SELECTIVE PRECONCENTRATION OF PLATINUM AND RHODIUM FROM HYDROCHLORIC ACID MEDIA CONTAINING TIN(II) CHLORIDE USING POLYURETHANE FOAM

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by

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ABSTRACT

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The potentially quantitative and selective sorption of chloro-(trichlorostannato)-platinum(II) and -rhodium (III/I) complex anions by polyurethane foams has been examined. Quantitative separation of platinum(II) from iridium and ruthenium has been achieved. Rhodium(III) is similarly sorbed by polyurethane foam in the presence of sufficient tin(II) chloride and its clean separation from iridium has been achieved using this method. Ruthenium, although not significantly sorbed under the same conditions as platinum and rhodium, appears to inhibit the extraction of the rhodium(III/I)-tin(II) species.

A procedure has been developed for the quantitative recovery of both platinum and rhodium. The polyurethane foams are dissolved in hot nitric acid, followed by flame AAS. Near-quantitative recovery of these metals has been achieved by means of foam stripping using a suitable eluent.

The rate of formation of the chloro-(trichlorostannato)-platinum(II) complex anions is rapid when $PtCl_4^{2-}$ is treated with an excess of tin(II) chloride. On the other hand, the reaction of cis-$Pt(NH_3)_2Cl_2$ with stannous chloride is very slow and forcing conditions are required to achieve quantitative sorption of the platinum(II)-tin(II) species by polyurethane foams for this complex

The potential of the foam to selectively extract platinum from solutions containing certain base metals was studied. Results obtained show that in all cases complete extraction of platinum was achieved. Of the base metals investigated, namely Fe(III), Co(II), Ni(II), Cu(II) and Zn(II), only copper(II) co-extracts to a small extent with the noble metal.

CHAPTER 1

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1. INTRODUCTION.

The platinum group metals - platinum, rhodium, iridium, ruthenium, palladium and osmium are rare elements; platinum, the most common with an abundance of *ca.* 10^{-6}% whereas the others have abundances of *ca.* 10^{-7}% of the earth's crust. They occur as metals, often as alloys such as osmiridium and in sulphides, arsenides, and other ores. The main sources of the metals are South Africa, the USSR and Canada.

There has been a substantial increase in the demand for the platinum metals in recent years [1]. The automotive industry in the United States is the principle consumer of the platinum group metals. Platinum and palladium are installed as oxidation catalysts in catalytic converters to treat automobile exhaust emissions. Oxidation catalysts are also used in many air-pollution abatement processes to remove organic vapours, odours or carbon monoxide [1].

The stability of platinum and platinum-rhodium alloys has led to their use in high temperature thermocouples, which are used in electrical and electronic apparatus. These metals have many uses in chemical laboratories because of their resistance to chemicals; for example crucibles, electrodes, instrument components, and similar applications. The platinum metals are also used in the glass industry, the manufacture of jewellery, the decoration of china, glass and ceramics, and have a variety of dental and medical uses. The demand for the platinum group metals has thus resulted in much interest being centred on the efficient recovery, separation and analysis of these metals.

Polyurethanes are manufactured in multimillion kilogram quantities annually for a wide range of markets. This availability merits their exploitation for separation and concentration processes in chemistry. The

polyurethane system is analogous to a solvent extraction system although the use of a solid organic polymer has numerous advantages over an organic solvent. The foams are inexpensive, relatively inert, and comparatively small volumes of foam are required due to its great sorption capacity. The physical structure of the foam permits high flow rates of solution through its bulk so that sorption takes place relatively quickly.

1.1 THE SEPARATION OF THE PLATINUM METALS.

The six members of the platinum group metals are usually found associated with one another in the earth's crust. Thus separation of these metals is imperative before the determination of each metal, as mutual interferences often occur. The chemical properties of the platinum elements are so strikingly similar that their separations from one another are among the most difficult of analytical procedures.

The selective oxidation of ruthenium and osmium to their tetroxides and subsequent extraction by chloroform or carbon tetrachloride has been utilized for the separation of these metals from other platinum metals in solution [2,3]. Platinum, palladium, rhodium and iridium can be further separated by another technique such as ion exchange or solvent extraction.

Ion exchange methods have been developed for most of the platinum metals, based either on differences in the affinity of similar complexes for the resin or on larger differences caused by varying the solution constituents. The method is rapid and offers separation from a variety of other ions.

MacNevin and Crummett [4] investigated the use of both anion and cation exchange systems for the separation of palladium from platinum, rhodium and iridium. The chloride complexes of all four metals are quantitatively retained by anion exchange resins. When these anions are treated with ammonium hydroxide, only palladium

converts to the cation $Pd(NH_3)_4^{2+}$ as the substitution reactions

$$MCl_n^{n-} + mL \longrightarrow ML_m^{n+}$$

for the other noble metals are slow. Thus palladium can be separated from iridium, from platinum and from rhodium singly and from a mixture of these metals by ion exchange.

One complication which arises when using the anion exchange technique on solutions containing iridium is that $IrCl_6^{3-}$ is strongly retained by anion exchange resins. Iridium can not be quantitatively removed from these resins by either strong acidic or strong alkali solutions. Hot (74 ^{o}C) concentrated nitric acid has been shown to remove the iridium but the reduction of Ir(IV) to Ir(III) and subsequent hydrolysis reactions to form $[Ir(OH_2)_nCl_{6-n}]^{(3-n)-}$ species on the resin must be kept to a minimum [5].

Solvent extraction has been widely used for the separation of the platinum metals [6,7]. The solvent extraction methods for the separation of binary or multicomponent systems of these metals use the differences in their kinetic behaviour for the formation of extractable species, as well as the strength of electrostatic interaction of their chloro-complexes with liquid ion-exchangers or with oxygen containing solvents [8].

A large number of organic solvents have been used for the extraction and separation of the platinum metals. These include tributyl phosphate(TBP) [9,10], methyl isobutyl ketone(MIBK) [11] and chloroform [12,13] to name but a few.

Berg and Senn [14] attempted the separation of the platinum metals by counter-current extraction using dilute hydrochloric acid and TBP as the two phases. Platinum and palladium separation was achieved as was platinum and rhodium separation. However, only partial

separation of rhodium and iridium occurred. Berg and Lau [15] obtained good separation of these two metals when using acid thiocyanate and TBP as the aqueous and organic phases respectively.

A recent review of Al-Bazi and Chow [8] gives details of most ion-exchange and solvent extraction schemes investigated between 1950 and 1983. These authors conclude by remarking "... there still remain several areas of separation which need considerable investigation and many where the chemistry of the method requires clarification".

A mixture of Au, Pd, Pt, Ir and Rh was successfully separated by column extraction chromatography on silica treated with TBP [16]. This procedure involved a number of column extractions and was time consuming. A more efficient column proved to be that of silica treated with trioctylammonium salts [17].

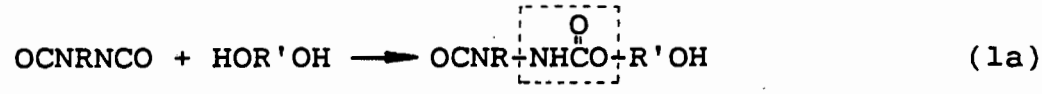
Other methods which have been used in the separation of the noble metals include partition chromatography on cellulose columns [18,19] and selective precipitation [20,21].

1.2 THE SORPTION OF METALS BY POLYURETHANE FOAMS.

1.2.1 *The Synthesis and Chemical Nature of Polyurethane Foams*.

Polyurethane foams are the most widely used cellular plastics in separation chemistry. Polyurethane is a cellular material which may be synthesised from a variety of polyester and polyether polyols (hydroxyl compounds) to produce soft, flexible or rigid foams [22]. The general principle in preparing these cellular materials is the dispersion of a gas within a liquid phase containing the monomer precursors to obtain a liquid foam which will then, on polymerisation, be solidified to a solid cellular plastic.

There are two important reactions in the preparation of urethane foams. The first is the reaction between diisocyanate and the hydroxyl compounds to form a urethane group. The basic urethane unit can react further with isocyanate to give a long, linear polymer.



(1a)

diisocyanate urethane

(1b)

urethane

where R = low molecular mass alkyl or aryl moiety
R'= alkyl polyester or polyether chain

The second reaction, between isocyanate and water is responsible for the foam formation by the liberation of carbon dioxide as an *in situ* blowing agent. The first step in this reaction is the formation of an unstable carbamic acid

(2)

carbamic acid

which decomposes to an amine and carbon dioxide

(3)

Alternatively, carbamic acid may react with another isocyanate molecule to produce carbamic acid anhydride which decomposes to substituted urea and carbon dioxide.

(4)

carbamic acid anhydride substituted urea

The amine from equation (3) reacts with isocyanate entities, resulting in chain extension with the insertion of urea bridges:

$$RNH_2 + RNCO \longrightarrow \underset{\text{substituted urea}}{RNHC(=O)NHR} \qquad (5)$$

In addition to the primary chain propagation steps, side reactions occur which lead to branching and cross-linking. Two of the most common reactions are those between isocyanate and urethane to form allophanate linkages,

$$RNHC(=O)OR' + RNCO \longrightarrow \underset{\text{Allophanate}}{R\text{-}NHC(=O)N(R)C(=O)O\text{-}R} \qquad (6)$$

and those between isocyanate and urea to produce biuret linkages.

$$RNHC(=O)NHR + RNCO \longrightarrow \underset{\text{Biuret}}{R\text{-}NHC(=O)N(R)CHN\text{-}R} \qquad (7)$$

Generally, the physical properties of the polyurethane foams depend on the method by which they are prepared. For example, the gas may be in continuous phase to give an open-cell material (Figure 1.1(a)) or it may be discontinuous, i.e. in the form of discrete, non-communicating cells (Figure 1.1(b)).

The chemical properties of polyurethane foams are also a function of the preparation process. For example, the solvent resistance of polyurethane increases at higher cross-link densities but is reduced with the use of a large excess of isocyanate. The mechanical properties of polyurethanes are highly dependant on the proportion of allophanate linkages which increase with time and temperature [23].

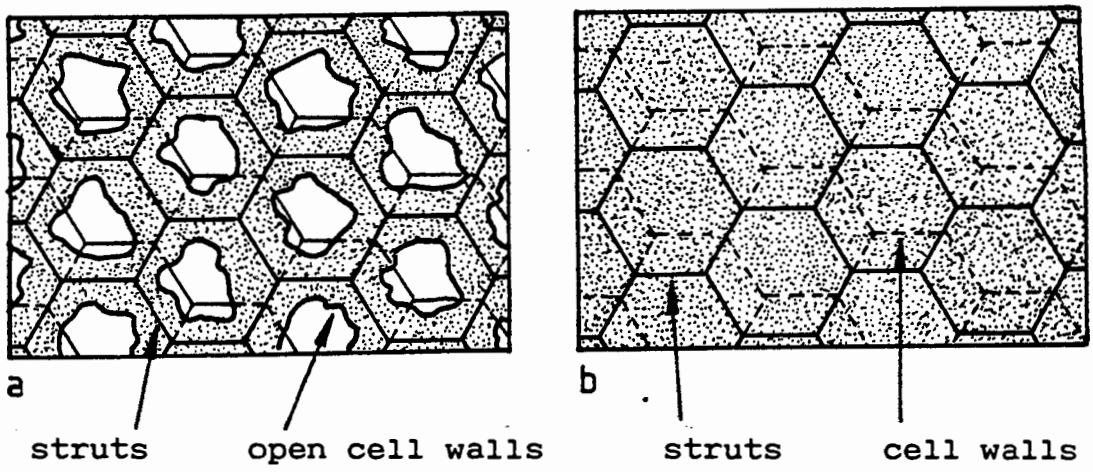


Figure 1.1 Cellular material
(a) Open-cell type polyurethane foam
(b) Gas filled non-communicating cell

Bowen [24] examined the chemical resistance of 27 batches of commercial polyurethane foams and found them to be relatively stable and inert. The foam batches tested degraded when heated between 180 °C and 220 °C, and slowly turned brown in ultraviolet light. They were dissolved by concentrated sulphuric acid, destroyed by concentrated nitric acid, and reduced alkali potassium permanganate. Bowen also noted that the foams are mostly unaltered, apart from reversible swelling, by water, hydrochloric acid up to 6M, sulphuric acid up to 4M, nitric acid up to 2M, glacial acetic acid, 2M ammonia, and 2M sodium hydroxide solutions, as well as by solvents such as light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, di-isopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate and the alcohols.

1.2.2 *General Review of the Use of Polyurethane Foams as an Extractant*.

The use of polyurethane foam in the sorption of a number of substances from aqueous solutions was first reported by Bowen [24] in 1970. Many other studies of the

extraction and separation of various inorganic and organic species from aqueous solutions have been reviewed by Braun [25-27] and Moody [28,29].

Polyurethane foams have been packed in columns used for gas chromatography [30,31], liquid chromatography [32-34] and ion-exchange chromatography [35,36]. Pulsed column redox techniques (treated foam is placed in a syringe and mechanically squeezed) [37] and column extraction techniques [38,39] have also been used for the extraction of metals onto polyurethane foam.

Most of these techniques make use of polyurethane foams impregnated with a reagent such as tri-n-octyl-amine [33] or tributylphosphate [40,41].

Gesser *et al.* [42] investigated the use of unloaded polyurethane foam for the extraction of gallium from acidic chloride solutions. The effect of hydrochloric acid on the extraction efficiency was found to be similar to that found in diethyl ether extractions. These authors concluded that polyether type polyurethane foams can be used as a convenient solid substitute for the liquid diethyl ether extraction system.

A number of other authors have subsequently reported the use of untreated polyurethane foams for the extraction of metals from aqueous solutions. These include the preconcentration of cobalt [43,44] and zinc, mercury and indium [45] from thiocyanate solutions; gold from thio-urea [46] and alkali cyanide media [47]; silver, thallium, barium and lead ions from picrate solutions [48] and tin from dilute acid [49].

A number of methods have been employed for determining the extracted component(s) on the foam. An indirect method involves determining the metal concentration in the solution before and after extraction [50]. Methods such as atomic absorption spectroscopy [43], radiochemical analysis [51] or spectrophotometry [52] rely on the recovery of the metal from the foam with a reagent such as methanol prior to analysis.

