ni 221.647 nm line which was selected offered sufficient sensitivity for trace analysis, but suffered from Ir, Cr and Co interferences. Correction factors were determined for each of these interferences.

During optimization, only those parameters which generally have a significant influence on the performance of an ICP-OES system were considered. These were optimized to obtain the best SBR-values, thereby ensuring that the best detection power was achieved. The final optimum conditions selected were:

**Table 6.5** : Optimum operating conditions for the ICP-OES system.

| Parameter | Pt<br>265.945 nm | Pd<br>340.458 nm | Rh<br>339.682 nm | Ni<br>221.647 nm |
|---|---|---|---|---|
| Power (kW) | 0.6 | 0.7 | 0.6 | 0.8 |
| Observation Height (mm) | 5 | 7 | 6 | 8 |
| Sample uptake rate (mℓ/min) | 1.5 | 1.5 | 1.5 | 1.5 |
| Aerosol gas flow (kPa) | 150 | 150 | 150 | 150 |
| Plasma gas flow (ℓ/min) | 15 | 15 | 15 | 15 |
| Intermediate gas flow (ℓ/min) | 1.5 | 1.5 | 1.5 | 1.5 |

The analytical performance of the optimized ICP-OES system was subsequently evaluated by calculating the detection limit and dynamic range for each element and are indicated in Table 6.6.

**Table 6.6** : Analytical performance of the optimized ICP-OES system.

| Parameter | Pt<br>265.945 nm | Pd<br>340.458 nm | Rh<br>339.628 nm | Ni<br>221.647 nm |
|---|---|---|---|---|
| Detection Limit (μg/ℓ) | 123 | 7.63 | 78.8 | 119 |
| Dynamic Range (μg/ℓ) | 4 - 400 | 0.5 - 400 | 9 -300 | 1 - 250 |
| Linearity ($r^2$) | 0.9884 | 0.9996 | 0.9821 | 0.9986 |

The precision obtained within the analytical range was generally good (eg. less than 1% RSD).

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# CHAPTER 7

# On-line Preconcentration of Platinum with Alumina

## 1. Introduction

The determination of trace levels of platinum in a variety of sample types generally require the use of sensitive analytical techniques. These include graphite furnace atomic absorption spectrometry (GFAAS), neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS). Despite the availability of such sensitive analytical techniques, a separation/preconcentration step is still often required prior to the final analysis. This is necessary to achieve the low detection limits required for the analysis of trace levels of Pt as well as to remove matrix interferences. Some of the most popular separation and preconcentration methods employed are liquid-liquid extraction and ion exchange.

There are a number of ion exchange resins available for the preconcentration of Pt. Strong base anion exchangers (eg. Dowex-1, BioRad AG1 and XAD-4) are for instance very effective in the preconcentration of Pt, but subsequent elution are generally quite difficult. Ion exchange procedures employing these resins are therefore mostly operated off-line and require considerable sample manipulation and long analysis times [1]. When preconcentration is performed on-line (eg. with FIA), it is possible to achieve high preconcentration factors with little sample manipulation and a high sample throughput. Ion exchangers used in FIA should however not only ensure quantitative adsorption of the analyte but also easy elution.

With regard to the FIA system proposed by Cantarero *et al* [1,2], alumina appeared to be a promising ion exchanger for the on-line preconcentration of Pt. Alumina, like most other metal oxides, provides a low ion exchange capacity and therefore requires less eluent for successful elution within a narrow elution band. Additionally, alumina has a rigid structure, undergoes little swelling or shrinking when solvent conditions are altered, shows favourable ion exchange selectivities and exhibits both anion and cation exchange characteristics [3]. Although alumina is also generally stable under acidic and basic conditions, it may become unstable below a pH of 2 and will be destroyed in strong alkalis such as 5 mol/ℓ KOH [4].

Although it has been suggested that ion retention on alumina is purely an adsorption or precipitation process, it is generally accepted that this is an ion exchange process. The analyte ion will therefore be retained via the formation of an electrical double layer at the alumina surface. Schmitt [3] suggested that a surface charge appears due to the dissociation of surface aluminiumhydroxide-groups. Depending on the solvent pH, either a proton or hydroxide ion, may subsequently be exchanged, allowing alumina to function as a cation or an anion exchanger. This process may be represented as follows [3]:

**Anion Exchanger :**

Dissociation : $\text{-Al-O-H} \rightleftharpoons \text{-Al}^+\text{OH}^-$

Anion Exchange : $\text{-Al}^+\text{OH}^- + \text{X}^- \rightleftharpoons \text{-Al}^+\text{X}^- + \text{OH}^-$

**Cation Exchanger :**

Dissociation : $-Al-O-H \rightleftharpoons -Al-O^{-}H^{+}$

Cation Exchange : $-Al-O^{-}H^{+} + X^{+} \rightleftharpoons -Al-O^{-}X^{+} + H^{+}$

where X is the analyte ion.

The isoelectric pH of alumina will depend on the type and treatment of the alumina as well as the type of buffer used with alumina and typically ranges between pH 3.5 and 9.2 [3]. The anion exchange capacity of alumina consequently increases with decreasing acidic pH, while the cation exchange capacity increases with increasing basic pH. Ion exchange of Pt(IV) as $PtCl_6^{2-}$ will therefore occur at low pH-values, where the alumina hydroxyl groups are dissociated. The divalent $PtCl_6^{2-}$ complex will therefore be strongly retained at low pH-values.

Due to the favourable characteristics exhibited by alumina, this ion exchanger was selected for the on-line preconcentration of Pt. A FIA system similar to the one proposed by Cantarero *et al* [1] was adopted. Since the acidity of the carrier stream, alkalinity of the eluent and the sample pH are all critical parameters which determines the performance of an ion exchanger, these parameters were optimized. Since Pt-complexes are generally inert, the kinetics of the ion exchange reactions are also important and the flow rates of the individual streams were also optimized. Finally, the analytical performance of the developed FIA-ICP system were evaluated according to parameters such as the accuracy, precision and detection limits obtained.

# 2. Experimental

## 2.1 Apparatus

### (i) ICP-OES

A Varian Liberty 220 Inductively Coupled Plasma Emission Spectrometer, equipped with a monochromator and a concentric glass pneumatic nebulizer was used as a detector for the FIA system. This instrument further scans a wavelength window around the selected wavelength to identify the position of maximum emission. Integration of the analyte peak are then performed at this position. Since the contribution of the background to the measured signal are generally significant and often structured, a dynamic background correction procedure was used for analysis. This procedure fits a polynomial to the background curve obtained before and after the maximum intensity. The background intensity below the peak maximum intensity can subsequently be estimated and subtracted from the measured signal intensity to yield the nett intensity.

During elution, 40 measurements with an integration time of 2 seconds each, were recorded. Since the peak position are determined during the initial wavelength scan, integration of the eluted peak could however only start once the Pt reached the plasma. A 22 second sample delay period was therefore incorporated before initiation of the wavelength scan. This ensured that the eluted Pt peaks were measured at the correct position.

The following optimum operating conditions were used during the analysis of Pt solutions at the 265.945 nm Pt-line:

**Table 7.1** : Operating conditions for the ICP-OES at Pt 265.945 nm.

| | |
|---|---|
| Input Power (kW) | 0.9 |
| Nebulizer Pressure (kPa) | 150 |
| Plasma gas flow (ℓ/min) | 15.0 |
| Auxiliary gas flow (ℓ/min) | 1.5 |
| Observation height (mm) | 3 |
| Sample introduction rate (mℓ/min) | 1.1 |

## (ii) FIA system

The FIA-ICP system used for the preconcentration of platinum is represented schematically in Fig. 7.1.

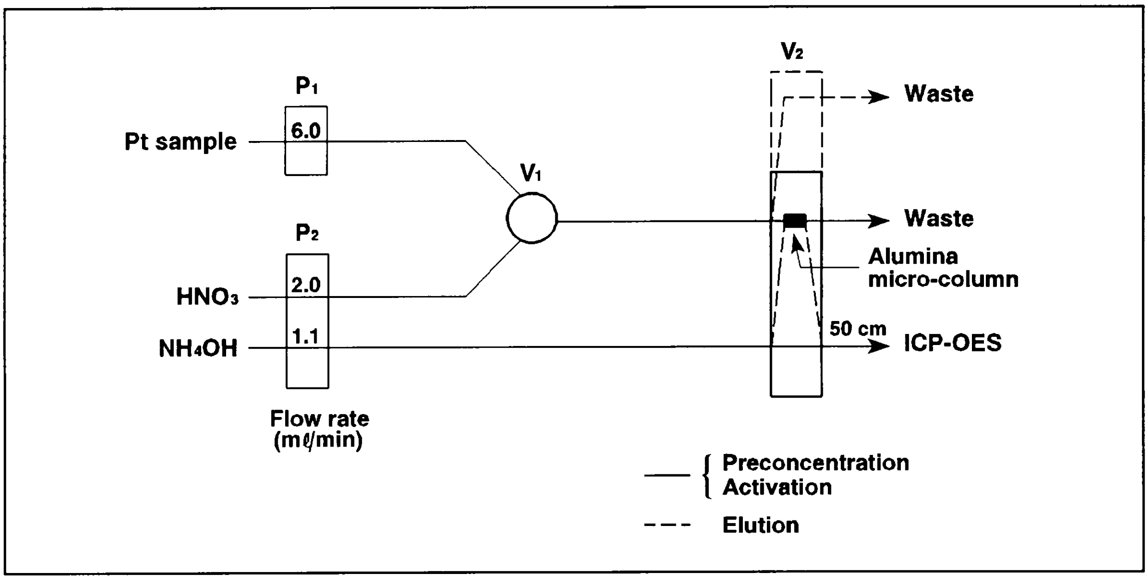

**Figure 7.1** Schematic representation of the FIA-ICP system used for the preconcentration of Pt.

A 6-port and a 1-port peristaltic pump were used in the system. Two individual pumps were needed since the first valve (V1), could only accommodate one flowing stream at a time (Fig. 7.2). During preconcentration it was therefore only possible to pump the sample stream, while the carrier ($HNO_3$) and eluent ($NH_4OH$) flows had to be stopped. This also meant that the eluent feed to the ICP was interrupted. During elution and activation it was however only necessary to stop the sample stream.

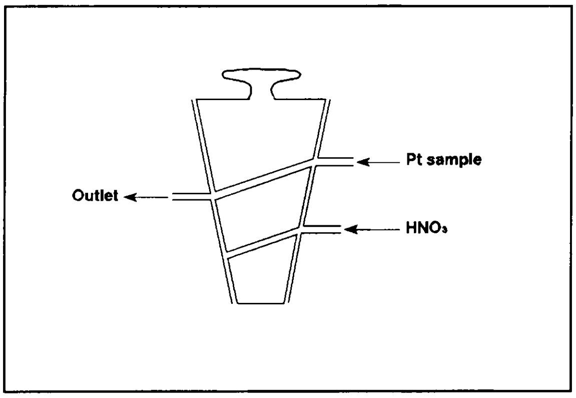

**Figure 7.2** Schematic representation of the first valve.

A VICI 2-position 10-port multi-functional valve (V2), which are capable of manipulating two flowing solution streams, was used as the second valve (Fig. 7.3). The alumina micro-column was attached to this valve and preconcentration and elution was subsequently effected by switching the valve. In the first position (load), the position of the first valve determined whether the column was being activated with nitric acid or if preconcentration was performed. In this position the eluent flowed directly to the ICP. In the second position (inject) of valve 2, the eluent was pumped via the column to the ICP, thus the adsorbed Pt was eluted in a reversed flow fashion. Apart from limiting the dispersion of the eluted Pt this also prevented the alumina-particles from becoming too firmly packed with time. During elution the $HNO_3$ stream was pumped to waste, while the sample stream did not flow at all.

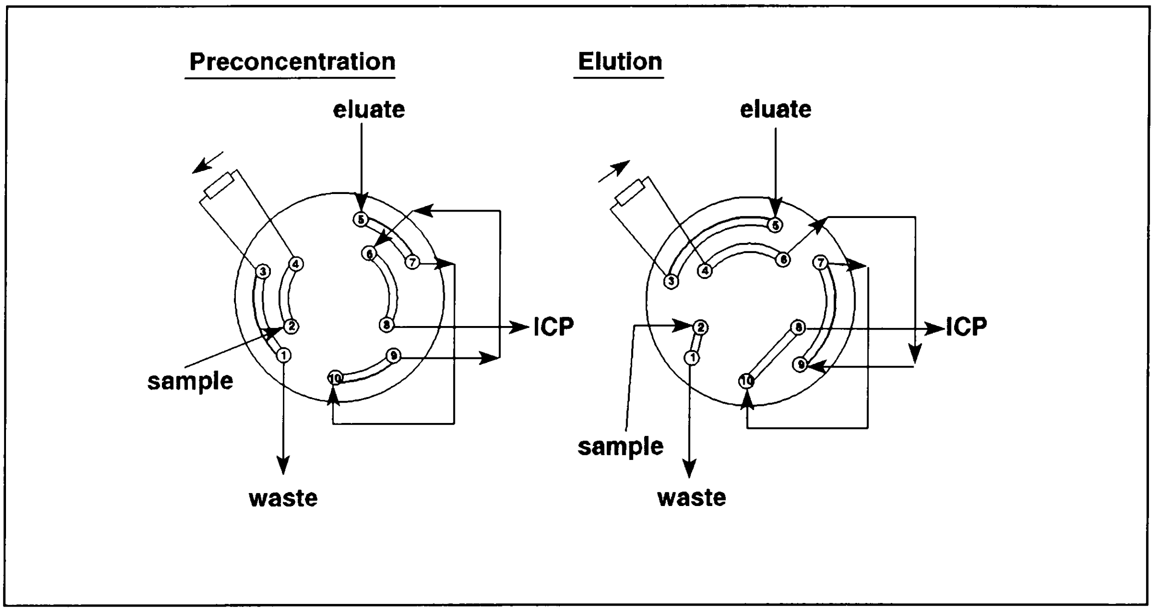

Figure 7.3 Schematic representation of the two positions of valve 2.

Before any experimental work could be undertaken a number of preconcentration/elution procedures first had to be evaluated to ensure that a reliable procedure was selected. Different activation and elution times were tested, while the necessity of the activation step was also confirmed experimentally. The best reproducibility was obtained using the following procedure:

Before any preconcentration could be performed, nitric acid had to be pumped through the alumina column for a 5 minute activation period. This was necessary to re-establish the acidity of the micro-column following elution with ammonium hydroxide. The sample was subsequently preconcentrated for 1 minute, after which an additional 15 seconds were allowed for the $HNO_3$ stream to flush the dead volume of the sample through the column. In the final step, elution was performed for a period of 4 minutes. A detailed description of the procedure is also given in Table 7.2.

**Table 7.2** : FIA-procedure for the preconcentration of Pt.

| Time | P1 | P2 | V1 | V2 | Procedure |
|---|---|---|---|---|---|
| 0:00 | On | Off | $HNO_3$ | Load | Activation |
| 4:57 | Off | Off | Pt | Load | Switching $P_1$ and $V_1$ |
| 5:00 | Off | On | Pt | Load | Preconcentration |
| 6:00 | Off | Off | $HNO_3$ | Load | Switching $P_2$ and $V_1$ |
| 6:03 | On | Off | $HNO_3$ | Load | Rinsing sample dead volume |
| 6:15 | On | Off | $HNO_3$ | Inject | Elution |
| 10:15 | On | Off | $HNO_3$ | Load | Activation |

Switching of the valves and starting and stopping of the pumps were operated manually and in certain cases 3 seconds was consequently allowed to perform this.

Tygon tubing were used as transport conduits between the pumps, valves and the detector. The length of tubing used were kept as short as possible. This was especially important for the connection between the micro-column and the ICP, as unnecessary dispersion of the eluted peak was avoided.

### (iii) Alumina micro-column

The micro-column (Fig. 7.4) used was constructed according to those described by Du Plessis [5] and Fang [6]. A screen taken from a Dionex OnGuard-H sample preparation column was inserted about 5 mm into a *ca* 8 cm length of tygon tubing (1.85 mm i.d.). A 6 cm piece of 0.53 mm i.d. tygon tubing was subsequently inserted into the first piece of tubing and sealed with cyclohexanone. Activated alumina (Merck, Brockman Grade I, basic form, particle size 63-200 $\mu$m) was sieved to obtain a particle size of 106-200 $\mu$m. The alumina was subsequently conditioned by leaving it overnight in 0.1 mol/ℓ $HNO_3$ and then slurry packed to fill a 7 cm section of the prepared column. The alumina was packed firmly by pumping water through the column (@ 2 mℓ/min) for a period of 6 to 8 minutes. The column was completed by sealing the open end with another screen as well as a 6 cm x 0.51 mm i.d. piece of tygon tubing.

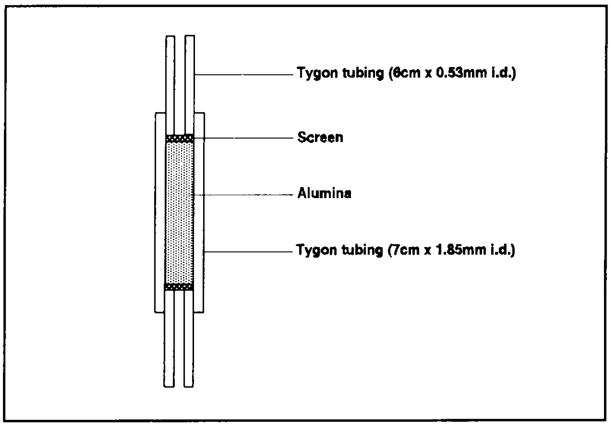

**Figure 7.4** Alumina micro-column.

Maintenance of the column was very straightforward and entailed rinsing it for approximately 5 minutes with nitric acid and water after it has been used.

## 2.2 Reagents

Analytical grade chemicals and deionized water were used in the preparation of all reagents.

***Standard Pt solutions*** : 1 mg/ℓ Pt solutions, in 0.01 mol/ℓ HCl, were prepared from a standard 2000 mg/ℓ Pt stock solution (Merck) and 32% HCl (SaarChem). This solution was prepared on a daily basis and was used for the optimization of the FIA-ICP system. Additionally, during the evaluation of the FIA-ICP system, Pt solutions with concentrations ranging from 0.05 to 40 mg/ℓ were prepared.

***Carrier solution*** : Nitric acid solutions (0.005 to 1.0 mol/ℓ) were prepared by dilution of appropriate volumes of 65% $HNO_3$ (Merck).

***Eluent solution*** : Ammonium hydroxide solutions (1.0 to 4.0 mol/ℓ) were prepared by the dilution of 25% ammonium hydroxide (BDH) with deionized water.

***Alumina anion exchange column*** : Activated alumina (Merck, Brockman Grade I, basic form, particle size 63 - 200 $\mu$m) were used. This was sieved to obtain a particle size of 106 to 200 $\mu$m and was then conditioned in 0.1 mol/ℓ $HNO_3$ before it was slurry-packed into the micro-column.

## 3. Optimization

### 3.1 HCl concentration in Pt sample

#### (i) Method

The FIA-ICP system, indicated in Fig. 7.1, was used according to the method described in section 2.1 (i). 1 mg/ℓ Pt solutions, with HCl concentrations ranging from 0.0005 to 1.0 mol/ℓ, were prepared and analyzed. 4 Repetitions were performed for each HCl concentration. Both the peak areas and maximum intensities were calculated and evaluated.

#### (ii) Results

Considering the response of the peak areas as well as the maximum intensities (Fig. 7.5), it is clear that the efficiency of the Pt preconcentration are practically constant over the concentration range of 0.0005 to 0.01 mol/ℓ HCl. However, at higher HCl concentrations the preconcentration of Pt decreases dramatically. This can be attributed to the increased concentration of the counterion ($Cl^-$), which will compete with the $PtCl_6^{2-}$ complexes for the available ion exchange positions on the alumina. This competition will however only become significant at HCl concentrations higher than 0.01 mol/ℓ HCl.

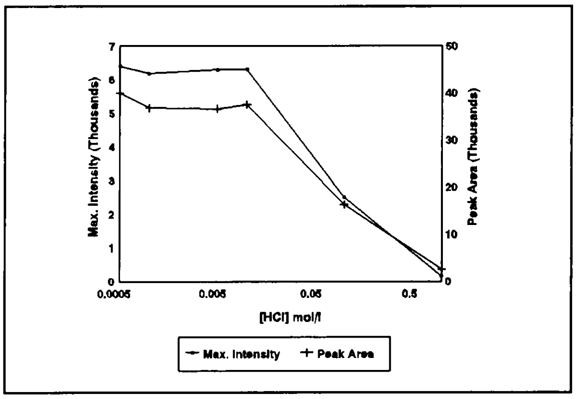

**Figure 7.5** Influence of HCl concentration on the preconcentration of Pt.

**Table 7.3** : %RSD-values at various HCl concentrations.

| HCl concentration (mol/ℓ) | %RSD (Maximum Intensity) | %RSD (Peak Area) |
|---|---|---|
| 0.0005 | 1.13 | 2.49 |
| 0.001 | 1.40 | 3.15 |
| 0.005 | 0.848 | 2.27 |
| 0.010 | 1.20 | 1.27 |
| 0.10 | 2.83 | 7.30 |
| 1.00 | 13.1 | 18.4 |

According to Blasius *et al* [7], $PtCl_6^{2-}$ will start to hydrolyse to $[PtCl_5(OH)]^{2-}$ and

$[PtCl_4(OH)_2]^{2-}$ at HCl concentrations lower than 3 mol/ℓ HCl. In HCl solutions with concentrations lower than 0.1 mol/ℓ, a significant portion of the Pt will be hydrolysed. Fortunately, the presence of these divalent species apparently do not lead to increased irreproducability (Table 7.3). In fact, poor RSD-values are actually associated with higher HCl concentrations.

The 0.005 mol/ℓ HCl concentration was selected as the optimum, since it yielded the best preconcentration efficiency of Pt as well as reproducible results.

### 3.2 Concentration of the Ammonium hydroxide eluent

#### (i) Method

When on-line preconcentration systems are used, it is critical that the adsorbed species ($PtCl_6^{2-}$) are eluted in a very sharp band (eg. as fast as possible). This ensures that the highest possible preconcentration factors are achieved. Since the concentration of the eluent plays a critical role in the speed of elution, this was an important parameter to optimize. The FIA-ICP system was operated using the same conditions as described in section 2.1 (i), except that the Pt sample contained only 0.005 mol/ℓ HCl. Optimization was subsequently performed with $NH_4OH$ concentrations ranging from 1 to 4 mol/ℓ.

## (ii) Results

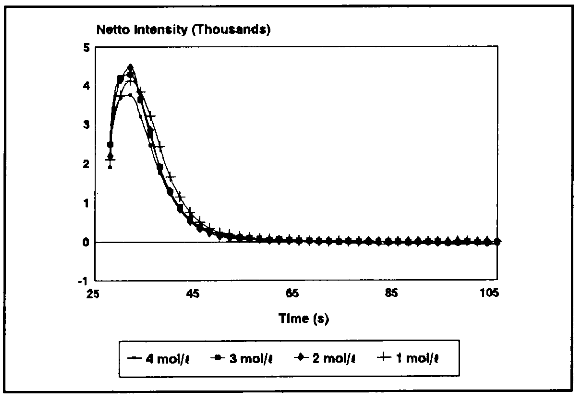

**Figure 7.6** Pt-Elution profiles with different ammonium hydroxide concentrations.

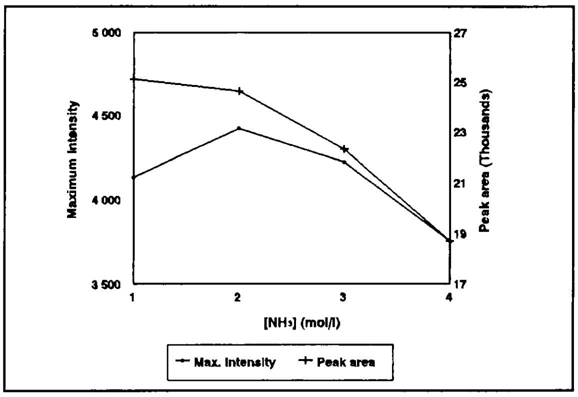

**Figure 7.7** Optimum ammonium hydroxide concentrations.

Contrary to expectations, increased $NH_4OH$ concentrations did not significantly increase the elution speed of Pt, in fact, all the maxima were observed at the same time. Increased eluent concentration did however cause an increase in the maximum intensities obtained up to concentrations of 2 mol/ℓ. In contrast to the maximum intensities, the peak areas generally decrease with increasing $NH_4OH$ concentrations and consequently has a maximum at 1 mol/ℓ $NH_4OH$. However, with 1 mol/ℓ $NH_4OH$, elution were not complete within a period of 4 minutes and the elution time had to be extended to 4 ½ minutes. Concentrations lower than 1 mol/ℓ were therefore not evaluated. This slower elution of Pt experienced with 1 mol/ℓ $NH_4OH$, could also explain the high peak areas obtained. Additionally, $NH_4OH$ concentrations higher than 4 mol/ℓ were also not considered in this investigation. This was not done since it has been reported that strong eluents, such as 5 mol/ℓ KOH, causes rapid destruction of alumina columns [3].

**Table 7.4** : %RSD-values at various $NH_4OH$ concentrations.

| $NH_4OH$ concentration (mol/ℓ) | %RSD (Maximum Intensity) | %RSD (Peak Area) |
|---|---|---|
| 1.0 | 3.60 | 5.26 |
| 2.0 | 2.14 | 5.95 |
| 3.0 | 3.10 | 5.89 |
| 4.0 | 2.42 | 5.97 |

The RSD-values obtained (Table 7.4) are relatively constant and only slightly favour the lower $NH_4OH$ concentrations. The 2 mol/ℓ $NH_4OH$ solution, which would ensure complete elution of the adsorbed Pt within a reasonable time, was selected as the best eluent. It should however be mentioned that even with the lower $NH_4OH$ concentration, aluminium could still be observed in the plasma during elution. Despite the gradual destruction of the column, the alumina columns still had lifetimes of between 1 and 2 months.

## 3.3 Optimum $HNO_3$ concentration

### (i) Method

After each elution step, the acidity of the micro-column had to be re-established to ensure that the pH of the alumina was below its isoelectric pH before preconcentration started. This was essential since the ion exchange positions of the alumina would otherwise not be ionized and available for ion exchange during preconcentration. The response of the FIA-ICP system was subsequently monitored, while $HNO_3$ solutions with concentrations ranging from 0.01 to 1.0 mol/ℓ were used to activate the alumina. Apart from the $NH_4OH$ concentration (optimum 2 mol/ℓ), the operating conditions of the FIA-ICP system were the same as in the previous section, while 4 repetitions were also performed for each concentration investigated.