The direct determination of the extracted component(s) in polyurethane foams has been achieved by neutron activation analysis [53], and X-ray fluorescence [44, 54]. Open cell polyurethane foam loaded with various organic reagents can be used to detect the metal ions present by spectrophotometry, making use of the colour which is formed [55].

Polyurethane foams have a number of commercial uses. The foams act as extraction materials in cigarette filters [56], oil spillage clean-ups [57,58] and in the removal of pesticides from water [59,60] and from the air [61,62].

1.2.3 *Use of Polyurethane Foam for the Separation of the Noble Metals*.

A number of authors have investigated the use of polyurethane and other foam materials for the separation of the noble metals.

Polyurethane foams treated with TBP were developed for use in the separation of palladium, nickel and bismuth by reverse phase chromatography [63]. Both palladium and bismuth were sorbed by the foam, whereas nickel remained in the thiourea/perchloric acid medium. The metals on the foam could easily be separated by elution under different conditions.

Moore and Chow [64] investigated the extraction by polyurethane foam of the platinum metals from organic solvents. The extraction of the palladium(IV) and rhodium(III) hexachloro-complexes was not possible because they were virtually insoluble in most organic solvents. Hexachloro-iridate(IV) was found to be stable in and extractable from ethyl acetate and acetone, and hexachloro-platinate(IV) from ethyl acetate.

Treated silicone rubber foams have also been employed for the separation of platinum and palladium [65] and for the separation of rhodium and iridium [66]. In the latter case, under suitable conditions, all the rhodium

remains in the aqueous phase, while the iridium is retained on the foam. Iridium can be recovered quantitatively from the foam by elution with small quantities of ethanol. This method requires the continuous treatment of the samples in dilute acid with chlorine gas to avoid the reduction of iridium(IV) to iridium(III). This restricts the general usefulness of the method and precludes its use with polyurethane foam since the foam reacts rapidly with chlorine and decomposes [64].

In recent years, Al-Bazi and Chow [67-72] have studied the extraction and separation of the platinum metals as their thiocyanate complexes using polyurethane foams.

In an attempt to separate rhodium and iridium [67], these authors found heating necessary to increase the rate of formation of the rhodium-thiocyanate complex. Under optimum conditions, 87% rhodium and 8% iridium extracted onto the foam. Under conditions where no iridium was sorbed, only 56% rhodium could be detected on the foam. In a later publication, Al-Bazi and Chow [68] reported that "the presence of lithium chloride or hydrochloric acid accelerates the reaction of rhodium with thiocyanate to form the extractable species. Furthermore, while the effect of lithium chloride is to facilitate the formation of the rhodium thiocyanate complexes it inhibits that of the iridium complexes and therefore makes the separation more efficient and quantitative".

Polyurethane foam has been found to be highly efficient for the preconcentration of palladium from thiocyanate solutions containing only hydrochloric acid and from those containing potassium chloride at high pH's [69]. Palladium(II) was found to form a complex with thiocyanate (probably $Pd(SCN)_4^{2-}$) immediately after the addition of thiocyanate. On the other hand, the rate of formation of the platinum(IV)-thiocyanate complex (probably $Pt(SCN)_6^{2-}$) is slow and highly dependant on the thiocyanate concentration. This difference was used

to separate platinum and palladium [70]. In order to avoid the reduction of platinum(IV) to platinum(II) in the presence of excess thiocyanate, it was necessary to add hydrogen peroxide to the aqueous phase.

Al-Bazi and Chow [71] have achieved the separation of osmium and ruthenium using conditions which inhibit the formation of the osmium-thiocyanate complexe. The separation of rhodium and ruthenium as their thiocyanate complexes have also been investigated using polyurethane foams [72]. Under optimum conditions, rhodium up to a threefold mole ratio to ruthenium had almost no effect on the extraction of ruthenium onto the foam. A qualitative study on the recovery of ruthenium from the foam showed that acetone can be used for this with high efficiency.

The use of thiocyanate as a ligand to convert the noble metals into extractable complex anions has some limitations. Firstly, the method is not selective towards the platinum group metals because various transition metals are also extracted efficiently from thiocyanate media [43-45]. Secondly, a thiocyanate-based extraction from highly acidic solutions is compromised to some extent by the formation of interfering thiocyanic acid and 5-amino-1,2,4-dithiazole-3-thione [69].

1.2.4 *Possible Mechanisms of the Sorption of Metals onto the Foam*.

A number of mechanisms for metal sorption from aqueous solutions by polyether-type polyurethane foams have been proposed. The predominant mechanism appears to depend upon the conditions of sorption and the species sorbed.

Bowen [24] concurred that absorption rather than adsorption processes were responsible for extraction, based on the fact that the capacities of the foam (0,5-1,5 $mol.kg^{-1}$) were far greater than could be expected from adsorption according to surface area considerations (about 3×10^{-4} $mol \cdot kg^{-1}$). This was confirmed by

microscopical examination of cross-sections of foam fibrils after iodine had been sorbed. The iodine colour was uniform throughout the section and not confined to the foam's surface.

Gesser *et al.* [42,73] studied the gallium chloride system. The phenomenon of gallium(III) sorption was considered to be an ether-like solvent extraction process in which $HGaCl_4$ was apparently the species extracted. In a detailed study of iron(III), Gesser and coworkers [74] inferred from the results that polyurethane foam can be regarded as a viscous liquid solvent of moderate dielectric constant, analogous to diethyl ether.

Similarly, the mechanism has been described by Lo *et al.* on tin(II) and tin(IV) [49], and on antimony(III) and antimony(V) [75] studies as solid solvent extraction. Braun and Farag [43], in their study of cobalt and iron described the extraction process as analogous to an "etheric" solvent extraction.

Moore and Chow [64] extended the use of polyurethane foam to the extraction of metal ions from organic solvents. These authors commented that the results could not be explained solely on the basis of an ether-like solvent extraction mechanism.

The presence of nitrogen and oxygen atoms in polyurethane foam led Bowen [24] to believe that the foam could behave as a weak-base anion exchanger. In acid solutions these atoms could become protonated, thus requiring the sorption of accompanying anion metal complexes to maintain electrical neutrality. This mechanism may contribute significantly to the sorption of anionic metal complexes at low pH's but in the absence of appreciable amounts of acid it does not play a significant role.

The ligand addition or exchange mechanism has been suggested [76] because of the large number of Lewis acid sites such as nitrogen and oxygen donor ligands in the

foam. These may be expected to be involved in coordinate bonding to the metal. However, the large distribution ratios measured, particularly for some metals, implied the existence of very strong ligands in the polymer. This situation seems doubtful, considering the structures typical of polyurethanes.

Another possible mechanism by which anionic metal complexes may be sorbed, which does not necessarily require protonation of polyurethane sites but is closely related to the weak-base anion exchange concept, is the cation chelation mechanism [76]. According to this mechanism, many cations such as Na^+, K^+, Ag^+, NH_4^+, RNH_3^+, Pb^{2+}, Ba^{2+} and H_3O^+ are capable of being multiply complexed by a helical arrangement of inwardly directed polyether oxygen atoms (Figure 1.2). The counter cations sorb onto the foam in a manner analogous to the uptake of cations be crown ethers [77,78].

It is further considered that the extent of sorption depends not only on the chelation affinity of the cation (which depends on its size and charge) but also on the nature and hydrophobicity of the anionic metal complex.

The main difference between the cation chelation mechanism and other ion-exchange mechanisms is that electroneutrality demands that both the cation and anion are simultaneously extracted by the polyurethane.

The order of affinity of polyurethane foam for various cations was shown to be $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ = NH_4^+ < Ag^+ = Tl^+ < Ba^{2+} < Pb^{2+}$. This order almost replicated that shown by 18-crown-6 derivatives [77].

Studies of the mechanisms of cobalt [79] and palladium [80] extraction by polyurethane foams have shown that the cation chelation mechanism may well be the operative means of sorption in these systems. The cation chelation mechanism does not, however, account for all observed extractions of metal ions or their apparent ionic species.

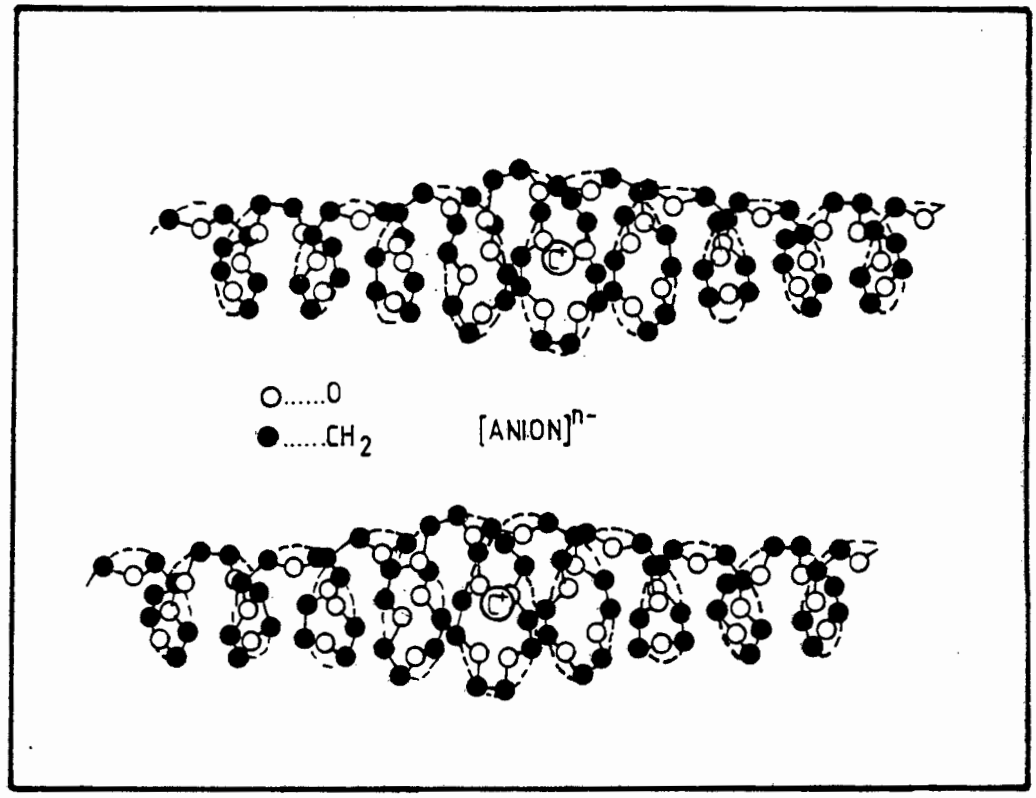


Figure 1.2 Metal ion sorption by polyurethane acccording to the cation chelation mechanism. The proposed helical structure (not to scale) of the long chain polyether section of a polyurethane foam is adapted from Hamon's work [76].

1.3 THE NOBLE METAL-STANNOUS CHLORIDE COMPLEXES.

1.3.1 *The Platinum-Stannous Chloride Complexes.*

The reaction of tin(II) chloride with the platinum group metals has been known for over a century [81,82]. The formation of intensely coloured compounds of the platinum metals with tin(II) forms the basis of familiar analytical methods [56]. These complexes are, in addition, of considerable interest because of their high catalytic activity towards hydrogenation and isomerisation reactions [83-85]. In spite of this, there is a lack of agreement on the composition and stability of the complexes formed in solution, due

chiefly to the difficulties encountered in the experimental study of these systems.

Wöhler [86] observed that platinum(IV) in hydrochloric acid, when treated with stannous chloride, gave a blood red colour which was extracted into ethanol. Wöhler and Spengel [87] considered the colour to be due to colloidal platinum, and concluded that the reaction was not suitable for the colourimetric determination of platinum.

This postulate was disproved by Ayres and Meyer [88] who found that the coloured material readily passes through semipermeable membranes such as collodion. Furthermore the reaction has been found to give rapid formation of stable yellow and red solutions suitable for colourimetric estimation [89-91].

Later authors attributed the red colour of the platinum-tin chloride complexes to platinum(II) [92] and to chloroplatinous acid [93,94]. Ayres and Meyer [88] investigated these findings. No colour developed when platinum(IV) chloride was evaporated with H_2SO_4 to expel HCl, and treated with tin(II) sulphate. Thus simple reduction to platinum(II) cannot account for the colouration. These authors also established that the colour in not due simply to chloroplatinous acid, but in some way involves tin.

The platinum-stannous chloride solutions were further studied to determine the reaction ratios of platinum:tin using both Pt(IV) and Pt(II) chlorides as starting materials [95,96]. A maximum of 5 moles of tin reacted with platinum(II) whereas a maximum of 6 moles of tin were consumed by platinum(IV). This difference is attributed to the reduction of Pt(IV) to Pt(II) by one mole of $SnCl_2$. It was suggested that one mole of tin(II) was oxidized to tin(IV) simultaneously with the reduction of platinum(II) to platinum(0), yielding a cationic product containing four moles of tin(II)

chloride associated with one mole of platinum, $[PtSn_4Cl_4]^{4+}$.

Lindsay *et al.* [97] obtained a complex anion, $[Pt_3Sn_8Cl_{20}]^{4-}$ by reacting stannous chloride with $PtCl_2$ or $[Cl_2Pt(SnCl_3)_2]^{2-}$ in acetone. They detected tin(IV) in the solutions and suggested that platinum is reduced to the zero valent state. In another study of the oxidation state of platinum in its compounds with tin(II) chloride by polarographic and potentiometric methods, a marked change in the potential for a tin:platinum ratio of 1 was observed [98]. Elizarova and Matvienko [98,99] attributed this to the reduction of platinum to the zero valent state.

Subsequent investigations of the reaction of platinum with tin(II) chloride by electrophoresis [100], ion-exchange [101] and by investigating the extractability of the platinum-tin complexes by various long chain high molecular weight amines into organic solvents [102], have suggested that these complexes are anionic.

Amongst the complexes which Young *et al.* [103] isolated from aqueous acid solutions containing platinum and stannous chloride were the proposed cis- and trans-isomers of $[PtCl_2(SnCl_3)_2]^{2-}$. They suggested that the trichlorostannato(II) ion is a donor ligand using its lone-pair electrons so that the usual common formal oxidation state and stereochemistry of the platinum metal can be preserved.