### (ii) Results

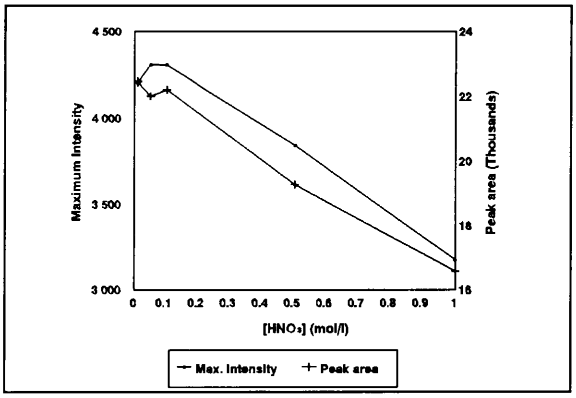

**Figure 7.8** Optimum nitric acid concentration.

Considering the maximum intensities obtained, the optimum $HNO_3$ concentration were between 0.05 and 0.1 mol/ℓ, while the peak areas generally decreased with increasing $HNO_3$ concentrations. It is clear that the lower $HNO_3$ concentrations provided the best results. Cantarero *et al* [1] attributed the lower Pt peak obtained with high $HNO_3$ concentrations to difficulties associated with the elution of Pt, therefore this is rather an elution effect than an activation problem.

**Table 7.5** : %RSD-values for various $HNO_3$ concentrations.

| $HNO_3$ concentration (mol/ℓ) | %RSD (Maximum Intensity) | %RSD (Peak Area) |
|---|---|---|
| 0.01 | 5.18 | 4.543 |
| 0.05 | 4.15 | 5.78 |
| 0.10 | 3.09 | 4.73 |
| 0.50 | 5.66 | 8.32 |
| 1.00 | 3.85 | 12.02 |

Since low RSD-values are also obtained for the 0.1 mol/ℓ $HNO_3$ solution, this concentration was selected as the optimum.

## 3.4 Optimum Pt sample flow rate

### (i) Method

Since the highest preconcentration factors are always required, it was important to determine the optimum sample flow rate. An increase in sample flow rate will typically increase the volume of sample concentrated and hence the preconcentration factor. The degree to which the sample flow rate can be increased, will however be limited by the kinetics of the ion exchange reaction as well as the back-pressure generated by the column. This is particularly important when Pt is analyses since its complexes are typically quite inert.

During this series of experiments the pump tubing of the 1-port pump were changed to obtain different flow rates. The actual flow rates achieved, were determined experimentally by measuring the volume of sample pumped in one minute, and ranged between 4.6 and 8.0 mℓ/min.

### (ii) Results

Both the peak areas and the maximum intensity of the eluted Pt peaks indicate (Fig. 7.9) that the optimum flow rate is reached at 6.0 mℓ/min. The steady increase in the Pt signals up to 6.0 mℓ/min can probably be attributed to the corresponding increase in the sample volume which is preconcentrated. At flow rates higher than 6.0 mℓ/min the sample passes through the column too rapidly and the Pt cannot be retained quantitatively, as a result both the peak areas and the maximum intensities decreased sharply at flow rates higher than 6.0 mℓ/min.

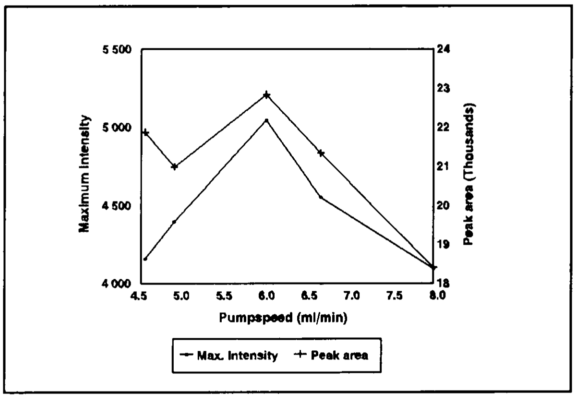

**Figure 7.9** Optimum Pt sample flow rate.

**Table 7.6** : %RSD-values at various Pt sample flow rates.

| Sample flow rate (mℓ/min) | %RSD (Maximum Intensity) | %RSD (Peak Area) |
|---|---|---|
| 4.6 | 1.02 | 3.87 |
| 4.9 | 1.80 | 4.07 |
| 6.0 | 3.18 | 3.22 |
| 6.7 | 4.78 | 4.53 |
| 8.0 | 4.78 | 6.99 |

The RSD-values of the maximum intensities generally decreases towards the lower flow rates, while those of the peak areas show a minimum at 6.0 mℓ/min. The latter flow rate was therefore chosen as the optimum sample flow rate.

## 3.5 Optimum Eluent flow rate

### (i) Method

As the sample flow rate, the optimum eluent flow rate will also be determined by the kinetics of the elution reaction. This is also particularly important for the elution of $PtCl_6^{2-}$, which is notoriously difficult to elute quantitatively within a reasonable period of time. Flow rates ranging from 0.9 to 1.8 mℓ/min were consequently evaluated during optimization. Since the eluent flow rate will also influence the time in which the eluted Pt will travel to the ICP, the sample delay time were changed for each flow rate tested.

### (ii) Results

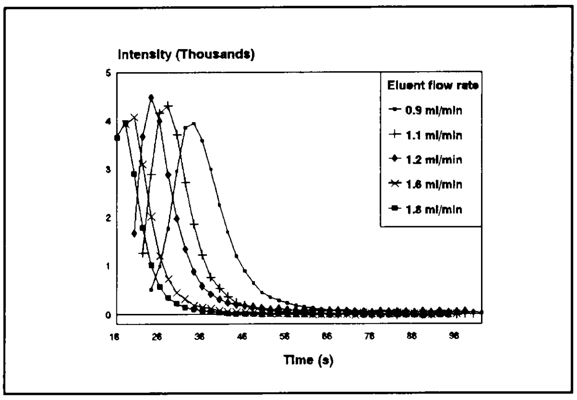

**Figure 7.10** Pt elution profiles at different eluent flow rates.

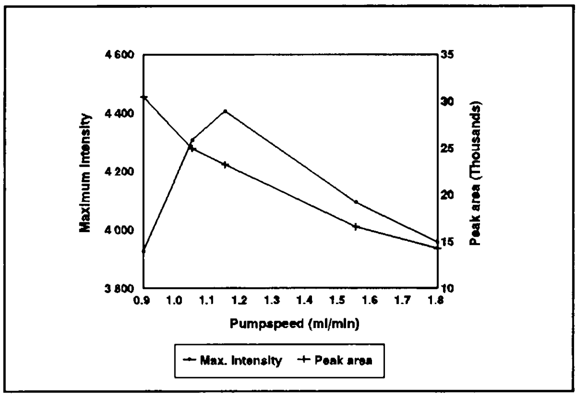

**Figure 7.11** Optimum ammonium hydroxide flow rate.

The Pt peak profiles obtained for the different flow rates indicate that the Pt are indeed eluted sooner at higher flow rates. Apart from this, the maximum intensity of these peaks also increase with increasing flow rates of up to 1.2 mℓ/min. However, if the flow rate is increased further, the maximum intensity decreases again. This can be attributed to the kinetics of the exchange reaction, which will limit quantitative elution as the contact time decreases. In contrast to the maximum intensities obtained the peak areas generally decreases with increasing flow rates. At low flow rates this can probably be ascribed to a narrower elution band, while at higher flow rates the reaction kinetics will become the limiting factor.

**Table 7.7** : %RSD-values for various $NH_4OH$ concentrations.

| $NH_4OH$ flow rate (mℓ/min) | %RSD (Maximum Intensity) | %RSD (Peak Area) |
|---|---|---|
| 0.9 | 1.35 | 2.02 |
| 1.1 | 1.26 | 1.21 |
| 1.2 | 2.65 | 3.53 |
| 1.6 | 2.68 | 2.35 |
| 1.8 | 0.708 | 5.16 |

Although the RSD-values which were obtained with this experiment were subjected to fluctuations, it appeared to be generally increasing towards the higher flow rates. The 1.2 mℓ/min flow rate was therefore selected as the optimum, despite the slightly higher RSD-value associated with it.

## 3.6 Optimum $HNO_3$ flow rate

### (i) Method

Since the activation of the alumina column is in principle a chemical reaction, the reaction-kinetics will once again determine the optimum $HNO_3$ flow rate. The flow rates were changed by changing the pump tubing used for the $HNO_3$ stream.

However, when the flow rate is changed while the activation time is kept constant, the volume of acid used will change accordingly. At lower flow rates this could mean that the acidity of the micro-column will not be re-established completely, while at higher flow rates the subsequent elution of the adsorbed Pt may become difficult [1]. The activation time was therefore changed according to the different flow rates tested to ensure that the volume of $HNO_3$ used, remained constant.

### (ii) Results

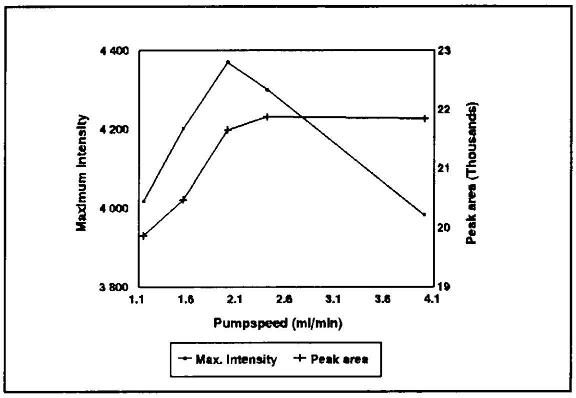

**Figure 7.12** Optimum nitric acid flow rate.

Both the peak areas and the maximum intensities indicate that with flow rates of up to 2 mℓ/min, the efficiency of the activation step increases with increasing flow rate. However, at higher flow rates the peak areas stabilize while the maximum intensity-values decrease again. This suggests that the activation of the activation reaction proceeds optimally when the nitric acid flow rate is 2.0 mℓ/min. The RSD at this flow rate is also the lowest and it was consequently selected as the optimum.

**Table 7.8** : %RSD-values for various $HNO_3$ flow rates.

| $HNO_3$ flow rate (mℓ/min) | %RSD (Maximum Intensity) | %RSD (Peak Area) |
|---|---|---|
| 1.15 | 1.09 | 7.21 |
| 1.55 | 3.62 | 11.47 |
| 2.00 | 0.779 | 3.93 |
| 2.40 | 1.54 | 6.84 |
| 4.00 | 3.96 | 6.60 |

# 4. Evaluation of the optimized FIA-ICP system

The analytical performance of the optimized FIA-ICP system was subsequently evaluated. The selected optimum operating conditions are summarized in Table 7.9.

**Table 7.9** : Operating conditions for the FIA-ICP system.

| Parameter | Optimum |
|---|---|
| HCl concentration in sample | 0.005 mol/ℓ |
| $NH_4OH$ concentration | 2 mol/ℓ |
| $HNO_3$ concentration | 0.1 mol/ℓ |
| Sample flow rate | 6.0 mℓ/min |
| $NH_4OH$ flow rate | 1.2 mℓ/min |
| $HNO_3$ flow rate | 2.0 mℓ/min |

During optimization, both the peak area and the maximum intensity of the eluted Pt peaks were determined. The reproducibility obtained with the maximum intensities were however consistently better than that obtained when the peak areas were evaluated. Only the maximum intensity of the eluted Pt peaks were consequently considered during the evaluation of the final FIA-ICP system.

### 4.1 Linear Range

Standard Pt solutions (0.05 - 40 mg/ℓ Pt) in 0.005 mol/ℓ HCl as well as a blank 0.005 mol/ℓ HCl solution were prepared and analyzed to determine the linear range covered by the FIA-ICP system. A calibration curve was constructed using the average maximum intensities obtained from 4 replicate analysis.

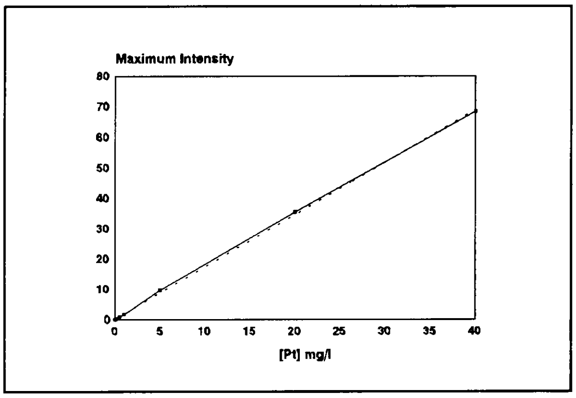

**Figure 7.13** Linear range of Pt.

The calibration curve obtained are indicated in Fig. 7.13, where the solid line represents the experimental values and the dotted line indicates the calculated calibration curve, eg.

$$y = 1716.6x + 322.3 \qquad with\ r^2 = 0.9994$$

It is clear that the calibration curve for Pt is linear over the 0.05 to 40 mg/ℓ concentration range investigated and probably extends beyond the maximum 40 mg/ℓ Pt concentration analyses. The linear regression coefficient ($r^2$) confirms the excellent fitting which is obtained over this concentration range.

## 4.2 Detection Limit

The detection limit was determined after 11 replicate analysis of a blank 0.005 mol/ℓ HCl solution. The value of the detection limit was calculated according to the definition in Chapter 6 (Eq. 1), eg.

$$C_{DL} = S(\overline{x_{bl}} + 3\sigma_{bl})$$

where S is the sensitivity (slope) of the calibration curve,

$\overline{x}_{bl}$ is the mean background intensity (maximum) and

$\sigma_{bl}$ is the standard deviation of the background intensity.

The detection limit for the preconcentration of Pt with the FIA-ICP system consequently was:

$$\boxed{C_{DL} = 5.88\ \mu g/\ell\ \mathrm{Pt}}$$

This is approximately 2 orders of magnitude lower than the 123 μg/ℓ obtained with the ICP-OES, without preconcentration.

## 4.3 Accuracy

The accuracy obtained with the developed system was first estimated by determining the concentration of two synthetic waste water samples with the normal calibration method. Additionally, the accuracy was also determined in terms of the recovery of Pt from one of the samples which had been spiked with known concentrations of Pt. The %Recovery was determined as:

$$\%Recovery = \frac{Pt_{Determined}}{Pt_{Added}} \times 100$$

In the first case a calibration curve was constructed, covering the concentration range of 0 to 1.0 mg/ℓ Pt. The two samples (0.72 and 0.44 mg/ℓ Pt respectively) were subsequently analyses and the results are given in Table 7.10.

**Table 7.10** : Accuracy of FIA-ICP system.

| $[Pt]_{sample}$ | $[Pt]_{calculated}$ |
|---|---|
| 0.72 mg/ℓ | 0.52 mg/ℓ |
| 0.44 mg/ℓ | 0.27 mg/ℓ |

In both cases the calculated Pt concentration were approximately 0.20 mg/ℓ lower than the actual concentration. A possible explanation for these low recoveries may be adsorption of Pt on the glass walls of the volumetric flasks used. Alternatively, this may also be due to suppression of the Pt preconcentration by interfering elements in the sample.

The concentration of the 0.72 mg/ℓ Pt sample was also determined using the standard addition method. The sample was therefore analyzed, followed by the analysis of the same sample to which increasing amounts of Pt of known concentration were added. The standard addition-calibration curve are shown in Fig. 7.14, where the Pt concentration of the sample are represented as the absolute value of the intersection with the x-axis, eg.

$$\boxed{[Pt]_{calculated} = 0.76\ mg/\ell}$$

This value is slightly higher than the real concentration and represents a 106% recovery of the added Pt. Since the Pt concentration obtained with the standard addition method is significantly more accurate than the normal calibrations method, it may be concluded that other species in the samples interfered with the preconcentration of Pt with the method.

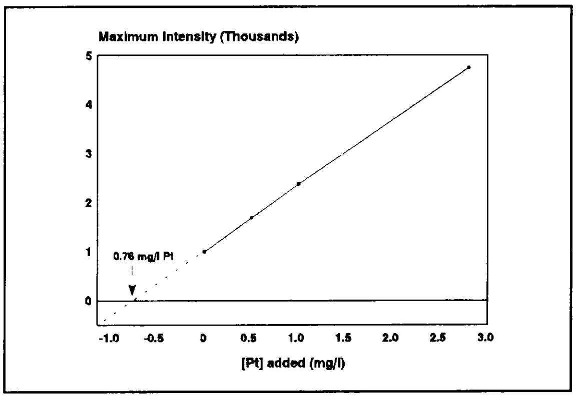

**Figure 7.14** Standard additions calibration curve for the 0.72 mg/ℓ Pt sample.

## 4.4 Precision

The precision obtained with the method was determined following the analysis of a 0.5 mg/ℓ Pt standard solution as well as the 0.72 mg/ℓ Pt sample solution. 11 Repetitions were performed with each sample and the corresponding RSD-values are represented in Table 7.11.

**Table 7.11** : Precision obtained with FIA-ICP system.

| Pt-Solution type | % RSD |
|---|---|
| 0.5 mg/ℓ Pt standard | 2.86 % |
| 0.72 mg/ℓ Pt sample | 4.97 % |

Considering that this system was operated manually, the precision obtained for the standard solution is quite acceptable. The RSD-value obtained for the sample is however higher than would be desired. The precision will however improve significantly if the system were coupled to a computer.

## 4.5 Sample interaction

The sample interaction between two consecutively analyzed samples, was calculated as follows:

$$\%\ Interaction = \frac{(A_3 - A_1)}{A_2} \times 100$$

where $A_1$ is the peak height of a sample with a low analyte concentration,

$A_2$ is the peak height of a sample containing ten times more analyte than the first sample analyses, and

$A_3$ is the peak height obtained when the first sample is analyses directly after the second sample.

For the purpose of this study, two samples with concentrations of 0.5 and 5.0 mg/ℓ Pt respectively, were analyzed. Since a negative value was obtained for the % Interaction (-0.76%), it was concluded that no sample interaction occurred between two consecutively analyzed samples. This confirmed that with the procedure used (Table 7.2), the elution of adsorbed Pt are complete.

# 5. Evaluation of the preconcentration performance of the FIA-ICP system

The effectivity with which the developed FIA-ICP system preconcentrates Pt, were determined according to the following criteria:

## 5.1 Enrichment Factor (EF)

Although the enrichment factor is formally defined as the ratio between the analyte concentration in the concentrate and the original sample, it can also be approximated by the ratio of the slopes of the linear sections of the calibration curves after and before preconcentration [6]. The enrichment factor obtained with this system consequently was:

$$\boxed{\text{EF} = 25.54}$$

It can therefore be said that with the FIA-ICP system the Pt concentration of a sample could be increased approximately 25 times. This value was obtained with only an one minute preconcentration time, it can easily be increased further by increasing the preconcentration time.

## 5.2 Concentration Efficiency (CE)

This parameter indicates the factor of enrichment which the system can achieve within one minute. However, before this parameter can be determined, the sample frequency obtainable with the system must be known. With this system a single sample could be analyzed within

10 ½ minutes. The sample frequency was consequently determined employing the following equation:

$$f = \frac{1}{t} \times 60$$

where t is the analysis time of a single sample and

f is the sample frequency in an hour.

A sample frequency of 5.7 samples an hour could be achieved with the system.

The concentration efficiency was subsequently determined using the following equation:

$$CE = EF \times \frac{f}{60}$$

According to Fang [6], this factor should be greater than 8 to ensure that an on-line preconcentration system are more advantageous than traditional batch procedures. The CE-value of 2.45 obtained for this system, is however significantly lower than 8. On-line preconcentration does however offer additional advantages such as reduced sample consumption and are also less labour intensive and should therefore not be discarded.

## 5.3 Consumptive Index (CI)

This parameter expresses the efficiency with which an on-line preconcentration system utilizes the sample available. This will be particularly important when a limited amount of sample is available.

The parameter was calculated according to the following equation:

$$CI = \frac{V_s}{EF}$$

where $V_s$ is the sample volume in millilitres (6.0 mℓ).

The consumptive index for the preconcentration of Pt was 0.235, indicating that only *ca* 0.24 mℓ of sample is needed to obtain an unit enrichment factor.

## 6. Conclusions

A FIA-ICP system was developed for the on-line preconcentration of Pt with an alumina micro-column. A number of parameters influencing the preconcentration and elution of Pt with a FIA-ICP system were optimized, as it was important to achieve the sensitivity required for trace analysis. The HCl concentration in the sample was found to be critical as the chloride ion started to compete with the anionic Pt complexes when the HCl concentration was too high. Preconcentration was subsequently performed at lower concentrations. The concentration of the $NH_4OH$ eluent also had a significant influence on the elution of the sorbed Pt. At low concentrations elution was very slow, while the eluent started to destroy the alumina column at high $NH_4OH$ concentrations. The influence of the $HNO_3$ concentration of the carrier was less prominent, although elution became difficult when high concentrations was employed. The optimum reagent flow rates were mainly determined by the kinetics of these reactions. At too high flow rates the kinetics of the preconcentration and elution reactions would for instance not permit quantitative preconcentration and elution, while at lower flow rates longer preconcentration and elution times were required. The optimum conditions selected for these parameters are summarized in Table 7.9.

The performance of the optimized FIA-ICP system was subsequently evaluated according to the linear range, detection limit, accuracy, precision, sample interaction as well as sample frequency obtained. Firstly, the linear range included concentrations ranging from 0.05 to 40 mg/ℓ Pt, while the detection limit of the ICP-OES was improved with 2 orders of magnitude to 5.88 μg/ℓ Pt. During the analysis of synthetic water samples, a 106% recovery of the added Pt was obtained. However, when standard addition procedures were not used, the Pt concentrations obtained were generally significantly lower than the actual concentrations. This has been attributed to the presence of interfering species present in the sample. The precision obtained with this system ranged between 2.86 and 4.97%, which were considered to be satisfactory for a manually operated FIA system. No sample interaction could be identified and a sample frequency of 5.7 samples/hour was obtained.

Finally, the preconcentration efficiency of the FIA-ICP system was also evaluated. The enhancement factor (EF) of 25.5 indicated that the system increased the Pt concentration in a sample more than 25 times. However, the concentration efficiency (CE) of 2.54 was lower than that typically associated with batch procedures. The consumptive index (CI) of 0.24, nevertheless still indicated efficient utilization of the available sample.

# 7. References

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# CHAPTER 8

# On-line Preconcentration of Platinum with POLYORGS IV

## 1. Introduction

Since the determination of noble metals in various materials usually require their preconcentration as well as separation from the sample matrix, methods such as ion exchange and solvent extraction are often used in conjunction with instrumental procedures. Alternatively, chelating sorbents are also very effective in the preconcentration and separation of the noble metals [1]. Sorbent extraction is in fact often preferred since it offers higher selectivity as well as high distribution coefficients for the analytes. Furthermore, these complexing sorbents generally exhibit good kinetic characteristics [2,3].

Various types of complexing sorbents are currently available for the preconcentration of trace metals from solutions. Some of these include natural and synthetic polymers as well as modified ion exchangers [3]. The selectivity of these sorbents depend on the complexing groups they contain. Since the noble metals generally have a greater tendency to form complexes than other metals, complex-forming sorbents are especially useful for the determination of these elements.

Sorbents containing nitrogen and sulphur donor atoms in the ionogenic groups are generally the most selective towards the noble metals, with those containing nitrogen atoms being more selective in the presence of metals such as Cu, Ni, Co, etc. The selectivity of these sorbents for the noble metals are also further increased if the nitrogen is contained within a heterocyclic group, while manipulation of the solution pH will also influence the selectivity [1].

A number of chelating sorbents (POLYORGS), specifically for the preconcentration of noble, rare and heavy metals, have recently been developed by the V.I. Vernadsky Institute of the USSR Academy of Science. These sorbents are synthesized by introducing pyrazole groups as substituents to polymeric molecules such as styrene-divinyl benzene. Of these sorbents, the POLYORGS IV are generally preferred for the preconcentration of Pt. This sorbent contains a 3- or 5-methyl pyrazole substituent and the structure of this chelate group are depicted in Fig. 8.1. Although pyrazole and its derivatives will generally form complexes with most transition metals, these sorbents are selective for the noble metals in the presence of Cu, Fe, Co, Ni, etc. This has been attributed to the fact that the introduction of a N-substituted 3- or 5-methyl pyrazole ligand to the aromatic polystyrene system causes a decrease in the reactivity of the ligand. Since the noble metals (eg. Pt) generally exhibit typical b-group behaviour, they will still interact strongly with the pyrazole ligands [4]. The sorption of base metals such as Fe and Cu will however become slight. This has in fact been confirmed by infrared spectroscopy, where the appearance of absorption bands in the 200 to 400 $cm^{-1}$ region of the spectra of the sorbents indicate the complexing of these metals with the nitrogen atom of the pyrazole ligand [4]. POLYORGS are consequently highly selective for the noble metals in the presence of non-noble metals. Additionally, these sorbents also have a high capacity and are stable over a wide range of acidities and temperatures [1].

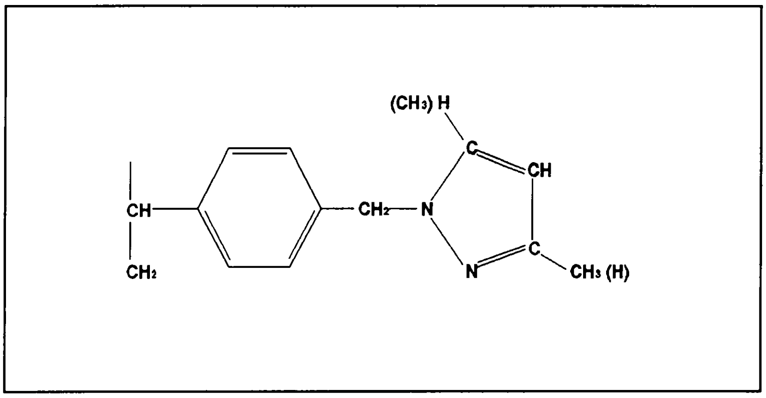

**Figure 8.1** Schematic representation of the structure of the POLYORGS IV-fibre [4].

POLYORGS sorbents are produced in the form of granules, powders, filters or fibrous materials. Of these, the former two types have been employed successfully for the preconcentration of Pt. Subsequent elution is however extremely difficult and the adsorbed Pt are generally recovered by destroying the sorbent through ashing at 450 to 500 °C or through heating it with a perchloric-sulphuric-nitric acid mixture [1].

Since the effectiveness of polymeric sorbents will generally depend on their kinetic properties, the sorbed metals should however be eluted easily. This is particularly important when sorbents are incorporated in on-line preconcentration systems. Granular and powder sorbents are therefore not suitable for use in FIA systems. In this respect, fibrous sorbents offer a number of significant advantages when compared with the former types of sorbents.