Young *et al.* [103] isolated two compounds, one red and the other yellow which they assigned as the trans- and cis-$[PtCl_2(SnCl_3)_2]^{2-}$ isomers. The yellow form was considered to be the cis-isomer due to its greater thermodynamic stability and solubility in polar solvents compared with the red complex. Both forms were found to exist in solutions at Sn:Pt mole ratios of 2 but at higher concentrations of tin, precipitation with tetramethylammonium chloride gave red salts which appeared to contain higher ratios, up to 5. This led to

the proposal that tin was coordinated to platinum to give a quinquecoordinate ion $[Pt(SnCl_3)_5]^{3-}$.

Cramer *et al.* [104] has also found the anion $[Pt(SnCl_3)_5]^{3-}$ to exist in solution. The determination of its configuration by X-ray diffraction has shown it to be trigonal bipyramidal, consisting of a central platinum atom surrounded by five $SnCl_3^-$ ligands attached through Pt-Sn bonds [105].

Young and coworkers [103] proposed that the following equilibria exist simultaneously in solutions containing platinum(II) chloride and tin(II) chloride.

$$SnCl_2 + Cl^- \longrightarrow SnCl_3^-$$

$$[PtCl_4]^{2-} + SnCl_3^- \longrightarrow [PtCl_3(SnCl_3)]^{2-} + Cl^-$$

$$[PtCl_3(SnCl_3)]^{2-} + SnCl_3^- \rightarrow trans\text{-}[PtCl_2(SnCl_3)_2]^{2-} + Cl^-$$

$$trans\text{-}[PtCl_2(SnCl_3)_2]^{2-} \longrightarrow cis\text{-}[PtCl_2(SnCl_3)_2]^{2-}$$

$$trans\text{-}[PtCl_2(SnCl_3)_2]^{2-} + 3SnCl_3^- \rightarrow [Pt(SnCl_3)_5]^{3-} + 2Cl^-$$

$$cis\text{-}[PtCl_2(SnCl_3)_2]^{2-} + 3SnCl_3^- \longrightarrow [Pt(SnCl_3)_5]^{3-} + 2Cl^-$$

However the existence of $trans\text{-}[PtCl_2(SnCl_3)_2]^{2-}$ has been questioned following the results of a Mössbauer study [106]. This red compound yields the identical Mössbauer and infrared parameters as the red petakis anion $[Pt(SnCl_3)_5]^{3-}$. Furthermore, Nelson *et al.* [107] performed ^{119}Sn and ^{195}Pt NMR studies on these compounds and found that red solutions of the proposed red trans-isomer isolated from 3M acid appear to be a mixture of red $[Pt(SnCl_3)_5]^{3-}$ and yellow cis- $[PtCl_2(SnCl_3)_2]^{2-}$.

It thus appears that although the platinum-tin system has been widely studied, the exact nature of the species formed in solution is not fully understood. In conclusion it may be said that the colour of such solutions is due to the formation of anionic platinum-

tin complexes which appear to exist as one of $[PtCl_{4-n}(SnCl_3)_n]^{2-}$ (n = 1-4) and $[Pt(SnCl_3)_5]^{3-}$ or a mixture of these.

1.3.2 *The Rhodium-Stannous Chloride Complexes.*

In 1918, Ivanov [108] observed that rhodium(III) salts in hydrochloric acid solution slowly developed a red colour when treated with tin(II) chloride. The reaction was initially used for the detection of rhodium [109]. A number of procedures have subsequently been proposed for the quantitative spectrophotometric determination of this metal [90, 110-113]. There does, however, appear to be a dispute on the optimum conditions for the formation of the coloured species.

Ayres *et al.* [114] found rhodium(III) and tin(II) chloride to react slowly at room temperature, taking 12 hours for the complete colour to develop, but to form rapidly at boiling point. No further colour change was found to occur after 5 minutes of boiling. This contradicts the finding of McBryde and Yoe [115] and Furlani *et al.* [116]. The latter authors were also of the opinion that the system they examined contained at least three rhodium complexes of stannous chloride.

Furlani and coworkers [116] performed spectrophotometric studies on the rhodium(III)-tin(II) chloride system and attributed the difference in findings to changes in the concentration of the reactants which affect complex formation.

Shukla [117] noted that the red compound formed from rhodium(III) and tin(II) chloride in hydrochloric acid could be converted into a yellow form by adding HCl, by extraction with butanol or by removing the Sn(II) by electromigration. The formation of the red or yellow species is reported to be principally dependent on the $SnCl_3^-$:Cl^- ratio [116]. The yellow complex is formed in solutions with a low concentration of the trichlorostannite ion, while the red complex is formed

in the presence of a large excess of the stannous chloride [103,110,116,118]. The yellow complex can be restored by dilution with hydrochloric acid, since the change is controlled by the $SnCl_3^-$:Cl^- ratio rather than the Rh(III):Sn(II) ratio.

Reactions of rhodium(III) with tin(II) bromide [119,120] and with a mixture of tin(II) chloride and tin(II) iodide [90] have also been described. The bromide medium appears to be useful for spectrophotometric determinations since its sensitivity is greater than that of chloride.

Davies *et al.* [101] were the first authors to suggest the structure of an ion existing in the rhodium(III)-tin(II) chloride system, namely $[Rh_2Cl_2(SnCl_3)_4]^{4-}$. Young and coworkers [103] regarded the trichlorostannato(II) ion as a donor anionic ligand of strength comparable to a Cl^- ion. Adams and Chandler [121] confirmed the existence of this anion using far infrared.

Furlani [116] reported the precipitation of the $[Rh(SnCl_3)_4]^{3-}$ anion with large cations from tin(II) chloride rich solutions. This anion has subsequently been identified by Young [122] who also reported the existence of the 6-coordinate rhodium complexes of $[RhCl_2(SnCl_3)_2$ (norbornadiene)$_2]$ and $[RhCl_2(SnCl_3)(PhMe_2As)_3]$.

Kimura *et al.* [123] also reported finding a 6-coordinate $[RhCl_3(SnCl_3)_3]^{3-}$ anion which they consider to be facial. In a further study, Kimura [124] isolated three other 6-coordinate rhodium(III) complex anions as their tetramethylammonium salts, *viz.* cis- and trans-$[Rh(SnCl_3)_2Cl_4]^{3-}$ and $[Rh(SnCl_3)Cl_5]^{3-}$. The 5-coordinate rhodium(I) complex $[Rh(SnCl_3)_5]^{4-}$ has also been described [125].

Results obtained from elemental analysis [126] and ^{119}Sn FT-NMR studies [127] confirm the existence of

rhodium(III) complexes in the form $[Rh(SnCl_3)_nCl_{6-n}]^{3-}$ (n = 1 to 5) and the rhodium(I) complex $[Rh(SnCl_3)_5]^{4-}$.

It is thus clear that the rhodium trichloride-stannous chloride-HCl-H_2O system is complex and there is still considerable uncertainty as to the exact experimental conditions required for each anionic species.

1.3.3 *The Ruthenium-Stannous Chloride Complexes.*

Ruthenium(III) chloride and tin(II) chloride in dilute hydrochloric acid, unlike platinum and rhodium, require heating on a water bath to give orange-red solutions [103].

Three ruthenium-tin(II) complexes with absorption maxima at 560 nm, 440 nm and 365 nm have been isolated from dilute acid [128]. The complex having its absorption maximum at 440 nm is reported to be the most stable [129]

Lederer and Shukla [130] were the first to report their observations on the ruthenium-tin(II) complexes formed in solution. Partition chromatography of ruthenium(II), $Ru(III)Cl_6^{3-}$ and the ruthenium-tin(II) compounds in butanol-3M hydrochloric acid showed clearly that a ruthenium-tin(II) compound is formed which differs in behaviour from both ruthenium(II) and ruthenium(III). Their results suggested that this complex would have a ruthenium(III) as the central atom.

Initially, Young *et al.* [103] formulated the anionic species as $[RuCl_2(SnCl_3)_2]^{2-}$ but on the basis of elemental analysis, later workers [131,132] preferred the octahedral formulation $[Ru(SnCl_3)_5Cl]^{4-}$. Recently, Farrugia and coworkers [133] characterized the octahedral anions $[M(SnCl_3)_5Cl]^{4-}$ (M = Ru, As) by ^{119}Sn Fourier Transform NMR and by X-ray crystallography.

Moriyama *et al.* [134] identified the complex $[Ru(SnCl_3)_6]^{4-}$ in 3M hydrochloric acid by means of ^{119}Sn NMR spectroscopy. These studies revealed the

stereochemical rigidity of the ruthenium(III)-tin(II) complex. This is in sharp contrast with the functional behaviour of the isoelectronic rhodium(III)-tin(II) complexes.

A number of complexes formed by the reactions of nitrosylruthenium(III) in hydrochloric acid with stannous chloride have been investigated [135]. On the basis of chemical and thermal analyses, magnetic properties, conductivities and infrared spectra, it is believed that these complexes contain terminal or bridging nitrosyl groups and/or a coordinating $SnCl_3^-$ group.

Ruthenium complexes with bivalent tin extract well with chloroform from hydrochloric acid in the presence of an organic base such as diphenylguanidine or diantipyrylmethane [136].

It appears that a number of ruthenium(III)-tin(II) species exist depending on the conditions in solution [130]. It is likely that more than one species exists in equilibrium in solution at any one time.

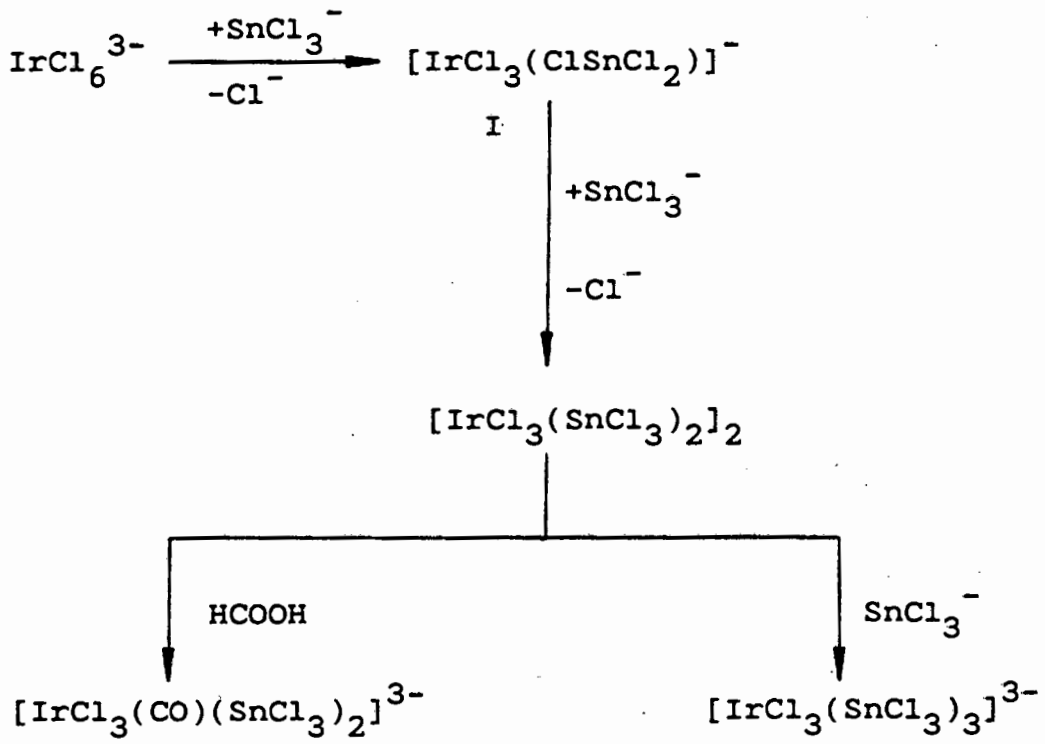
1.3.4 *The Iridium-Stannous Chloride Complexes.*

As with ruthenium, iridium(IV) and tin(II) chloride in hydrochloric acid require heating to form amber-coloured solutions [103]. The complexes of iridium(III) and iridium(IV) vary in nature according to the Ir:Sn(II) ratio, length of heating and age of the solution [137]. Simple ion-exchange experiments have shown that the coloured complexes formed in aqueous acid solution are anionic [101].

Furlani *et al.* [138] found spectral changes when the $SnCl_3^-$:Cl^- ratio is varied in the iridium(III)-tin(II) chloride system at room temperature. These authors had found similar spectral changes for the rhodium(III)-tin(II) system [116]. However, only one spectrum results on heating these solutions. Whereas Young *et al.* [103] isolated the binuclear species

$[Ir_2Cl_6(SnCl_3)_4]^{4-}$ from heated solutions, Furlani and coworkers [138] reported the isolation of $[Ir_2Cl_2(SnCl_3)_4]^{3-}$ as their double salts with $SnCl_2$.

Elizarova *et al.* [139] studied the sequence of formation of the tetraethylammonium salts of $[IrCl_3(CO)(SnCl_3)_2]^{2-}$ and $[IrCl_3(SnCl_3)_3]^{3-}$ prepared in formic acid. In formic acid at room temperature, as in aqueous solution [138], two complexes are formed (λ_{max} = 345 nm and 420 nm). Heating the solution resulted in a band at 285 nm. The authors assumed that a complex of Ir:Sn of 1:1 (420 nm) is formed first, followed by a 1:2 complex, which may be carbonyl (285 nm) or non-carbonyl (345 nm) depending on the conditions. They suggested an overall scheme for complex formation:



The authors believe that the formation of the $SnCl_3^-$ ligand is preceded by the binding of tin to iridium through a chlorine atom (Complex I).

A number of authors [120,140,141] have studied the reactions of iridium with tin(II) bromide and tin(II) iodide. Unfortunately, no detailed investigations as to the structures of these anions have been reported.

In conclusion, it appears that two or more species of iridium-tin(II) chloride exist at room temperature whereas only one seems to exist after heating the dilute acidic solutions. The nature of this complex depends on the conditions of the iridium-tin(II) chloride-hydrochloric acid system. Further work on the systems will be required for a more detailed understanding of not only the iridium-tin(II) complexes, but also those of the other platinum group metals.