Fibrous sorbents consist of a powder chelating polymer which is retained in a fibrous polymer. These sorbents are characterized by large well-developed surfaces within which the chelating powders are well dispersed. This ensures good contact with solutions and fast metal sorption kinetics [2].

Due to the excellent kinetics attributed to these fibrous sorbents, the POLYORGS IV-fibre was consequently selected for the on-line preconcentration of Pt. This has however not been performed previously and a procedure, similar to one which had previously been used for the preconcentration of gold, was consequently developed [2]. In this system gold were eluted with a 2% thiourea solution in 0.1 mol/ℓ HCl. The corresponding reaction of Pt is however very slow and a number of parameters which may increase the reaction rate were consequently investigated.

## 2. Experimental

### 2.1 Apparatus

### (i) ICP-OES

A Spectro "Spectroflame" inductively coupled plasma-optical emission spectrometer, equipped with a monochromator and polychromator, was used as a detector with the FIA-ICP system. The Pt 265.945 nm line on the polychromator was selected for analysis with the following optimum operating conditions:

**Table 8.1** : Optimum operating conditions of ICP-OES at Pt 265.945 nm.

| | |
|---|---|
| Input Power | 1.36 kW |
| Nebulizer gas flow | *ca* 650 mℓ/min |
| Plasma gas flow | 9.0 ℓ/min |
| Auxiliary gas flow | 6.5 ℓ/min |
| Observation height | 13 mm |
| Sample introduction rate | 2.06 mℓ/min |

Peak profiles were obtained by taking either 40 or 60 measurements (with a 1 second integration time) after elution was initiated. In certain cases, the peak area was determined through integration of the peak profile obtained within a period of 36 seconds, following a 4 second sample delay period.

A commercial cross-flow nebulizer from Spectro was used with the ICP system.

### (ii) FIA-ICP system

The FIA system used with the POLYORGS micro-column are represented in Fig. 8.2. In this system Pt samples containing 0.1 mol/ℓ HCl were preconcentrated. Subsequent elution was performed with thiourea solutions which also contained 0.1 mol/ℓ HCl. This elution reaction of Pt with thiourea involves the reduction of Pt(IV) to Pt(II) as well as the formation of a Pt-thiourea complex which can be eluted. Since the kinetics of these reactions are slow, this system was operated in the stopped flow mode. During elution, the eluent was therefore only pumped until it filled the column (within 5-9 seconds), before the flow was stopped to allow the elution reaction to proceed. In order to ensure a continuous feed to the ICP during this waiting period, a second pump (P2) and valve (V2) were incorporated into the FIA system. The valve was also used with the alumina system and has been schematically represented in Fig. 7.2. A VICI 2-position 10-port valve (Fig. 7.3) was used as the first valve (V1) and also incorporated the POLYORGS micro-column. Depending on the position of the valve, either preconcentration (load) or elution (inject) was consequently performed.

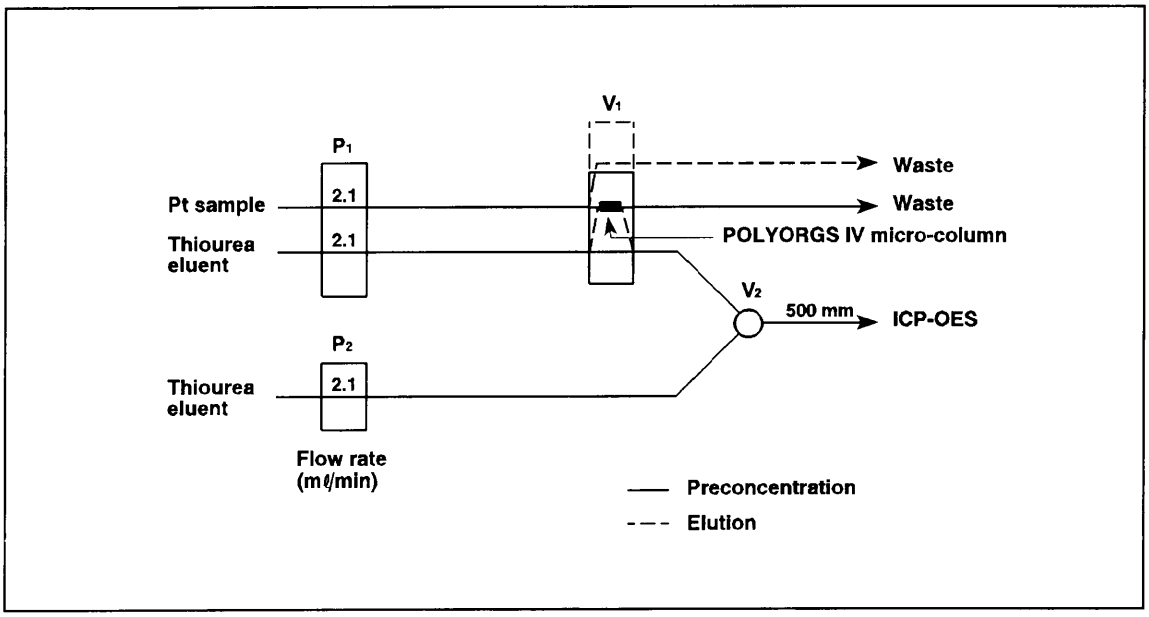

**Figure 8.2** Schematic representation of FIA-ICP system using a POLYORGS IV micro-column.

Apart from the second valve, the stopped flow system also required two pumps. An 1-port and a 6-port pump were therefore used in the system. The first pump (P1) was responsible for pumping both the sample and the eluent. When this pump were stopped to allow the elution reaction to proceed, the second pump was activated to provide a continuous eluent feed to the ICP. During this period it was consequently possible to measure the background intensity of the eluent. This was essential since drifting of the instrument had a significant influence on the measured intensities. The measured background intensities were subsequently subtracted from the signal intensities measured during elution. To ensure that the measured background signal of pump 2 were comparable to the actual background originating from the first pump, the pumps were adjusted to deliver identical flow rates. The selected flow rate (2.1 mℓ/min) was also very close to the optimum sample introduction rate of the ICP.

After the 3 minute waiting period, elution was performed for 1 minute, during which either the elution profile or the peak area were measured. Following the initial elution step, the first pump was stopped again to initiate a second 3 minute waiting period. This process was repeated at least 7 times until no more Pt could be detected in the eluent. The complete procedure, for a 2 minute preconcentration period, is represented in Table 8.2.

**Table 8.2** : On-line Preconcentration procedure with POLYORGS IV.

| Time | P1 | P2 | V1 | V2 | Procedure |
|---|---|---|---|---|---|
| 0:00 | On | Off | Load | P1-eluent | Preconcentration |
| 2:00 | On | Off | Inject | P1-eluent | Elution (start) |
| 2:05 | Off | On | Inject | P2-eluent | Measure background |
| 5:05 | On | Off | Inject | P1-eluent | Elution no.1 |
| * 6:05 | Off | On | Inject | P2-eluent | Measure background |
| * 9:05 | On | Off | Inject | P1-eluent | Elution no. 2 |

* These two steps were repeated 5 more times to ensure complete removal of the sorbed Pt from the column.

Tygon tubing were used as transport conduits between the pumps, valves and ICP-OES. The length of these tubing were always kept as short as possible. This is especially critical for the distance between the column and the detector, in order to limit unnecessary dispersion of the concentrated. This length is indicated in Fig. 8.2.

This system was also operated at elevated temperatures. During these investigations the reagents and conduits of the FIA system were immersed in a waterbath. Parts which could not be immersed were isolated with aluminium foil.

### (iii) POLYORGS IV micro-column

The construction of a micro-column with a fibrous sorbent (POLYORGS IV) is very straightforward. A square piece of the fibre (*ca* 0.05 mg) was cut, rolled into a cylindrical shape and inserted into a 38 mm x 1.59 mm i.d. piece of tygon tubing. Each column outlet was formed by inserting a 6 cm long tygon tube (0.51 mm i.d.) into a 5 mm x 1.42 mm i.d. piece of tubing. These constructed tubes were consequently inserted at both ends of the column. Cyclohexanone was used to seal the column (Fig. 8.3).

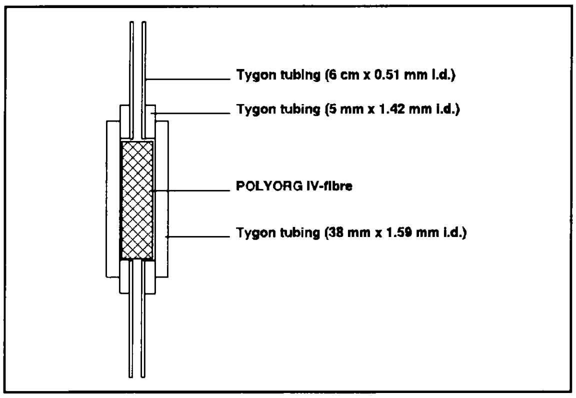

**Figure 8.3** Schematic representation of POLYORGS IV micro-column.

## 2.2 Reagents

Analytical grade chemicals and deionized water were used in the preparation of all reagents.

***Standard Pt solution*** : 0.5 mg/ℓ Pt solutions in 0.1 mol/ℓ HCl were prepared from a standard 2000 mg/ℓ Pt stock solution (Merck) and a 32% HCl solution (SaarChem). This solution was prepared on a daily basis and was used during the development and evaluation of the FIA-ICP system.

***Eluent*** : 2 to 5% m/v Thiourea solutions were prepared by dissolving weighed amounts of thiourea (Merck) in 0.1 mol/ℓ HCl, diluted from 32% HCl (SaarChem).

***POLYORGS IV micro-column*** : A 38 x 34 $mm^2$ piece (*ca* 0.05 g) of POLYORGS IV fibre (synthesized by the V.I. Vernadsky Institute, USSR Academy of Science), was inserted into a piece of tygon tubing to produce the micro-column. Before being used, the complexing sorbents contained in the fibre were converted to the $Cl^-$-form through conditioning with 0.1 mol/ℓ HCl.

# 3. Developing a FIA-ICP system for the preconcentration of Pt with a POLYORGS IV micro-column

## 3.1 Column Capacity

Since a POLYORGS IV micro-column had not previously been used for the preconcentration of Pt within a FIA system, it was first necessary to develop a preconcentration procedure for the designed system (Fig. 8.2). In order to determine the preconcentration time required, it was consequently necessary to estimate the capacity of the column under dynamic conditions. This was done by monitoring the column outlet during the preconcentration of a 0.5 mg/ℓ Pt solution. Preconcentration continued for 10 minutes at a flow rate of 2.1 mℓ/min, while the signal intensity was measured at 5 second intervals. An increase in the measured Pt signal would thus indicate the point where the column becomes saturated.

Apart from the Pt sample which was initially present in the conduits, it can be seen that Pt intensity did actually not increase during the 10 minute preconcentration period (Fig. 8.4). Therefore it could be concluded that the dynamic column capacity was greater than 0.226 mg Pt/g fibre. Under the prevailing conditions the capacity of the column would therefore not be exceeded within a 10 minute preconcentration period.

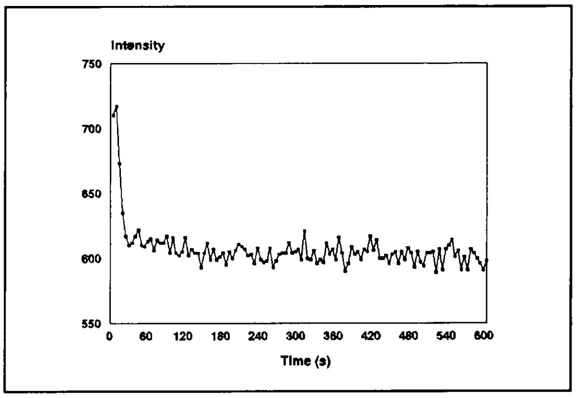

**Figure 8.4** Preconcentration profile of Pt, indicating that no breakthrough occurs within 10 minutes.

### 3.2 Preconcentration time

Although it have been determined that preconcentration times of up to 10 minutes may safely be used for the preconcentration of Pt, the subsequent difficulty associated with the elution makes this unpractical. Shorter preconcentration times were therefore compared to select the preconcentration time which yielded sufficient preconcentration without being too difficult to elute. Since a 1 minute preconcentration time gave poor Pt profiles, only 90 and 120 second preconcentration periods were consequently evaluated. The peak areas calculated from 60 measurements with an integration time of 1 second each, are represented in Fig. 8.5.

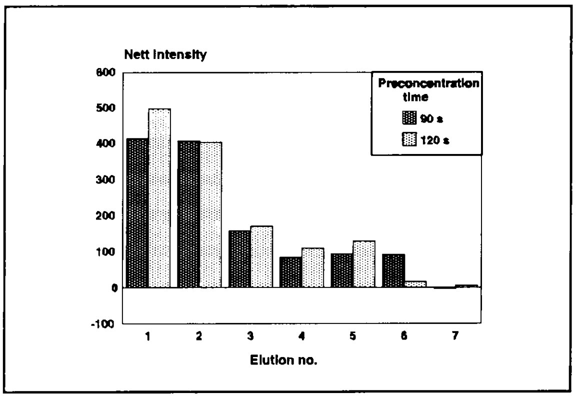

**Figure 8.5** Influence of different preconcentration times on the Pt peak areas obtained.

As expected, the 120 second preconcentration time yielded the most sensitive results. Furthermore, 7 elution steps were required for complete elution of the sorbed Pt, with both these preconcentration times. Longer preconcentration times were not considered, since the procedure already required 30 minutes for a single analysis. The 120 second preconcentration time, which offered a higher sensitivity without an associated increase in elution time, was subsequently chosen.

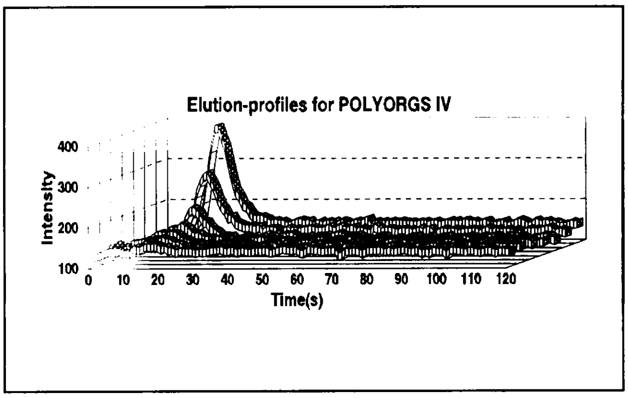

**Figure 8.6** Pt elution profiles obtained after a single 120 second preconcentration period.

### 3.3 % Thiourea in eluent

When a 5% thiourea eluent in 0.1 mol/ℓ HCl was used, problems were experienced since thiourea precipitated in the injector tube. This caused severe instability of the plasma, making it impossible to perform any analysis. Despite the slow elution obtained with the 5% thiourea eluent, it was therefore necessary to select an eluent with a lower thiourea concentration. The elution obtained with a 5% thiourea eluent was consequently compared with that obtained with 1 and 3% thiourea solutions. The peak areas corresponding to the different elution steps are indicated in Fig. 8.7.

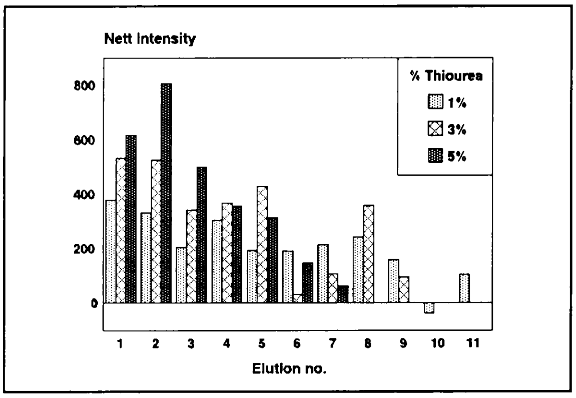

**Figure 8.7** Influence of the %thiourea on the elution of Pt.

From these results it is clear that the 5% thiourea eluent do indeed give the best elution. However, since this concentration cannot be used, either the 1 or 3% thiourea eluents had to suffice. The elution profiles obtained with these two eluents are however fluctuating while up to 11 elution steps were required for complete elution of the sorbed Pt with the 1% thiourea solution. Since the 3% thiourea eluent offered slightly better sensitivity and complete elution were obtained faster (9 steps), this eluent was used in all subsequent procedures.

### 3.4 Reaction Temperature

According to Korkisch [5], reduction and substitution reaction rates of Pt with thiourea can be increased at elevated temperatures. Additionally, this will also prevent the formation of a precipitate of Pt and thiourea in the column. The efficiency of the elution process at room temperature (22 °C) and at an elevated temperature of 60 °C, was consequently compared. The peak area profiles obtained are represented in Fig. 8.8.

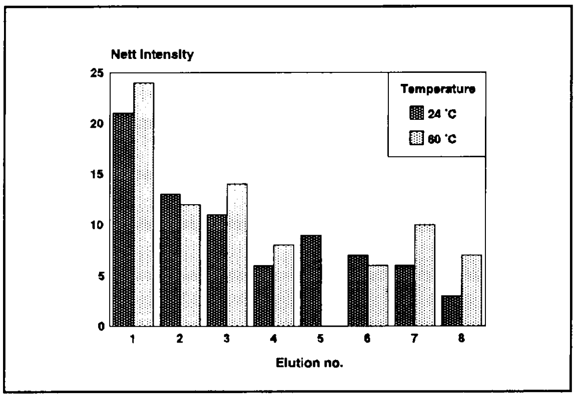

**Figure 8.8** Influence of reaction temperature on the elution of Pt.

It can the seen that the sorbed Pt will initially elute more efficiently at higher temperatures. However, after 8 elution steps, significant quantities of Pt are still eluted from the column. This may possibly be due to Pt which had not been completely eluted from the column in previous preconcentration steps and which will start to elute at higher temperatures.

Despite the apparent improvement of the elution efficiency obtained with the increase in the temperature, the overall elution process is still extremely inefficient. Experimental work with this system was consequently discontinued.

## 4. Conclusions

Since POLYORGS IV-sorbents have previously been used successfully for the preconcentration of Pt in batch processes, the suitability of the sorbent fibres for an on-line preconcentration system was investigated. Under dynamic conditions, these fibrous materials were found to have an excellent capacity for Pt. Subsequent quantitative elution of the sorbed Pt were however extremely difficult and several elution steps were required. It was further also not possible to increase the concentration of the thiourea eluent, since this caused blockage of the injector tube of the plasma torch. The elution rate could however be slightly increased at elevated temperatures, although the sample frequency was still only 2 samples/hour at 60 °C. It was therefore concluded that the use of POLYORGS IV fibres in the on-line preconcentration of Pt, was not viable.

# 5. References

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[3] G.V. Myasoedova, **Fresenius Journal of Analytical Chemistry**, **341**, (1991) 586-591.

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# CHAPTER 9

# On-line Preconcentration of Platinum with Dowex 1

## 1. Introduction

The analysis of Pt in geological material and industrial products generally require the determination of trace quantities of Pt within an interfering matrix. These interferences can however be eliminated through ion exchange procedures. Since Pt readily forms stable, anionic complexes, particularly in hydrochloric media, it will be strongly adsorbed by anion exchange resins. Apart from the platinum group of metals (PGM), most other elements will not form anionic complexes in dilute hydrochloric acid solutions, thus allowing the selective preconcentration of the PGM [1].

Of the strongly basic anion exchange resins available, the Dowex 1 resin are employed most frequently for the preconcentration of Pt [1]. The distribution coefficients of Dowex 1 for Pt(IV) are represented in Table 9.1. According to these coefficients, $PtCl_6^{2-}$ will be strongly adsorbed from all HCl concentrations, with adsorption generally decreasing with increasing molarity of HCl. $PtCl_6^{2-}$ will even be retained from 12 mol/ℓ HCl solutions and elution are consequently not possible with pure HCl solutions. Under these conditions Pt may however be separated from the other PGM's [1].

**Table 9.1** : Distribution coefficients of Platinum on Dowex 1 [2].

| [HCl] (mol/ℓ) | 12 | 9 | 6 | 3 | 1.2 |
|---|---|---|---|---|---|
| Distribution coefficient | 430 | 870 | 1900 | 3600 | $10^4$ |

The excellent adsorptive characteristics exhibited by strong basic anion exchangers such as Dowex 1, do however have an important drawback. According to Korkisch [1], the elution of the PGM (especially Pt), which have been adsorbed as anionic chloro complexes, are generally complicated and often not complete. Some of the eluents which had been employed with varying degrees of success, include 50% $HClO_4$ [3], 1% thiourea in 0.5 mol/ℓ HBr [4] as well as 12 mol/ℓ $HNO_3$ at 90 °C [5,6]. These eluents and the conditions at which elution are performed, are however not ideally suited for FIA systems. Elution with thiourea had also previously proved to be extremely slow.

As an alternative, Korkisch *et al* [2] have suggested that Pt may also be eluted with mixed aqueous-organic solvents. This group, systematically investigated the anion exchange behaviour of the PGM and Au on Dowex 1, when various combinations of 7 selected organic solvents in hydrochloric acid were used as the mobile phase. The adsorption characteristics and separation possibilities obtainable with each of these were subsequently evaluated according to the distribution coefficients determined. Of the solvents considered, only dimethylformamide (DMF) and pyridine appeared to be suitable as eluting agents for Pt (Table 9.2). DMF was subsequently selected as eluent for the on-line preconcentration of Pt with a Dowex 1 micro-column.

**Table 2 :** Distribution coefficients of Pt on Dowex 1 in organic solvent-HCl solutions [2]

| Organic solvent | Concentration HCl (%v/v organic solvent) | | | |
|---|---|---|---|---|
| | 9(25) | 6(50) | 3(75) | 0(100) |
| Dimethylformamide | 100 | 40 | 17 | 0.7 |
| Pyridine | 32 | 1 | 1 | --- |

A FIA-ICP system, which incorporated a Dowex 1-X8 micro-column, was subsequently developed. Since a mixed aqueous-organic solvent solution was selected as eluent, it was necessary to optimize the ICP for these conditions. Following the optimization, a procedure was developed for the on-line preconcentration of Pt. Important parameters which received attention, included the concentration of the DMF and HCl in the eluent, the capacity of the column as well as the time required to ensure complete elution.

## 2. Experimental

### 2.1 Apparatus

#### (i) ICP-OES

A Varian Liberty 220 Inductively Coupled Plasma Emission Spectrometer, equipped with a monochromator and a standard concentric pneumatic nebulizer was used as a detector. The Pt 265.495 nm line was used during analysis while the exact position of maximum emission intensity was determined automatically with each wavelength scan performed. To avoid possible off-peak measurements when an on-line preconcentration system is coupled to the

ICP, it is therefore important that the eluted peak will reach the plasma before the wavelength scan is performed. A sample delay period of 8 seconds consequently preceded the wavelength scan. Additionally, the ICP also estimated the background intensity beneath the measured signal and subtracted it to report the nett signal intensity. For each elution profile, 100 measurements with an integration time of 1 second each, were taken. As most of the Pt were eluted between the 5th and 30th seconds, the intensities measured during this period were used to calculate the peak areas associated with the Pt eluted.

### (ii) FIA-ICP system

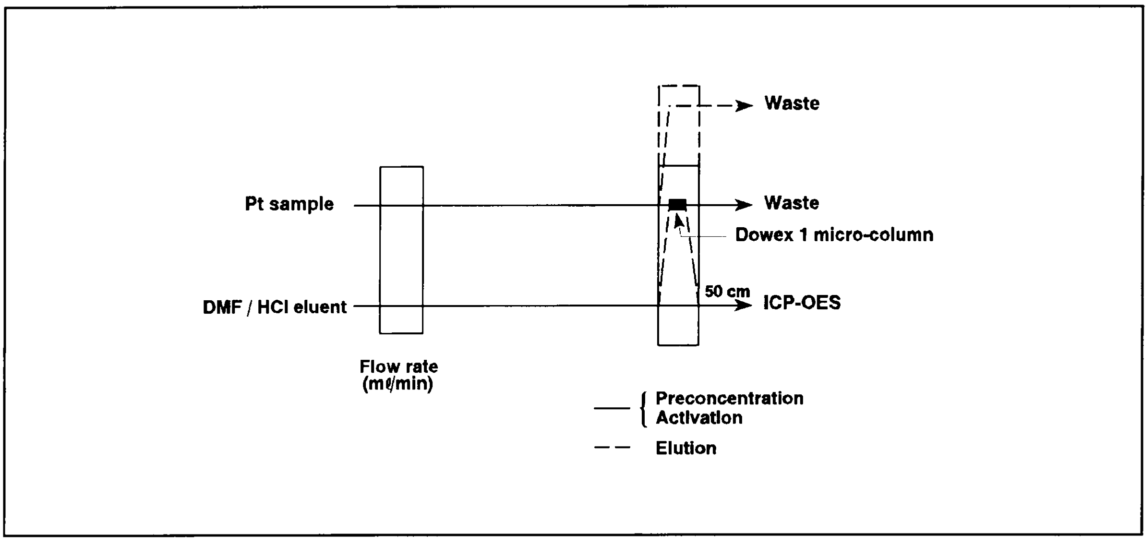

**Figure 9.1** Schematic representation of the FIA-ICP system used with the Dowex 1 micro-column.

A 6-port DESAGA peristaltic pump and a VICI 2-position 10-port multi-functional valve were used in the FIA system (Fig. 9.1). The Dowex 1 micro-column was incorporated on the valve, thus allowing easy manipulation of the preconcentration (load) and elution (inject) cycles. The configuration as well as the operation of this valve has been represented schematically in Fig. 7.3. Preconcentration and elution were performed counter currently to prevent firm packing of the resin as well as unnecessary dispersion of the concentrated Pt zone during elution.