1.4 RESEARCH OBJECTIVES.

Stannous chloride in hydrochloric acid media is known to react selectively with the platinum metals to form trichlorostannato anionic complexes. A preliminary study by Nel [142] has shown that polyurethane foams extract these platinum-tin(II) complexes from dilute acid solutions. A further study [143] indicated that platinum is quantitatively sorbed by the foam and that these loaded foams can be degraded using concentrated nitric acid and analysed by atomic absorption spectroscopy. In the light of the above, it was decided to study the preconcentration, separation and recovery of four platinum group metals, namely platinum, rhodium, ruthenium and iridium, using polyurethane foams.

The objectives can be summarized as follows:

(1) To investigate the selective extraction from dilute acid solutions of one or more of the platinum metals by polyurethane foams as their chloro-(trichlorostannato)-metal complex anions.

(2) To evaluate a means of recovering the metal(s) from the loaded foams by:

   (a) decomposing the foams

   (b) removing the metal(s) by foam stripping with a suitable solvent.

(3) To devise a suitable analytical method for the determination of the platinum group metals recovered from the foams and in the aqueous phases.

CHAPTER 2

CHAPTER 2

2. METHODS OF ANALYSIS.

In this study a method of analysis was required to determine quantities of platinum, rhodium, ruthenium and iridium in the presence of one another. The conventional gravimetric and colourimetric methods of determining the noble metals are often time-consuming, tedious and subject to considerable interferences [57]. With the advent and development of the atomic absorption methods, this difficult task has been considerably simplified. A comparison of flame emission and absorption data [144, 145] shows that noble metals are more sensitive to flame absorption methods than to emission. Atomic absorption spectroscopy (AAS) is a popular technique used in the analysis of over 60 elements [146, 147]. The platinum group metals have been determined by AAS in a large variety of matrices [148, 149]. This technique has been considered suitable for our requirements, after a careful examination of its applicability.

The atomic absorption technique relies on the absorption of energy by valence electrons of ground state atoms. A monochromatic light source supplies the characteristic radiation which is absorbed by the atoms. The amount of light absorbed is a function of the number of absorbing atoms. The only interferences encountered are caused by those chemical and physical processes which inhibit the formation of ground state atoms in the flame. This can usually be minimized or eliminated by careful choice of flame type or the use of a releasing agent [147].

The absorbance A is given by the logarithmic ratio of the intensity of the incident light signal I_o to that of the transmitted light I_t.

$$A = \log (I_o/I_t) = kcl$$

where k = absorption coefficient at a particular wavelength
c = concentration of absorbing atoms
l = length of the absorption path.

For small absorbance values, the absorbance is proportional to concentration for any given pathlength at any given wavelength. Thus, because concentration is a linear function of absorbance, it is only necessary to compare the absorbance of the sample with that of known standards.

2.1 THE ATOMIC ABSORPTION OF PLATINUM.

Atomic absorption method have been applied to determine platinum using a number of flames, for example butane-propane-air [150], air-propane [151], air-acetylene [152] and nitrous oxide-acetylene [153]. Strasheim and Wessels [150] and Ginzburg *et al.* [151] found serious interelement interferences in the determination of platinum, not only from other noble metals, but also from a number of other metal salts using the cooler flames. These authors also found the platinum sensitivity to be poor. It was suggested that a flame with a higher temperature such as air-acetylene might reduce these effects.

Pitts *et al.* compared the atomic absorption of platinum using an air-acetylene flame [152] with that of a nitrous oxide-acetylene flame [153]. The authors found that although the nitrous oxide-acetylene flame reduces interelement interferences, it also reduces the sensitivity of platinum, presumable owing to the increased ionization of the analyte at higher temperatures. The interferences found using the air-acetylene flame can be eliminated by using a suitable releasing agent.

Although in the earlier works on interference studies, Lockyer and Hames [154] and Menzies [155] did not find

any interelement interferences in the atomic absorption analysis of platinum, rhodium, palladium, silver and gold; depressive interferences were first noted by Strasheim and Wessels [148] in their determination of platinum and rhodium in the presence of other noble metals. These authors added a wide variety of base elements to the analyte solutions in an effort to eliminate the problem of mutual interferences (interferences caused by other noble metals). The addition of 20 000 ppm copper added as the sulphate, overcame the reduction in the platinum absorption readings. Slavin [156] also recommends the addition of 0,2% w/v copper sulphate for the determination of platinum in the presence of palladium and gold. Although effective, this high salt concentration leads to some problems such as burner clogging.

Schnepfe and Grimaldi [157] used a mixture of 0,5% w/v copper and 0,5% w/v cadmium, added as their sulphates, to remove mutual and base metal interferences in the determination of platinum and palladium. These authors also noted an increase in sensitivity.

Janssen and Umland [158] found that interelement interferences in the determination of platinum metals could be prevented by the addition of a mixture of 1% w/v sodium and 1% w/v copper as their sulphates. Moreover, this addition increases the sensitivity of platinum, rhodium and iridium.

One percent lanthanum (added as its chloride) was shown by Van Loon [159] to suppress the interference effects in the determination of platinum. Sen Gupta [160] investigated 0,5% w/v $CuSO_4$ mixed with 0,5% w/v $CdSO_4$ as well as lanthanum and strontium chlorides. The author found platinum to be equally sensitive with both the lanthanum and strontium chlorides.

Macquet *et al.* tested the use of a mixture of lanthanum(2%) and potassium phosphate(3%) to prevent

interferences when analysing platinum in platinum complexes [161, 162].

Pannetier and Taffoli [163] added 0,5% w/v lithium sulphate to both enhance the sensitivity of platinum, rhodium and iridium and to eliminate interelement interferences in the determination of these elements and palladium. Adriaenssens and Verbeck [164] found that in 2% potassium cyanide solution the majority of interelement interferences observed during the analysis of noble metals do not occur.

Mallett *et al.* [165] investigated a number of releasing agents including lanthanum chloride, copper sulphate, a mixture of copper and cadmium sulphates, uranium in aqua regia and vanadyl chloride. In general, the additives were found to be effective for one of more of the noble metals in the air-acetylene flame. Only lanthanum chloride and uranium were found to be effective for all four noble metals being studied. In the presence of relatively large amounts of base metals, uranium could not remove the significant interferences which occurred. Vanadyl chloride prepared in perchloric acid was found to remove these interelement interferences.

Vasilyera *et al.* [166] investigated the use of lanthanum and neodymium chlorides, sulphates and nitrates as releasing agents in a study of the noble metals, as well as a number of the additives used by Mallett *et al.* [165]. Of the compounds studied, lanthanum and neodymium nitrates were the only releasing agents found to successfully lower the detection limits for Pt, Rh, Ir and Ru and inhibit the effect of Co, Cu, Ni, Fe, Bi, Zn and Na on their determination. The other releasing agents studied produced effects which varied for different platinum metals. For example, where $LaCl_3$ and $NdCl_3$ were more suitable additives for platinum and rhodium; cupric, lanthanum and neodymium sulphates were found to be better for ruthenium and iridium.

We chose to use the cooler air-acetylene flame in the determination of platinum and relied upon a releasing agent to remove the interelement interferences. The platinum resonance line at 265,9 nm was chosen for its sensitivity. Strongly oxidizing air-acetylene mixtures resulting in lean, blue flames were found to provide maximum sensitivity for platinum.

To overcome the depressive interferences from various metals, we chose lanthanum nitrate as an interference suppressant. The presence of $La(NO_3)_3$ also serves to enhance the platinum absorption and was thus also used in experiments where no mutual interferences were present (Figure 2.1).

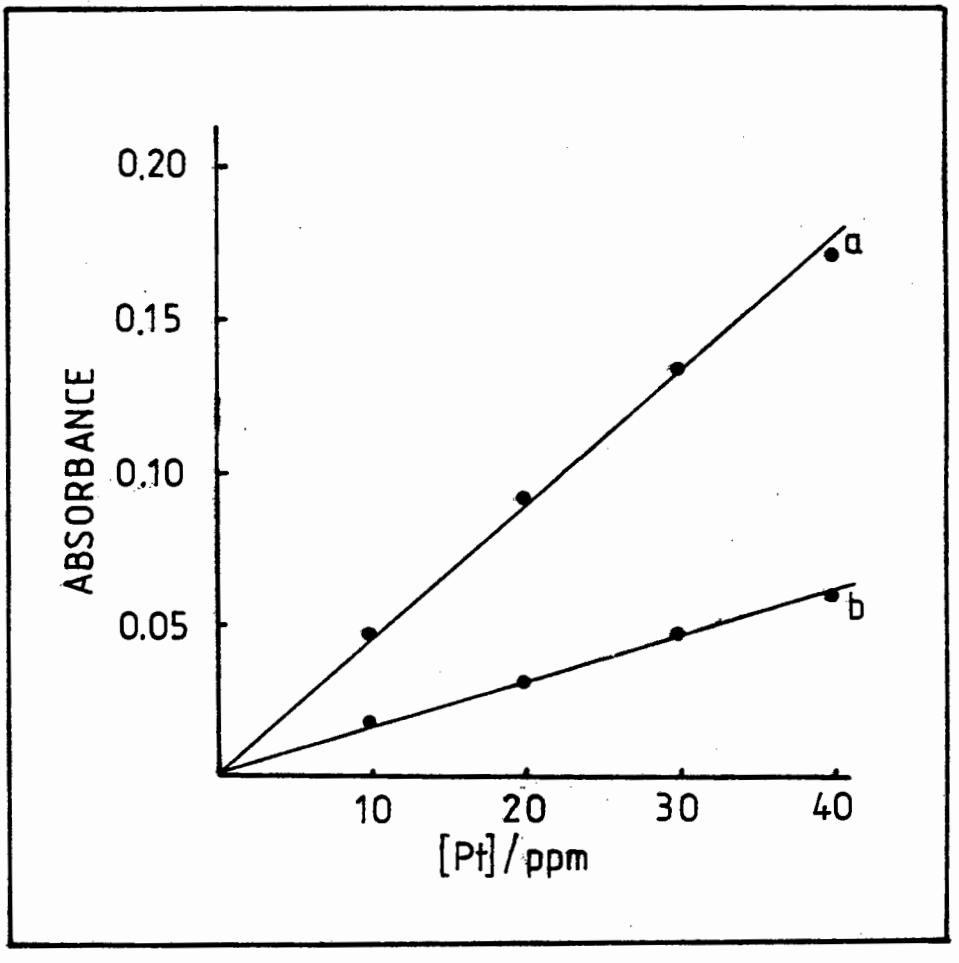


Figure 2.1 Platinum calibration curve in (a) the presense of 0,2% w/v $La(NO_3)_3$ and (b) the absence of $La(NO_3)_3$, [HCl] = 2 M.

Yates [167] showed that 0,2% w/v $La(NO_3)_3$ is suitable to suppress the interference of tin on platinum solutions of 1,0 to 3,0M HCl with tin:platinum mole ratios of up to 10. We carried out investigations on the use of 0,2% w/v $La(NO_3)_3$ as a releasing agent for platinum in the presence of higher ratios of tin:platinum, and in the presence of other noble metals. Results showing the effect on the absorbance value due to variations in the platinum:tin mole ratios and the presence of other noble metals are shown in Tables 2.1 and 2.2.

Pt:Sn ratio	Absorbance
1:0	0,076
1:10	0,075
1:20	0,077
1:30	0,077
1:40	0,076
1:40	0,076
1:50	0,076

Table 2.1 The effect of stannous chloride on the absorbance of platinum solutions in 2M HCl with 0,2% w/v $La(NO_3)_3$; [Pt] = 20 ppm.

Concentrations of element added/ppm				Absorbance
Pt	Rh	Ru	Ir	
10	-	-	-	0,051
10	10	-	-	0,051
10	-	10	-	0,051
10	-	-	10	0,052
10	10	10	10	0,052
50	-	-	-	0,245
50	50	-	-	0,246
50	-	50	-	0,245
50	-	-	50	0,245
50	50	50	50	0,244

Table 2.2 Absorbance of platinum in the presence of interfering noble metals in 2M HCl with 0,2% w/v $La(NO_3)_3$.

Results from Tables 2.1 and 2.2 show that 0,2% w/v lanthanum nitrate is suitable to suppress mutual interferences in platinum solutions of 2M hydrochloric acid with tin:platinum mole ratios up to 50.

An experiment was performed to establish whether polyurethane foam, decomposed in nitric acid, would affect the atomic absorption of platinum.

Results in Table 2.3 show that there is a marked decrease in platinum sensitivity as the mass of foam is increased. To overcome this effect, the standards and samples were matrix matched as closely as possible in such a way that both sets of solutions contained the same amount of polyurethane foam.

[Pt]/ppm	mass foam/mg	absorbance
60	0,0	0,201
	0,1	0,199
	0,2	0,172
	0,3	0,160
	0,6	0,143
80	0,0	0,265
	0,1	0,240
	0,2	0,224
	0,3	0,206
	0,6	0,178

Table 2.3 The effect of nitric acid dissolved foam on the absorbance of platinum solutions in 2M HCl with 0,2% w/v $La(NO_3)_3$.

Organic solvents have been found to increase the sensitivity of platinum 2 to 4 times more than the aqueous solutions [168,169]. Mulford [170] suggests that the organic solvent forms more small sized droplets during aspiration, and these are more likely to pass through the burner mixing chamber without condensing.

It therefore follows that if the metal standards and samples to be analysed are in different solvent systems, a significant solvent interference could be expected.

An experiment was performed to investigate the effect of 10% v/v hydrochloric acid in ethanol on the calibration curve. Platinum standards in 2M hydrochloric acid were analysed followed by those in ethanol with 10% HCl. Since the organic solvents act as fuel when aspirated into the burner, the acetylene fuel flow had to be lowered and strictly monitored in order to compensate for the organic solvent present in the solution and to maintain reproducible flame conditions. Results accompanying the platinum absorbance values are shown in Figure 2.2.