### (iii) Dowex 1 micro-column

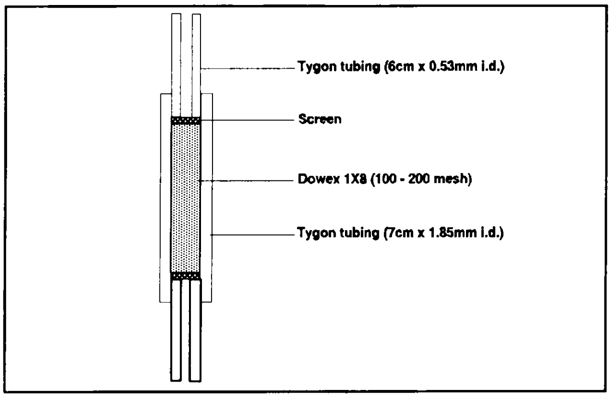

**Figure 9.2** Schematic representation of the Dowex 1 micro-column.

The Dowex 1 micro-column was constructed in the same fashion as the alumina column, described in Chapter 7. A screen taken from a Dionex OnGuard-H sample preparation column and a 6 cm x 0.51 mm i.d. tygon tube were inserted into a 2.0 mm i.d. piece of tygon tubing. The Dowex 1-X8 resin (Fluka AG, 100-200 mesh) were activated by leaving it in 6 mol/ℓ HCl overnight. This was performed to ensure maximum ionization of the ion exchange positions of the resin, before it was slurry packed into a 4 cm section of the column. Packing was performed at a flow rate of *ca* 4.0 mℓ/min and continued for 1 minute. To ensure firm packing of the resin, water was pumped counter currently through the column for another 5 minutes. The column was completed by sealing the open end with a second screen and 6 cm x 0.51 mm i.d. piece of tubing. All connections were sealed with cyclohexanone.

## 2.2 Reagents

Analytical grade chemicals and deionized water were used in the preparation of all reagents.

***Standard Pt solutions*** : Initially, a 5.0 mg/ℓ Pt solution was prepared in 50% DMF and 3 mol/ℓ HCl. This standard was used during the optimization of the ICP. For the development of the on-line preconcentration system, a 0.5 mg/ℓ Pt solution was prepared in 1.5 mol/ℓ HCl. Both these solutions were prepared on a daily basis by the appropriate dilution of a 2000 mg/ℓ Pt standard solution (Merck) and a 32 or 37% HCl solution (Saarchem).

***Dimethylformamide/HCl eluent*** : Appropriate volumes of DMF (Saarchem) and 32 or 37% HCl (Saarchem), were diluted to produce eluents which contained 30 to 75% DMF in 0.5 to 3.0 mol/ℓ HCl.

***Dowex 1 micro-column*** : Dowex 1-X8 (Fluka AG, $Cl^-$-form, particle size 100-200 mesh) were used to prepare the micro-column. These particles were activated by soaking them, overnight, in 6 mol/ℓ HCl, before they were slurry packed into the micro-column.

## 3. ICP-OES Optimization

Since special care has to be taken when organic solvents are analyzed with the ICP, it was necessary to optimize the operating conditions of the ICP especially for these conditions. The input power, observation height and the plasma-, intermediate- and the nebulizer gas flow were subsequently optimized with the 5 mg/ℓ Pt standard solution in the selected DMF/HCl solution. The optimum conditions were selected after evaluation of the nett intensities, signal-to-background ratios (SBR) and the relative standard deviation (RSD) values were evaluated. The influence of the individual parameters on the performance of the ICP system are subsequently discussed individually.

## 3.1 Input Power

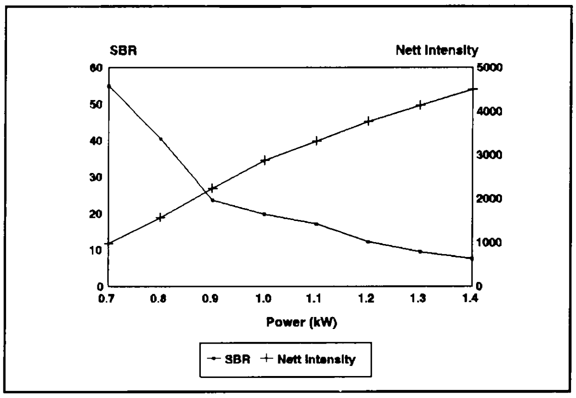

**Figure 9.3** Optimum input power with a 50% DMF in 3 mol/ℓ HCl solution.

When organic solvents are analyzed, the operating power of the ICP will have the most significant influence on the performance of the ICP. Higher operating powers are further preferred, since this will ensure that the organic solvent are completely pyrolysed in the plasma [7]. The influence of this parameter was consequently evaluated first.

Operating powers investigated, ranged from 0.7 to 1.4 kW (Fig. 9.3). As expected, the nett signal generally increased with increasing power, reaching a maximum at 1.4 kW. The associated increase in the background intensity was however even more pronounced, and the SBR-values consequently decreased over the range investigated, indicating a possible optimum of 0.7 kW.

**Table 9.3** : %RSD-values obtained at various power levels.

| Input Power | % RSD |
|---|---|
| 0.7 kW | 1.42 |
| 0.8 kW | 1.28 |
| 0.9 kW | 1.43 |
| 1.0 kW | 0.78 |
| 1.1 kW | 0.65 |
| 1.2 kW | 0.97 |
| 1.3 kW | 1.03 |
| 1.4 kW | 0.82 |

When the RSD-values were taken into consideration it became clear that the precision obtained at lower operating powers are the worst. According to Table 9.3, the best precision was obtained at intermediate power levels of 1.0 and 1.1 kW. An input power of 1.0 kW was subsequently selected.

## 3.2 Observation Height

Since the excitation conditions in the plasma will change when organic solvents are analyzed, the optimum observation height will also change accordingly [7]. It was therefore also necessary to determine the optimum observation height again. An automatic viewing height package, which is available with the instrument's software, was used for this purpose. The observation height corresponding to the highest SBR-value was subsequently selected as the optimum.

Optimum observation height = 9 mm

## 3.3 Intermediate gas flow rate

The main effect of this gas flow is to lift the plasma away from the torch. When aqueous solutions are analyzed this is normally not very important. However, when organics are analyzed this gas flow becomes very important in preventing the deposition of carbon on the injector tube [7]. The optimum intermediate gas flow rate was subsequently determined.

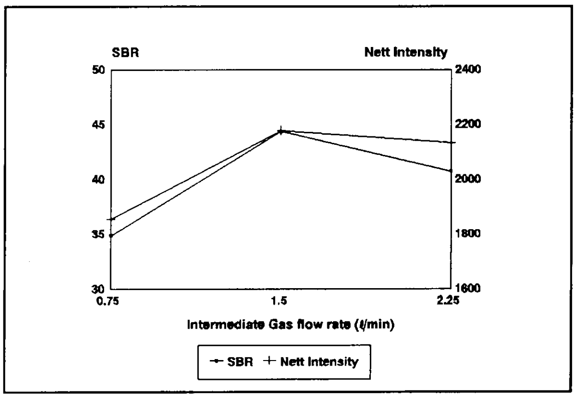

**Figure 9.4** Optimum intermediate gas flow rate with a 50% DMF in 3 mol/ℓ HCl eluent.

The response of the system, as reflected by the nett intensities and the SBR-values, are depicted in Fig. 9.4. In this case, both these parameters indicate an optimum flow rate of 1.5 ℓ/min. Since the RSD-values associated with the latter flow rate was also the lowest, an intermediate gas flow rate of 1.5 ℓ/min was selected as the optimum.

**Table 9.4** : RSD-values obtained at different intermediate gas flow rates

| Intermediate gas flow rate (ℓ/min) | %RSD |
|---|---|
| 0.75 | 4.87 |
| 1.5 | 1.08 |
| 2.25 | 1.33 |

## 3.4 Plasma gas flow rate

Higher plasma gas flow rates are generally preferred for the analysis of organics. This will not only reduce the background intensity but will also prevent carbon build up on the injector tube [7]. The optimum plasma gas flow was consequently determined by increasing the plasma gas flow rate from 15.0 to 22.5 ℓ/min. The results are represented in Fig. 9.5.

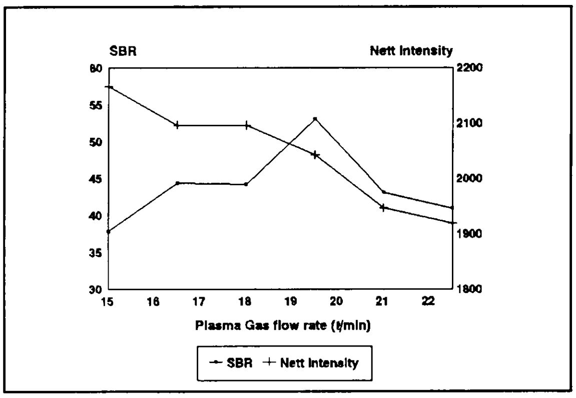

**Figure 9.5** Optimum plasma gas flow rate with a 50% DMF in 3 mol/ℓ HCl eluent.

Although the nett intensities generally decreased with increasing gas flow rates the SBR-values reached an optimum at a flow rate of 19.5 ℓ/min. The decreasing nett intensities can possibly be attributed to the fact that an increase in the plasma gas flow rate will lead to a decrease in the sample residence time in the plasma, which will in turn lead to lower emission intensities. Since the RSD-values are generally low at flow rates higher than 16.5 ℓ/min, an optimum flow rate of 19.5 ℓ/min was selected.

**Table 5** : RSD-values obtained at different plasma gas flow rates

| Plasma gas flow rate (ℓ/min) | %RSD |
|---|---|
| 15.0 | 2.41 |
| 16.5 | 3.21 |
| 18.0 | 0.892 |
| 19.5 | 1.36 |
| 21.0 | 1.11 |
| 22.5 | 1.09 |

## 3.5 Nebulizer Pressure

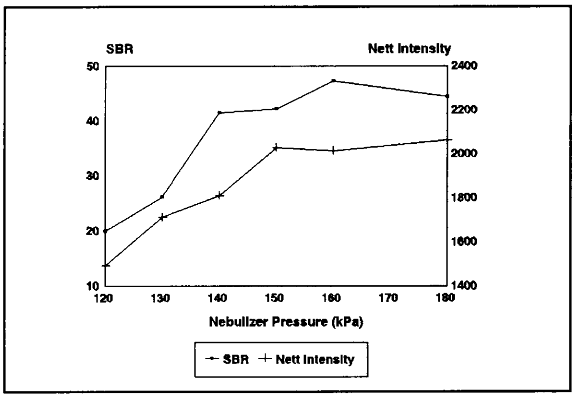

**Figure 9.6** Optimum nebulizer pressure for a 50% DMF in 3 mol/ℓ HCl eluent.

When organic solvents are analyzed with ICP-OES, problems are typically experienced with the associated high solvent load to the plasma. By lowering the nebulizer pressure it is however possible to decrease the nebulization efficiency which will in effect cause an increase in the average droplet size of the aerosol. This will in turn lead to a reduction in the number of aerosol droplets which are small enough to ultimately reach the plasma, thus reducing the solvent load to the plasma. The reduced nebulizer pressure will furthermore also reduce the background intensity and will once again also prevent carbon build up on the injector tube [7].

**Table 6** : RSD-values obtained at different nebulizer pressures.

| Nebulizer Pressure (kPa) | %RSD |
|---|---|
| 120 | 3.28 |
| 130 | 2.37 |
| 140 | 1.45 |
| 150 | 1.31 |
| 160 | 1.37 |
| 180 | 2.13 |

The influence of the nebulizer pressure on the analytical performance of the ICP-OES was subsequently investigated. These results are represented in Fig. 9.6. According to the nett intensities the optimum is reached at a 180 kPa, while the SBR-values indicate an optimum at 160 kPa. Since the RSD-value corresponding to the latter pressure was lower it was selected as the optimum pressure.

# 4. Developing a FIA-ICP system for the preconcentration of the Pt with a Dowex 1 micro-column

## 4.1 Column Capacity

Although Dowex 1 is a strong base anion exchanger which do have a high capacity, it was necessary to establish the point at which the column became saturated when on-line preconcentration was performed. A 0.5 mg/ℓ Pt solution was consequently preconcentrated at a flow rate of 1.6 mℓ/min for a period of 10 minutes. During this time the Pt-intensity of the column outlet was measured at 5 second intervals. An increase in the Pt signal would indicate saturation of the column.

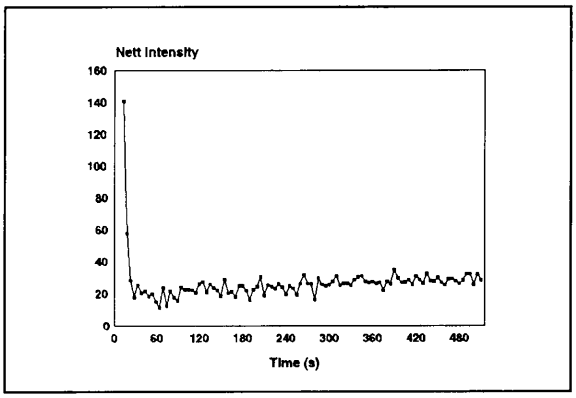

**Figure 9.7** Pt intensities as measured during the determination of the column capacity.

According to the preconcentration profile obtained (Fig. 9.7), it can be seen that the column capacity was in fact not exceeded during a 10 minute preconcentration period. To avoid lengthy elution procedures, a 90 second preconcentration period was subsequently selected.

## 4.2 Elution Procedure

Since quantitative elution of the sorbed elements (Pt) is essential in any on-line preconcentration system, it was further necessary to establish the elution time required for a 90 second preconcentration period. The elution profile obtained with a 50% DMF in 3 mol/ℓ HCl eluent was therefore evaluated (Fig. 9.8) and it was concluded that all the sorbed Pt were eluted quantitatively within 4 to 5 minutes. A 6 minute elution period was selected to ensure quantitative elution of all Pt samples which might be analyzed in future.