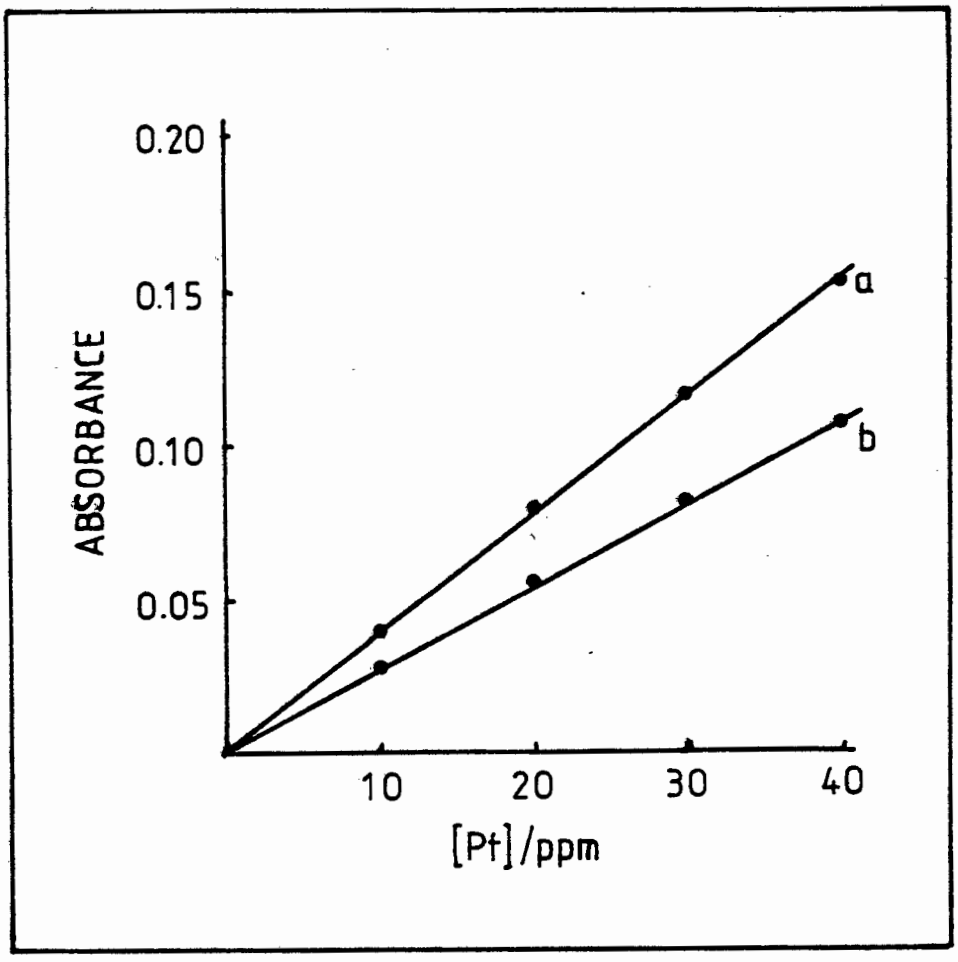


Figure 2.2 Platinum calibration curve with 0,2% w/v $La(NO_3)_3$ in (a) 2M HCl and (b) 10% v/v HCl in ethanol.

Contrary to other findings discussed previously [168-170], we observed a decrease in sensitivity when

platinum was analysed in a solution containing ethanol, as shown in Figure 2.2. There are a number of possible explanations for this effect.

Firstly, none of the authors who determined the platinum group metals in organic solvents used the mixture of 10% v/v hydrochloric acid in ethanol. Pitts *et al.* [168] who did study ethanol, used mixtures of up to 80% v/v ethanol with 0,1 M HCl as opposed to concentrated HCl as the aqueous component.

Secondly, there is a possibility of platinum-carbide compounds forming in organic solvents which may be more refractive than the platinum chloride compounds formed in 2M HCl. The presence of lanthanum nitrate may not be sufficient to remove these refractory compounds. If this were a factor, one would expect the sensitivity of platinum to decrease as the carbon chain length of the alcohol increases. Although the sensitivity of platinum increased in the presence of methanol, ethanol and propanol from that in aqueous solutions, Pitts *et al.* [168] observed a decrease in the absorbance of platinum for the longer chain alcohols. We also observed that as the mass of foam (i.e. carbon content) increases, so the platinum absorbance decreases (Table 2.3).

Thirdly, since the ethanol acts as a fuel when aspirated into the burner, the flame may become cooler and possibly more reducing in nature. The fact that the acetylene flow had to be adjusted for maximum sensitivity indicates such to be the case. However, there still may have been a decrease in temperature which would result in a decrease in platinum absorption.

Throughout this work we attempted to match standards and samples as closely as possible in view of the results obtained in the above experiments. The standards used contained K_2PtCl_4 and 0,2% w/v $La(NO_3)_3$ in the appropriate medium.

2.2 THE ATOMIC ABSORPTION OF RHODIUM.

The depressive interferences on the noble metals were first noted by Strasheim and Wessels [150] in their determination of platinum and rhodium in the presence of other noble metals and base metals. The authors were able to remove the mutual interferences with platinum by the addition of copper sulphate. In the case of rhodium, although the enhancement of absorbance was achieved by the addition of a number of base metals, it was not possible to eliminate the interference effects of the noble metals. Thus rhodium had to be detected by the standard addition technique. The interferences are believed to be due to the formation of complex compounds in solution, which are less amenable to thermal decomposition [171].

Scarborough [172] studied the feasibility of determining Rh, Ru, Mo and Pd in uranium alloys. The mutual interferences of the elements present were prevented by maintaining the concentration of uranium from 1 to 15 mg per ml. Stewart [173] noted that a mixture of uranium and arsenic at a ratio of 9:1 completely removed interferences. Ginzburg *et al.* [174] recommended the addition of 1% w/v magnesium for analysing rhodium.

The mutual interferences studied by Sen Gupta [160] were mostly removed by a mixture of 0,5% w/v copper and cadmium (added as their sulphates) or by 1% w/v lanthanum or 1% w/v strontium (added as their chlorides). Lanthanum chloride was found to be the most affective for rhodium. However, in order to avoid serious interelement interferences in the determination of rhodium in osmiridium, sperrylite and native platinum, the sample solutions had to be diluted to appropriate levels to reduce the salt concentration.

Mallett *et al.* [165] obtained a poor recovery for rhodium (55%) when copper plus cadmium (added as their sulphates) was tested, and although a full recovery was obtained by the use of copper sulphate, the sensitivity

of rhodium was significantly lowered. Lanthanum chloride and uranium were the most effective releasing agents.

The latter was preferred because of its slight superiority in removing the mutual interference effects of all the noble metals and because it offered a greater improvement in sensitivity. With uranium as a releasing agent, it was observed that rhodium was particularly prone to serious interferences in the presence of relatively large amounts of some base metals. Vanadyl chloride in perchloric acid medium removed mutual interference effects and considerably improved the recoveries of the noble metals in the presence of base metals. However, unknown amounts of hydrochloric and nitric acids were undesirable when the vanadium-perchloric acid method was being used, as they interfered with the determination of the noble metals.

Releasing agents such as 1% w/v Na plus 1% w/v Cu (as sulphates) [158], 0,5% w/v $LiSO_4$ [163], lanthanum and neodymium chlorides, sulphates and nitrates [166] have also been investigated as releasing agents for rhodium and other noble metals. These have been discussed in some detail in section 2.1.

Many interferences occurring in cooler flames can be reduced or eliminated by the use of hotter flames. Atwell and Herbert [175] observed interelement interferences in air-acetylene flames during the determination of rhodium in the presence of Cu, Cr, Pd, Pt, Ru, Ir, Ti and Zn. Although interferences from most elements disappeared in a nitrous oxide-acetylene flame, ruthenium and iridium still interfered. The reduction of interferences in nitrous oxide-acetylene flames has also been noticed by Mallett *et al.* [165] and Pitts *et al.* [153]. However, the sensitivity of rhodium was reduced by the use of this flame, presumably due to an increased ionization of the analyte at higher temperatures.

Kallmann and Hobart [176] noted that a nitrous oxide-acetylene mixture consistently gives low rhodium absorbance values, even in the presence of ionization depressing alkali salts. They also noted that the absorbance of rhodium is substantially increased when the air-acetylene flame is as lean and oxidizing as possible. This is in keeping with the observations of Heneage [177].

We chose the cooler air-acetylene flame in the determination of rhodium and relied upon a releasing agent to remove the interelement interferences. The rhodium 343,5 nm resonance line was used for all measurements since it is the most sensitive and has the lowest background noise. Strongly oxidizing air-acetylene mixtures resulting in lean, blue flames were found to provide maximum sensitivity for rhodium.

We chose lanthanum nitrate as an interference suppressant. The presence of $La(NO_3)_3$ also serves to enhance the rhodium absorbance readings and was thus used in experiments where no mutual interferences were present (Figure 2.3).

Wyrley-Birch [178] showed that 0,2% w/v lanthanum nitrate is suitable to suppress the interference of tin on rhodium in acidic solutions with tin:rhodium mole ratios of up to 20. We carried out investigations on the use of 0,2% w/v $La(NO_3)_3$ as a releasing agent for rhodium in the presence of higher ratios of tin:rhodium and in the presence of other noble metals. Results showing the effect on the absorbance signal due to variations in the rhodium:tin mole ratios and the presence of other noble metals are shown in Tables 2.4 and 2.5.

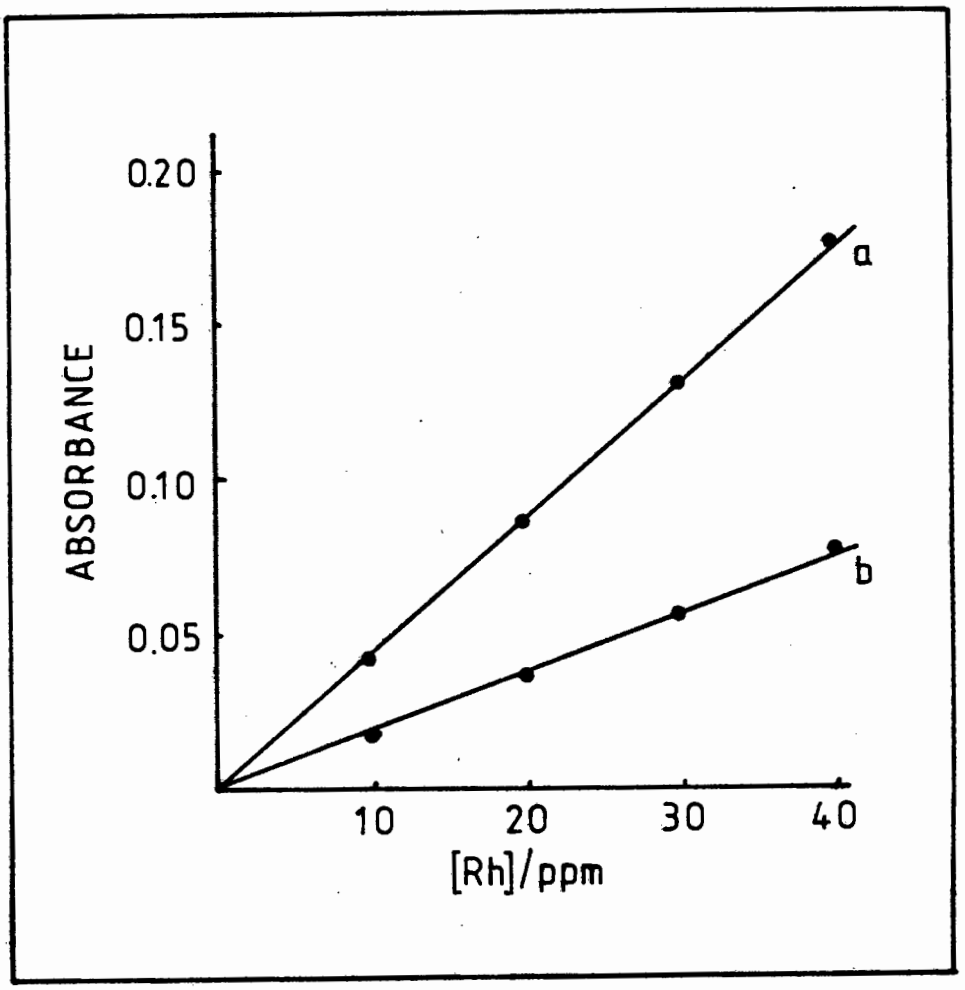


Figure 2.3 Rhodium calibration curve in (a) the presence of 0,2% w/v $La(NO_3)_3$ and (b) the absence of $La(NO_3)_3$, [HCl] = 2 M.

Rh:Sn mole ratio	Absorbance
1:0	0,146
1:10	0,147
1:20	0,147
1:30	0,147
1:40	0,146
1:50	0,147

Table 2.4 The effect of stannous chloride on the absorbance of rhodium solutions in 2M HCl with 0,2% w/v $La(NO_3)_3$ and [Rh] = 20 ppm.

Concentration of element added/ppm				Absorbance
Rh	Pt	Ir	Ru	
10	-	-	-	0,076
10	10	-	-	0,077
10	-	10	-	0,076
10	-	-	10	0,076
10	10	10	10	0,076
50	-	-	-	0,360
50	50	-	-	0,359
50	-	50	-	0,360
50	-	-	50	0,361
50	50	50	50	0,359

Table 2.5 Absorbance of rhodium in the presence of interfering noble metals in 2 M HCl with 0,2% w/v $La(NO_3)_3$.

Results from Tables 2.4 and 2.5 show that 0,2% w/v lanthanum nitrate is suitable to suppress mutual interferences in rhodium solutions of 2M hydrochloric acid with tin:rhodium mole ratios up to 50.

An experiment was performed to establish whether the addition of nitric acid dissolved foam to the solutions would affect the atomic absorption values of rhodium. Results showing this effect are shown in Table 2.6.

[Rh]/ppm	mass foam(g)	Absorbance
20	0,0	0,086
	0,2	0,077
	0,4	0,073
	0,6	0,067
40	0.0	0,170
	0,2	0,140
	0,4	0,127
	0,6	0,117

Table 2.6 The effects of nitric acid dissolved foam on the absorbance of rhodium solutions in 2M HCl with 0,2% w/v $La(NO_3)_3$.

Results in Table 2.6 show a serious decrease in the rhodium absorption as the mass of foam is increased as

in the case of platinum. To overcome this effect, it was necessary to matrix match the samples and standards as closely as possible, in such a way that both sets of solutions contained the same amount of foam.

Deily [179] investigated the optimum flame conditions and burner positions for determining rhodium in organic solvents. The leanest flame obtainable is required due to the added fuel contributed by the organic solvent.

An experiment was performed to investigate the effect of 10% v/v hydrochloric acid in ethanol on the rhodium calibration curve, by comparing the absorbance values of rhodium in this medium with those in 2M hydrochloric acid. From Figure 2.4 it can be seen that there is a marked decrease in the absorption of rhodium when analysed in a solution of ethanol with 10% HCl (v/v). A similar observation was made for platinum (Figure 2.2). A number of speculations concerning these findings have been discussed in Section 2.1.

The absorbance of rhodium in 3,5M H^+ and 0,5M Cl^- was investigated. This medium consists of a mixture of hydrochloric and sulphuric acids in the appropriate concentrations. Figure 2.5 compares these absorbance values to those of rhodium in 2M hydrochloric acid. Results showing the effects on the absorption of rhodium by ruthenium and iridium in 3,5 M H^+ and 0,5 M Cl^- are shown in Table 2.7.

It can be seen from Figure 2.5 that a decrease in sensitivity of rhodium absorbance is obtained when analysed in media containing a higher H^+ ion concentration. This is in keeping with the findings of other authors [150-152] who also observed that the presence of sulphuric acid causes a depressive effect on the absorbance of the noble metals. Pitts *et al.* [152]

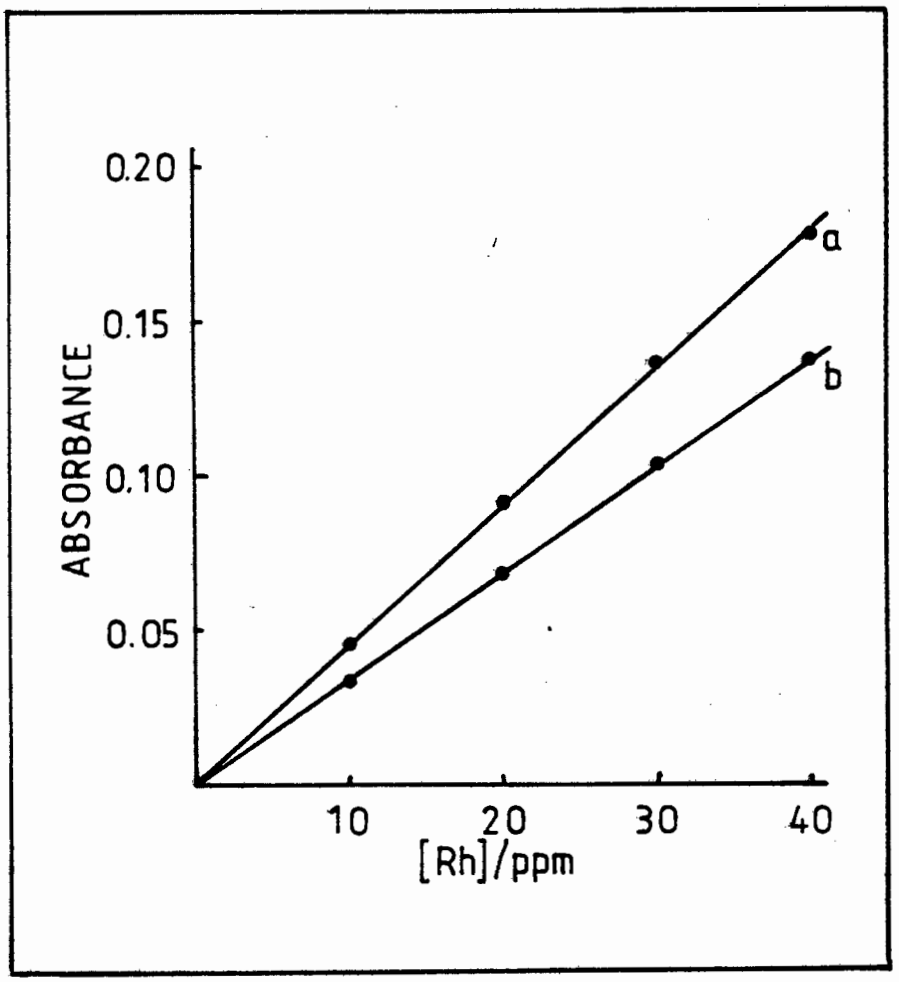


Figure 2.4 Rhodium calibration curve with 0,2% w/v $La(NO_3)_3$ in (a) 2M HCl and (b) 10% v/v HCl in ethanol.

offered the following explanation for the decrease in platinum absorbance in solutions containing sulphuric acid even at low concentrations: Evaporation of platinic acid solutions in the presence of sulphuric acid is known to yield platinum sulphate ($H_2[Pt(SO_4)_2(OH)_2]$) [180]. Although the reaction may not occur appreciably in solution, the evaporation of $H_2[PtCl_6]$ in the presence of sulphuric acid in the flame could yield a considerable quantity of non-volatile platinum sulphate. Since the noble metals behave in many similar ways chemically, this postulate may also be applied to rhodium. However the precise nature of supposedly simple compounds which could be formed such as rhodium sulphate are complicated and often unknown [181].

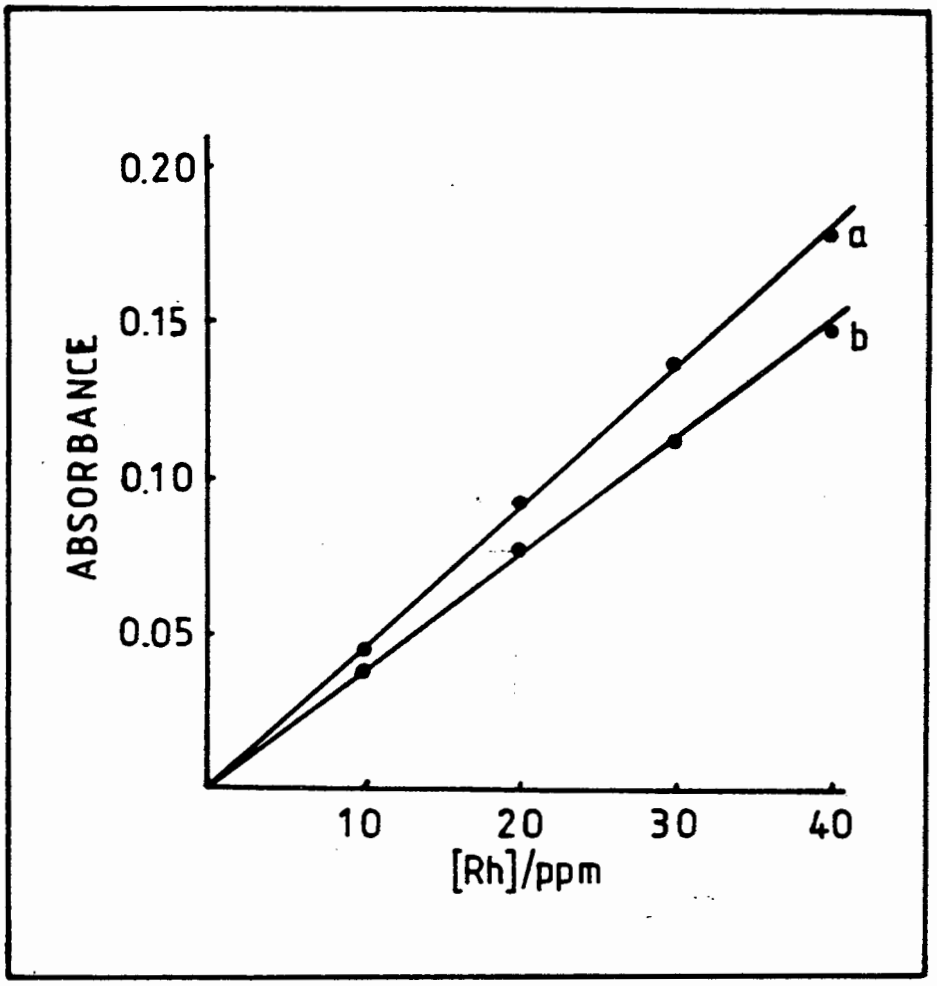


Figure 2.5 Rhodium calibration curve with 0,2% w/v $La(NO_3)_3$ in (a) 2M HCl and (b) 3,5 M H^+ and 0,5 M Cl^-.

Concentration of element added/ppm			Absorbance
Rh	Ru	Ir	
10	-	-	0,059
10	10	-	0,059
10	-	10	0,058
10	10	10	0,058
20	-	-	0,110
20	20	-	0,110
20	-	20	0,111
20	20	20	0,110

Table 2.7 Absorbance of rhodium in the presence of interfering noble metals in 3,5M H^+ and 0,5M Cl^- with 0,2% w/v $La(NO_3)_3$.

Results in Table 2.7 indicate that 0,2% w/v lanthanum nitrate is sufficient to overcome the mutual interferences from ruthenium and iridium on rhodium in 3,5M H^+ and 0,5M Cl^-.

Throughout this work we attempted to match standards and samples as closely as possible in view of the results obtained in the above experiments. The standards used contained $RhCl_3 \cdot nH_2O$ (n = 3 or 4) and 0,2% w/v $La(NO_3)_3$ in the appropriate medium.

2.3 THE ATOMIC ABSORPTION OF RUTHENIUM.

Ruthenium can be determined gravimetrically or colourimetrically [5] but atomic absorption is attractive as a rapid means of determining this element. When using this method one has to guard against serious depressive interelement interferences which occur if ruthenium is not separated from other elements prior to analysis [182-184].

Peterson and Smith [185] observed that the presence of uranium resulted in the elimination of interferences on ruthenium. This is in keeping the the findings of Scarborough [172].

Rowston and Ottaway [182] determined ruthenium in air-acetylene and used a mixture of 0,5% w/v Cu and 0,5% w/v Cd (added as their sulphates) to eliminate the numerous interferences encountered. Makarov *et al.* [183] recommended the addition of 0,5% lanthanum for Ru, Pt and Ir determinations.

The use of cyanide ions for the elimination of interfering effects has been studied [186] because of the great stability of the cyanocomplexes of ruthenium [187]. Potassium cyanide was found to considerably increase the absorption of ruthenium, and iridium was the only noble metal found to seriously interfere [181].

Schwab and Hembree [188] found that lanthanum nitrate stabilized ruthenium in simulated waste solutions from

the re-processing of nuclear reactor fuels and enhanced the sensitivity of the determinations by 100%. Preliminary ruthenium determinations by atomic absorption were found to give erroneous results when samples containing no lanthanum nitrate were aspirated into a reducing air-acetylene flame. Heinig and Mauersberger [189] successfully used lanthanum chloride as a releasing agent in synthetic Purex waste solutions to remove all interelement interferences on ruthenium except for cesium.

Ruthenium and iridium were determined in anode coatings by Harrington and Bramstedt [190]. The use of a titanium-potassium matrix was found to eliminate all the interelement interferences encountered. Titanium chloride was found to be the effective releasing agent for ruthenium whereas potassium chloride was more efficient for iridium. The enhancement of the ruthenium absorption in the presence of titanium chloride appears to be due to an increase in the dissociation of ruthenium rather than to a spectral interference.

There seem to be some contradictions in the findings on the effects of air-acetylene versus nitrous oxide-acetylene flames on the absorption of ruthenium. Sen Gupta [160], in the studies on osmiridium, native platinum and sperrylite, found that the sensitivity of ruthenium was the same in air-acetylene and nitrous oxide-acetylene flames when using a mixture of 0,5% w/v Cu and 0,5% w/v Cd (as their sulphates) as the releasing agent. In their study of Au, Pt, Pd, Rh and Ru, Mallett *et al.* [191] found that the nitrous oxide-acetylene flame reduces the metal interferences, except for ruthenium. It did, however, strongly reduce the sensitivity, again with the exception of ruthenium.

Montford and Cribbs [184] also noted that there was little improvement in respect of interferences using nitrous oxide-acetylene flames, but they noted a decrease in sensitivity when studying ruthenium solutions containing excess uranyl nitrate. Heinig and

Mauersberger [189], on the other hand, found no interferences on ruthenium while studying Purex waste solutions containing lanthanum chloride using nitrous oxide-acetylene flames. They did, however, find that the sensitivity was lower and the signal to noise ratio poor.

We chose the cooler air-acetylene flame in the determination of ruthenium and relied on a releasing agent to remove the interelement interferences. The resonance line at 349,9 nm was used for all measurements since it is the most sensitive and has the lowest background noise. Stoichiometric air-acetylene flames were found to provide maximum sensitivity for ruthenium.

We chose lanthanum nitrate as an interference suppressant. The presence of $La(NO_3)_3$ also serves to enhance the ruthenium absorbance signal.

Wyrley-Birch [178] established that the interference of stannous chloride on ruthenium could be eliminated by the use of 0,2% w/v $La(NO_3)_3$. The effect of stannous chloride on the analysis of ruthenium in the presence of $La(NO_3)_3$ is shown in Table 2.8 while Table 2.9 shows the effect of other noble metals on the absorption of ruthenium.

Ru:Sn ratio	Absorbance
1:0	0,092
1:10	0,091
1:20	0,091
1:30	0,092
1:40	0,092
1:50	0,092

Table 2.8 The effect of stannous chloride on the absorption of ruthenium solutions in 2M HCl with 0,2% w/v $La(NO_3)_3$ and [Ru] = 20ppm.

Concentrations of element added/ppm				Absorbance
Ru	Pt	Rh	Ir	
10	-	-	-	0,068
10	10	-	-	0,068
10	-	10	-	0,069
10	-	-	10	0,067
10	10	10	10	0,069
50	-	-	-	0,311
50	50	-	-	0,310
50	-	50	-	0,311
50	-	-	50	0,310
50	50	50	50	0,309

Table 2.9 Absorbance of ruthenium in the presence of interfering noble metals in 2M HCl with 0,2% w/v $La(NO_3)_3$.

Results from Tables 2.8 and 2.9 show that 0,2% w/v $La(NO_3)_3$ is suitable to suppress mutual interferences in ruthenium solutions of 2M hydrochloric acid with tin:ruthenium mole ratios of up to 50.

The absorbance of ruthenium in 3,5M H^+ and 0,5M Cl^- was investigated. This medium consisted of a mixture of hydrochloric and sulphuric acids in the appropriate concentrations. Figure 2.6 compares these absorption values to those of ruthenium in 2M hydrochloric acid.