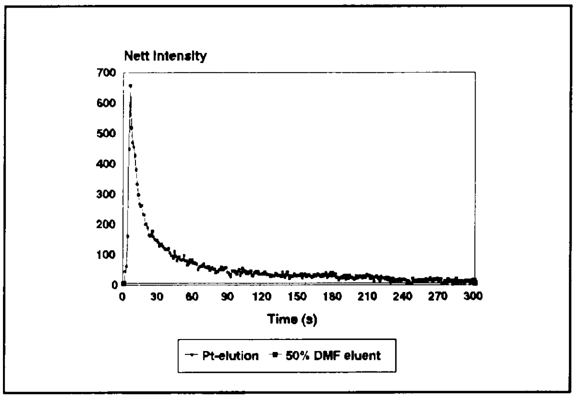

**Figure 9.8** Pt elution profile with 50% DMF in 3 mol/ℓ HCl.

When this procedure was initially employed, serious problems were experienced as elution peaks continued to decrease with each repetition performed. Since it appeared as if the column lost some of its activity during the elution, a 2 minute conditioning period was subsequently incorporated between consecutive elution steps. This would ensure that all the ion exchange positions of the resin are ionized, before the next preconcentration step is initiated. During the conditioning a 1.5 mol/ℓ HCl solution was pumped through the column at a flow rate of 1 mℓ/min.

## 4.3 Optimum Eluent Concentration

According to Korkisch *et al* [2], the distribution coefficient of the Dowex 1 resin for Pt decreases with increasing DMF concentration (Table 9.2). Under these conditions Pt would therefore be eluted faster. The influence of the %DMF in a 3 mol/ℓ HCl eluent was consequently investigated to determine the concentration with which the best elution was obtained. According to the peak areas obtained, it appears as if the 60% DMF eluent yielded the best elution (Fig. 9.9). However, when the peak profiles are also taken into consideration (Fig. 9.10), it is clear that the fastest elution are actually obtained with the 75% DMF eluent. This is also in agreement with the results of Korkisch *et al* [2].

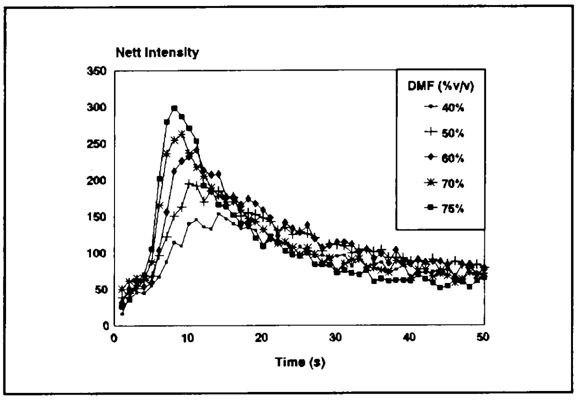

**Figure 9.9** Pt elution profiles obtained at different DMF concentrations.

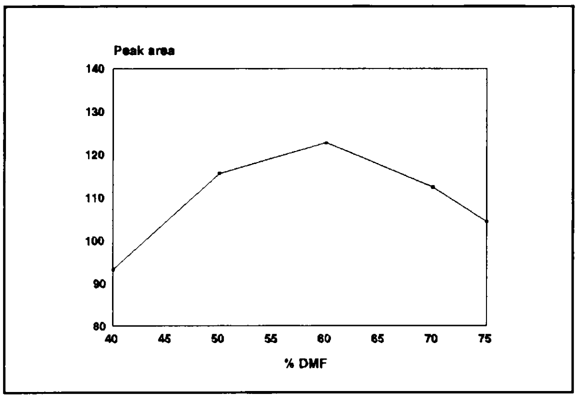

**Figure 9.10** Influence of different DMF concentrations on Pt elution peaks.

The concentration of the HCl in the 75% DMF eluent selected, was also optimized. According to the elution profiles obtained (Fig 9.11), the 1 mol/ℓ HCl eluent clearly yielded the most intense elution peak, although elution appeared to be faster with the 3 mol/ℓ HCl eluent. According to the peak areas it would however appear as if the elution efficiency decreased with increasing HCl concentration (Fig. 9.12, Day 1). On repetition of the experiment, exactly the opposite trend was however observed (Fig. 9.12, Day 2), with the peak areas this time increasing with increasing HCl concentrations. Since the only difference between these two experiments had been the sequence in which the eluents were evaluated, it could be concluded that quantitative elution was not obtained with the elution procedure selected.

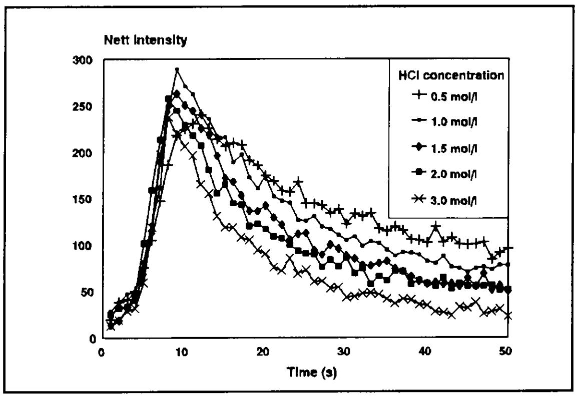

**Figure 9.11** Pt elution profiles obtained with different HCl concentrations.

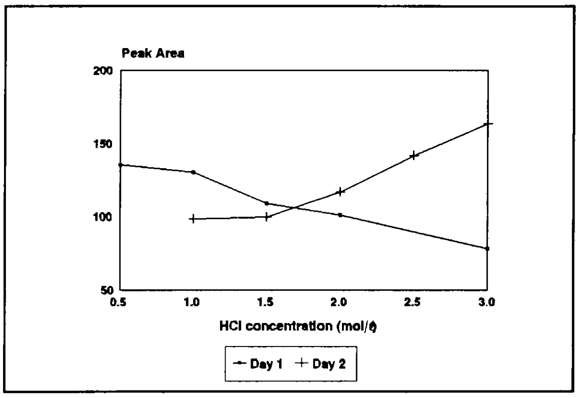

**Figure 9.12** Influence of different HCl concentrations in a 75% DMF eluent.

## 4.5 Evaluation of other possible eluents

Since complete elution was apparently not possible with the DMF/HCl eluent, another eluent had to be selected. Nitric acid and ammonium hydroxide solution had previously been used successfully for the elution of Pt from Dowex 1 in batch processes. The effectiveness of these two eluents in an on-line preconcentration system were consequently evaluated. Of these two only the 2 mol/ℓ $HNO_3$ solution succeeded in eluting the sorbed Pt within a reasonable period of time. Since elution was still slow, the concentration of the eluent was increased to 4 mol/ℓ $HNO_3$. The elution obtained with the latter eluent was subsequently compared with that previously obtained with the 75% DMF in 2.5 mol/ℓ HCl eluent (Fig. 9.13). According to these profiles it is clear that the DMF eluent still yielded the best elution. Since none of the eluents evaluated could ensure quantitative elution of the sorbed Pt, it was concluded that the Dowex 1 resin is not suitable for the on-line preconcentration of Pt.

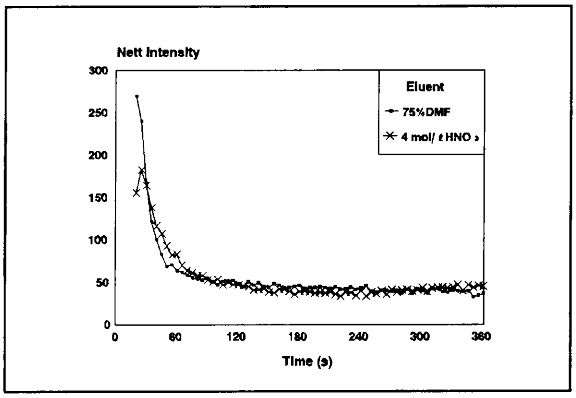

**Figure 9.13** Elution of Pt with different eluting agents.

## 5. Conclusions

Since Dowex 1 are most often employed in the batch preconcentration of Pt, an attempt was made to also use it in the on-line preconcentration of Pt. This resin offers the advantage of selective preconcentration of Pt (as well as the other PGM) from all HCl solutions, but very strong eluents are often required for their subsequent elution. As an alternative, Korkisch *et al* [2] suggested that elution may also be performed with mixed solvents. Considering the distribution coefficients available for various HCl/organic solvent mixtures [2], a HCl/dimethylformamide eluent was subsequently selected for the on-line preconcentration of Pt.

Results obtained with the FIA-ICP system, indicated that quantitative preconcentration of Pt could be achieved with the Dowex 1 micro-column. Serious problems were however experienced with the subsequent quantitative elution of the sorbed Pt. Although elution of the sorbed Pt appeared to be complete when Pt elution profiles were evaluated, the column became saturated after a few preconcentration steps had been performed. Optimizing the DMF and HCl concentrations in the eluent did not improve this situation and other eluents were subsequently also evaluated. Of these the DMF/HCl eluent still yielded the best elution and it was therefore concluded that quantitative, on-line elution of Pt was not possible when the Dowex 1 resin was used for preconcentration.

# 6. References

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# CHAPTER 10

# Final Conclusions

During the last few decades, the demand for the platinum group of metals (PGM), particularly Pt, have increased dramatically. This can largely be attributed to the use of Pt, Pd and Rh rich catalytic converters in the control of automobile exhaust emissions. Since significant amounts of Pt have subsequently been released into the environment, it has become necessary to determine trace and ultra-trace levels of Pt in environmental samples. The increased demand for Pt, has also highlighted the existing need for effective, rapid analytical methods for the determination of Pt in geological samples. Since the levels of Pt in these samples are also extremely low, the analysis thereof represents a significant challenge. Even with the most sensitive analytical techniques, eg. ICP-OES and ICP-MS, preliminary separation and preconcentration of Pt is normally required.

Ion exchange resins are consequently often employed during the determination of Pt in most sample types. Conventional batch preconcentration procedures are however generally slow and labour intensive, while the high degree of sample manipulation significantly increases the risk of sample contamination. When preconcentration is performed on-line, most of these disadvantages may be overcome. Three different ion exchange resins were consequently evaluated for the on-line preconcentration of Pt with a FIA-ICP system.

Activated alumina (basic form) was the first anion exchange resin tested with an on-line preconcentration system for Pt. A description of this system and the design of the micro-column used, are given in Chapter 7. In order to ensure optimum preconcentration and elution of Pt, certain selected parameters of the system were optimized. These parameters included the concentration of the HCl in the sample, the $HNO_3$ carrier as well as the $NH_4OH$ eluent. The influence of the flow rates of the sample, carrier and eluent streams were also determined.

After optimization had been completed, the analytical performance of the final FIA-ICP system was evaluated. One of the most important features of any preconcentration system, is its ability to lower the detection limit of the detector selected. With this system the detection limit of the ICP-OES was lowered with two orders of magnitude, while the linear range spanned four orders of magnitude. Standard addition procedures yielded a 106% recovery with an associated precision of lower than 5% RSD. An acceptable level of accuracy and precision was therefore obtainable with this system. Although it was only possible to analyze 5.7 samples/hour, no sample interaction could be identified with this procedure.

After the alumina anion exchange resin had been used successfully for the on-line preconcentration of Pt, the preconcentration ability of the POLYORGS IV-fibre was also evaluated. This is a chelating ion exchanger and are available in a variety of physical forms (eg. granules and fibres). In the granular form, this resin had previously been used successfully for the preconcentration of Pt as well as the other precious metals. Elution of sorbed species (especially Pt) from this resin are however quite difficult. In an effort to improve the kinetics of these ion exchange reactions, the resin particles had therefore been incorporated into a fibre. This fibre was consequently used in the micro-column of the FIA-ICP system described in Chapter 8.

Despite the superior kinetic characteristics of the POLYORGS IV-fibre, the thiourea elution reaction was still extremely slow. In an effort to improve the elution rate of the sorbed Pt, the concentration of the thiourea in the eluent was optimized, while the temperature at which the system was operated was increased. Although a slight improvement could be observed with an increase in temperature, this was counteracted by a decrease in the thiourea concentration. However, this was unavoidable since the injector tube became blocked at higher concentrations (eg. 5% thiourea). After optimisation of these parameters, a sampling rate of only 2 samples/hour was possible. It could therefore be concluded that the POLYORGS IV-fibre was not suitable for the on-line preconcentration of Pt.

Finally, the performance of a strong base anion exchange resin in the on-line preconcentration of Pt was also evaluated. For this purpose the Dowex 1-resin, which are frequently used for the batch preconcentration of Pt, was selected. The eluents and elution conditions generally used with this resin are however not suitable for FIA systems. The ability of a mixed aqueous HCl and dimethylformamide (DMF) eluent was consequently selected as an alternative. Initial work indicated that quantitative elution could in fact be obtained with this eluent. After optimization of the HCl and DMF concentrations, it did however become clear that Pt could not be eluted quantitatively under these conditions. Although other possible eluents were also evaluated, the DMF eluent still yielded the best elution. The Dowex 1 resin was therefore also not suitable for the on-line preconcentration of Pt.

In conclusion, it is clear that of these ion exchangers evaluated, the alumina anion exchange resin was clearly the best suited for the on-line preconcentration of Pt with a FIA-ICP system.

Additionally, an interfering line was also identified during the optimization of the ICP for the Pt 265.945 nm line. It has been proposed that this line corresponds to the 265.93 nm band head of the fourth positive system of $N_2$. This conclusion was supported by the fact that this line formed part of a molecular spectrum, while the intensity of the line increased with increasing observation heights and power levels. As this line is present at low power levels and observation heights (optimum conditions for Pt), this interference will not be significant if the ICP-system has been optimized.