Figure 2.6 shows that there is a decrease in ruthenium sensitivity when analysing solutions containing a high H^+ ion concentration. This is in keeping with other authors [150-152] who observed decreases in the sensitivities of the noble metals in the presence of sulphuric acid. An explanation for this effect could be the formation of the more refractory ruthenium sulphate. Montford and Cribbs [184] found the atomic absorption behaviour of ruthenium to be as complicated as its solution chemistry.

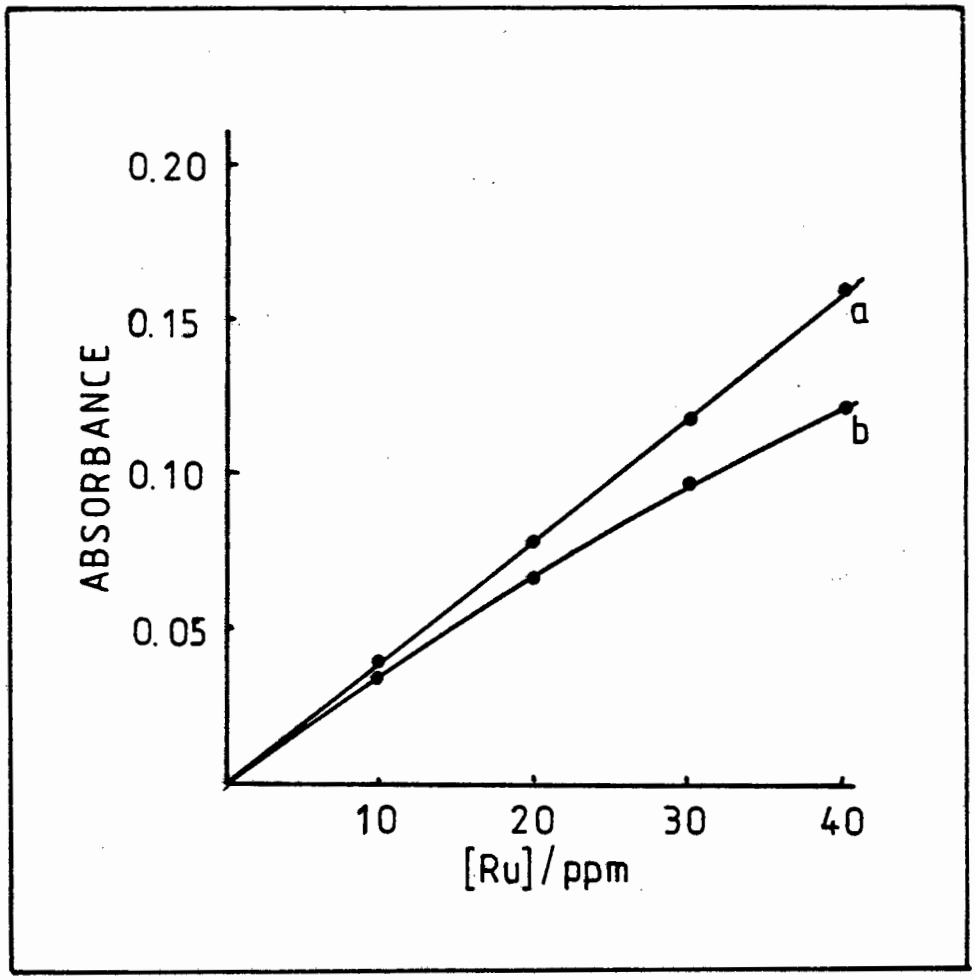


Figure 2.6 Ruthenium calibration curve with 0,2% w/v $La(NO_3)_3$ in (a) 2M HCl and (b) 3,5M H^+ and 0,5 M Cl^-.

Results showing the effects on the absorption of ruthenium by rhodium and iridium in 3,5M H^+ and 0,5M Cl^- with 0,2% w/v $La(NO_3)_3$ are shown in Table 2.10.

Results in Table 2.10 indicate that 0,2% w/v lanthanum nitrate is sufficient to overcome the mutual interferences from rhodium and iridium in 3,5M H^+ and 0,5M Cl^-.

Concentration of element added/ppm			Absorbance
Ru	Rh	Ir	
10	-	-	0,031
10	10	-	0,030
10	-	10	0,031
10	10	10	0,031
20	-	-	0,056
20	20	-	0,056
20	-	20	0,056
20	20	20	0,055

Table 2.10 Absorbance of ruthenium in the presence of mutual interferences in 3,5M H^+ and 0,5M Cl^- with 0,2% w/v $La(NO_3)_3$.

Throughout this work we attempted to matrix match standards and samples as closely as possible in view of the results obtained in the above experiments. The standards used contained $RuCl_3.nH_2O$ (n = 3 or 4) and 0,2% w/v $La(NO_3)_3$, in the appropriate medium.

2.4 THE ATOMIC ABSORPTION OF IRIDIUM.

The well-established spectrophotometric method with tin(II) bromide [192,193] for the determination of iridium is accurate and highly sensitive. However, this method suffers from a lack of selectivity, thus necessitating the complete removal of other platinum metals prior to iridium complex formation.

For a long time, iridium was considered indeterminable by atomic absorption spectroscopy. The first success was obtained by Mulford [194] who examined this element in more detail. Later Manning and Fernandez [195] made a thorough study and recommended the use of an air - acetylene flame rich in fuel and the use of the 264,0 nm resonance line. The 208,9 nm line was found to be twice as sensitive, but the signal:noise ratio was considerably worse.

Van Loon [196] investigated the determination of iridium in the presence of a large variety of both base and

other noble metals. The addition of a mixture of copper and sodium ions was sufficient to eliminate the interferences on iridium except for calcium and magnesium if their content was greater than 600 ppm. Janssen and Umland [158] also recommend a mixture of these ions as a releasing agent for iridium. Grimaldi and Schnepfe [197] added copper and sodium ions to their solutions when they determined iridium in mineralized mafic rocks. An increase in iridium sensitivity was also noted.

Fuhrman [198] found the sensitivity of iridium determined could be doubled by adding mixtures of potassium and lanthanum or sodium and lanthanum salts. The addition of Na or K alone, on the other hand, reduced the signal considerably. Further, in the presence of K and La, no influences owing to platinum or titanium could be observed on the absorption of iridium.

Other releasing agents found to eliminate interelement interferences on iridium include a mixture of 0,5% w/v $CuSO_4$ plus 0,5% w/v $CdSO_4$ [160], 0,5% w/v $LiSO_4$ [163,199], cupric nitrate [200] and potassium-titanium mixtures [190].

The use of uranyl or lanthanum chlorides as releasing agents for the platinum group metals in the presence of the interfering Na^+, Ba^{2+} and SO_4^{2-} ions has been tested [201]. Uranium was found to eliminate the cations interfering with iridium more easily than lanthanum. Sulphate ions were still found to interfere when either lanthanum or uranyl chlorides were present in solutions.

Diamantatos [202] developed a method for the rapid isolation of iridium from other platinum metals as well as a number of base metals. The method comprises the initial removal of ruthenium and osmium by volatilization of their tetroxides followed by the simultaneous extraction of Pt, Pd, Rh and Au into chloroform. In this way, iridium can be determined in the absence of interfering elements.

Luecke and Zielke [203] observed that the iridium sensitivity is reduced by about 50% when using a nitrous oxide-acetylene flame, except when the iridium was in the form $(IrCl_6)^{2-}$. Iridium as this complex exhibits the same sensitivity in this flame and in air-acetylene. Furthermore, the numerous interferences present during the determination of iridium disappeared when using the hotter flame.

We chose the cooler air-acetylene flame in the determination of iridium and relied on a releasing agent to remove the interelement interferences. The 264,0 nm resonance line was chosen as it is both cleaner and more intense than the 208,9 nm line. The slight decrease in sensitivity is offset by the improvement in signal to noise ratio. Reducing air-acetylene flames were found to provide maximum sensitivity for iridium.

We chose lanthanum nitrate as an interference suppressant. The presence of $La(NO_3)_3$ also serves to enhance the iridium absorbance signal.

Experiments were performed to establish whether 0,2% lanthanum nitrate is sufficient to remove interferences from stannous chloride and from other noble metals on the analysis of iridium. Table 2.11 shows the effect of tin(II) on the absorbance of iridium while Table 2.12 shows the absorbance of iridium in the presence of other noble metals.

Ir:Sn ratio	Absorbance
1:0	0,044
1:10	0,044
1:20	0,043
1:30	0,044
1:40	0,045
1:50	0,043

Table 2.11 The effect of stannous chloride on the absorbance of iridium solutions in 2M HCl with 0,2% w/v $La(NO_3)_3$ and [Ir] = 20 ppm.

Concentrations of element added/ppm				Absorbance
Ir	Pt	Rh	Ru	
10	-	-	-	0,030
10	10	-	-	0,029
10	-	10	-	0,030
10	-	-	10	0,031
10	10	10	10	0,029
50	-	-	-	0,133
50	50	-	-	0,133
50	-	50	-	0,132
50	-	-	50	0,131
50	50	50	50	0,132

Table 2.12 Absorbance of iridium in the presence of interfering noble metals in 2M HCl with 0,2% w/v $La(NO_3)_3$.

Results from Tables 2.11 and 2.12 show that 0,2% w/v $La(NO_3)_3$ is suitable to suppress mutual interferences in iridium solutions of 2M hydrochloric acid with tin:iridium mole ratios of up to 50. The absorbance of iridium in 3,5M H^+ and 0,5M Cl^- was investigated. This medium consisted of a mixture of hydrochloric and sulphuric acids in the appropriate concentrations. Figure 2.7 compares these absorption values with those of iridium in 2M hydrochloric acid. It can be seen that there is a serious decrease in iridium sensitivity when analysing the solutions containing sulphuric acid. This is in keeping with the findings of Mallett and Dubois [201] who observed the following: At very low concentrations of sulphate ions ($[H_2SO_4] < 0,1$ M) the sensitivity of iridium is enhanced, although this is followed by suppression with the increase of the sulphate ion concentration. Results showing the effects on the absorption of iridium by rhodium and ruthenium in 3,5M H^+ and 0,5M Cl^- with 0,2% w/v $La(NO_3)_3$ are shown in Table 2.13.

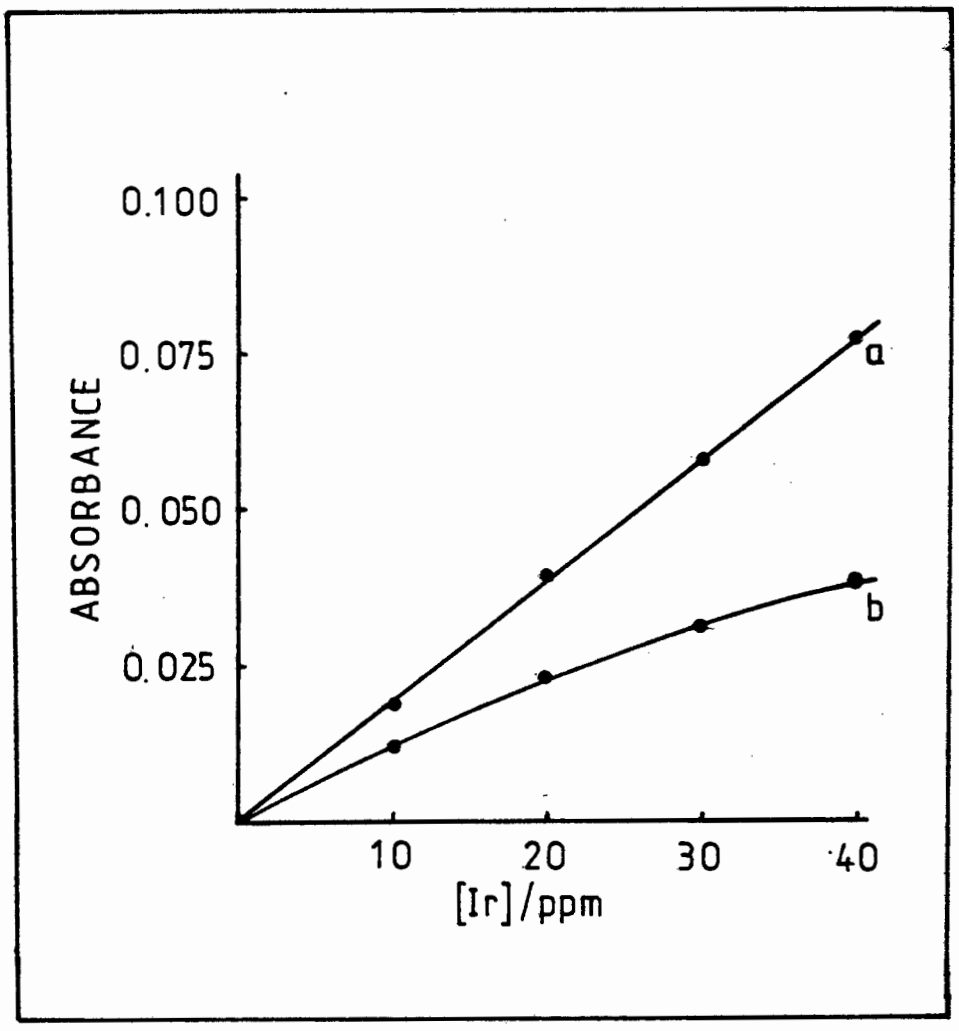


Figure 2.7 Iridium calibration curve with 0,2% w/v $La(NO_3)_3$ in (a) 2M HCl and (b) 3,5M H^+ and 0,5M Cl^-.

Concentration of element added/ppm			Absorbance
Ir	Rh	Ru	
10	-	-	0,022
10	10	-	0,018
10	-	10	0,020
10	10	10	0,019
20	-	-	0,035
20	20	-	0,029
20	-	20	0,032
20	20	20	0,030

Table 2.13 Absorbance of iridium in the presence of rhodium and ruthenium in 3,5M H^+ and 0,5M Cl^- with 0,2% w/v $La(NO_3)_3$.

Results in Table 2.13 show that there is a slight depressive effect from rhodium and a greater depressive effect from ruthenium on the absorbance of iridium in 3,5M H^+ and 0,5M Cl^- with 0,2% w/v $La(NO_3)_3$. This indicates that 0,2% w/v lanthanum nitrate is not a suitable releasing agent for iridium in a H_2SO_4/HCl medium.

Throughout this work we attempted to matrix match standards and samples as closely as possible in view of the results obtained in the above experiments. The standards used contained K_2IrCl_6 and 0,2% w/v $La(NO_3)_3$ in the appropriate medium.

2.5 THE ATOMIC ABSORPTION OF THE BASE METALS.

The base metals, Fe, Co, Ni, Cu and Zn in dilute hydrochloric acid solutions are readily determined by atomic absorption spectroscopy. The conditions under which they are analysed are shown in Table 2.14.

Base Metal	Absorption wavelength	Burner head configuration
Fe	372,0	normal
Co	304,4	normal
Ni	232,0	rotated 90°
Cu	324,7	rotated 45°
Zn	213,9	rotated 90°

Table 2.14 AAS conditions for determining the base metals.

The platinum group metals being studied have no effect on the determination of the base metals at these selected wavelengths, using the air-acetylene flame [146].

2.6 ERRORS AND STATISTICS OF QUANTITATIVE ANALYSIS.

The terms used and the statistical methods employed throughout this work are given below.

The error in a measurement is the difference between the observed, i.e. measured value, and the true value of the quantity measured. Errors can be divided into two classes: (1) Determinate errors, and (2) Indeterminate (random) errors.

Determinate errors are those errors whose magnitude can be determined (at least in principle) and the measurements thereby corrected. These errors are rather numerous in chemical analysis and some possible errors occurring in this study may include: impurities in a reagent used, the use of improperly calibrated glassware, mechanical loss of material in various steps of the analysis and inherent errors in the method.

We tried to remove or reduce these errors with the use of A grade glassware and analytically pure chemicals and reagents as far as possible.

Indeterminate or random errors are revealed by small fluctuations in the successive measurements made by the same observer with the greatest care under conditions as nearly the same as possible. These errors include for example variations in the atomic absorption spectrophotometer and in the weighing of hydroscopic substances such as stannous chloride. It is generally stated that it is beyond the power of the observer to prevent or allow for random errors.

The calibration curves of the platinum metal concentration versus absorbance were constructed by finding the best straight line throughout the series of points. The values of the constants in the equation for this line,

$$Y = a + bX$$

are found from the relations

$$a = y - bx \qquad b = \frac{\sum xy - \frac{\sum x \cdot \sum y}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}}$$

where X = absorbance
Y = concentration

Typical calibration curves for the individual noble metals showing the variation of absorbance measured are shown in Figure 8.2.

All the results obtained in this work are given in the form

$$\bar{x} \pm s$$

which are calculated from the formulae:

$$\bar{x} = \frac{\sum x}{n} \quad \text{and}$$

$$s = \frac{\sum (x - \bar{x})^2}{n - 1}$$

where x = a measured value
$\bar{x}$ = the arithmetic mean of a series of measurements
n = the number of samples
s = sample standard deviation

All confidence intervals quoted are at the 95% confidence level. These are calculated as follows:

$$\bar{x} \pm t_{\alpha\phi} \frac{s}{n}$$

where α = n-1 (numbers of degrees of freedom)
ϕ = 0,025 at 95% confidence level
t = appropriate value from students t table [204].

CHAPTER 3

CHAPTER 3

3. THE EXTRACTION, SEPARATION AND RECOVERY OF PLATINUM USING POLYURETHANE FOAMS.

Having established suitable analytical methods for the determination of the platinum metals being studied, we proceeded to make a detailed study of the extraction and subsequent recovery of platinum from acidic solutions containing stannous chloride using polyurethane foams. The feasibility of the selective extraction of platinum from solutions containing other noble and base metals by this method was also of great interest.

All work involving the preconcentration of platinum onto the foams was carried out under nitrogen and strict precautions were taken to exclude air as far as possible. Details of the actual procedures used in the loading and subsequent degradation of the foams are given in Chapter 8.

3.1 PRELIMINARY INVESTIGATIONS.

When solutions of $PtCl_4^{2-}$ and $SnCl_2$ are mixed in hydrochloric acid, the orange-red colour of the mixture gradually becomes more intense. The ultraviolet-visible absorbance spectra of freshly prepared aqueous solutions containing a Sn:Pt mole ratio, R_a(Pt), of 2 at various acid concentrations were determined as a function of time by Yates [167]. Steady state was reached in 10 and 20 minutes from solutions of 1M and 1,5M hydrochloric acid respectively. The spectroscopic determination of mixed platinum and tin(II) solutions at higher acid concentrations (2,3M and 6M HCl) was found to be somewhat complicated, probably due to the rapid oxidation of Sn(II) at higher acidities. The complicated spectra obtained suggest that steady state was not reached as certain absorbances increased with time whereas others decreased accordingly.

In conclusion, it was found that at low R_a(Pt) values, the formation of the platinum-tin complex anions is presumably a relatively slow process which, if not taken into consideration could result in incomplete extraction of platinum. At high R_a(Pt) values, the rate of formation of the platinum-tin(II) species may be expected to be more rapid due to the presence of excess $SnCl_3^-$.

Ahmed [205] performed extraction experiments in 1,4M HCl at various R_a(Pt) values with and without pre-equilibration of the aqueous phases. The results clearly illustrated that the amount of platinum extracted is lower at R_a(Pt) values between 2 and 5, with no pre-equilibration of the aqueous phase. This observation may be attributed to the relatively slow rate of formation of the chloro-(trichlorostannato)-platinum(II) complex anions. However, high Sn:Pt mole ratios (*ca.* 10) resulted in complete extraction of platinum irrespective of whether the aqueous phase had been pre-equilibrated or not. Presumably this is due to the more rapid formation of platinum(II)-tin(II) complex anions, as well as the "completeness" of the formation of the extractable chloro-(trichlorostannato)-platinum(II) species.

Ahmed [205] also noted that even after sufficient equilibration time, the rate of extraction of platinum increased as the R_a(Pt) value was increased up to 5, whereas no significant increase in the extraction was observed between Sn:Pt mole ratios of 5 and 10. This suggests that at R_a(Pt) > 5, platinum is coordinately saturated with respect to the $SnCl_3^-$ ligand and any further increase in the tin(II) concentration has no significant effect on the extraction.

This effect was also observed by Brackenbury [206] in a study of the extraction of the chloro-(trichlorostannato)-platinum(II) species by polyurethane foams. Results showed that both the rate of sorption and the sorptive capacity of the foam was greater at

R_a(Pt) = 5 than for R_a(Pt) = 2. At R_a(Pt) = 5, the anion $[Pt(SnCl_3)_5]^{3-}$ is believed to be the predominant species in hydrochloric acid. This led Brackenbury to conclude that the quinquecoordinate complex may have a greater tendency to be extracted by the foam than the possible square-planar $[Pt(SnCl_3)_nCl_{4-n}]^{2-}$ (n = 1-4) species.

The rates of many chemical reactions increase with higher temperatures. The rate of sorption of the chloro-(trichlorostannato)-platinum(II) species by polyurethane foam follows this trend. However, the sorptive capacity of the foam was found to decrease with increasing temperatures [206].

The effect of the hydrochloric acid concentration on the extraction has also been previously studied. Solutions of platinum(II) and tin(II) are known to be unstable at low acid concentrations as a result of hydrolysis to form complexes of type $H_{n-2}[PtSn(OH)_3)]_n$ (n = 4 or 5) [207].

Ahmed [205] investigated the effect of HCl concentration on the extraction of platinum into 40% MIBK in hexane. An increase in the amount of platinum extracted was observed with higher acid concentrations; this effect being more pronounced at high R_a(Pt) values. In a study of the sorptive capacity of polyurethane foam for platinum(II)-tin(II) species [206], a maximum capacity was reached at 0,75M HCl, after which the quantity of platinum extracted gradually decreased. At hydrochloric acid concentrations greater than 2M, the sorptive capacity remained essentially constant.

Under optimum conditions (25 ^{o}C, R_a(Pt) = 5, [HCl] = 0.75M) Brackenbury [206] achieved a maximum capacity value of 0,68 moles of Pt per kg of foam. Thus in order to obtain quantitative extraction of platinum by polyurethane foams under any given conditions, we chose to use an excess of foam (*ca.* 400 mg per 5 mg Pt).

It was also decided to use Sn:Pt mole ratios > 10 for a number of reasons. Firstly, tin is easily oxidized by trace amounts of oxygen. Although care was taken at all times to exclude air, it was felt that an excess of tin(II) would ensure the complete formation of chloro-(trichlorostannato)-platinum(II) complex anions even in the presence of small amounts of any oxidizing species which may have been present in the solutions. Secondly, the rate of formation of the extractable platinum(II)-tin(II) species appears to increase at higher Sn:Pt mole ratios. Pre-equilibration prior to extraction becomes unnecessary for R_a(Pt) > 10 [205]. Thirdly, no steady state appears to be reached for solutions with HCl concentrations greater than 1,5M containing low R_a(Pt) values [167]. On the other hand at a lower HCl concentration, the chloro-(trichlorostannato)-platinum(II) complex anions are prone to hydrolysis and are not as easily extracted by the foam [206]. Thus at small Sn:Pt mole ratios, the hydrochloric acid concentration is significant. Equilibrium of the platinum(II)-tin(II) complex anions is reached at higher HCl concentrations provided that sufficient tin is present [205]. It was accordingly decided to use Sn:Pt mole ratios $\geq$ 10 and higher HCl concentrations to prevent hydrolysis.

3.1.1 *The Rate of Extraction of Platinum by Polyurethane Foams.*

The time required for polyurethane foams to quantitatively sorb the chloro-(trichlorostannato)-platinum(II) complex anions was investigated spectroscopically. A freshly prepared solution with a Sn:Pt mole ratio of 40 in 2M HCl was equilibrated for 30 minutes prior to determining its ultraviolet-visible spectrum. The spectrum shows two distinct maxima for platinum between 250 nm and 650 nm (Figure 3.1(a)). We chose to use the peak at 400 nm as the fixed wavelength for subsequent experiments.

Various solutions of 2M HCl containing known masses of between 1,5 and 5 mg platinum and R_a(Pt) = 40 were loaded onto polyurethane foam blocks at room temperature. The platinum-tin(II) solutions were simultaneously pumped through a flow-through cell in the spectrophotometer and through the foam. Details of the procedure and apparatus employed are given in Section 8.4.

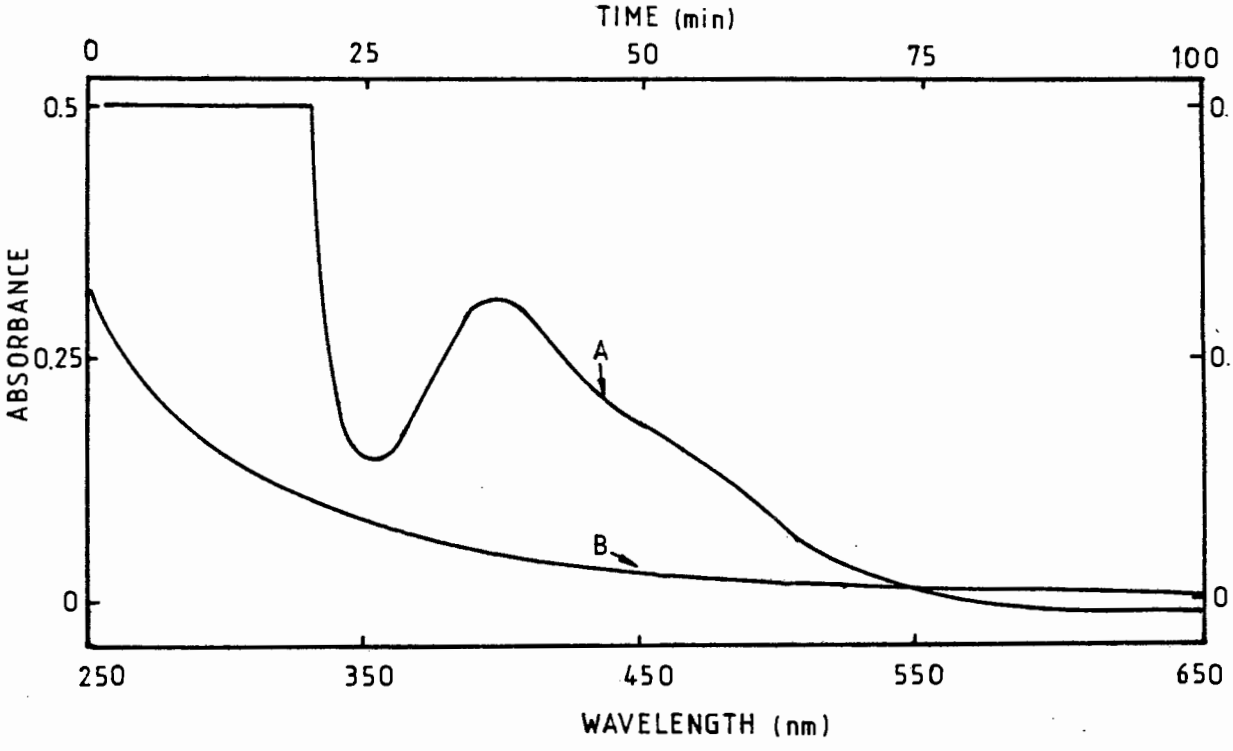


Figure 3.1 A typical absorption spectrum. (a) wavelength scan, (b) time scan at a fixed wavelength of 400 nm.

It may be seen from Figure 3.1(b) that 100 minutes is sufficient time for the polyurethane foam to extract the chloro-(trichlorostannato)-platinum(II) complex anions, with the bulk of the species being immobilised onto the foam in the first 20 minutes. A further aliquot of stannous chloride was added to determine whether any platinum remained in the solution. No coloured species were formed which suggests that the platinum had been quantitatively extracted by the foam. Consequently, in subsequent extraction studies polyurethane foam blocks were shaken in contact with platinum-tin(II) solutions for a period of 90 minutes.

3.1.2 *The Recovery by Foam Degradation of Platinum Immobilised on the Foam.*

A number of foam ashing techniques were investigated to degrade the loaded foams in order to determine by AAS the platinum content sorbed by polyurethane foams. These methods included the decomposition of the foams by:

(1) heat only

(2) hot concentrated nitric acid

(3) wet ashing using digestion bombs

An outline of the experimental procedures is given in Figure 3.2

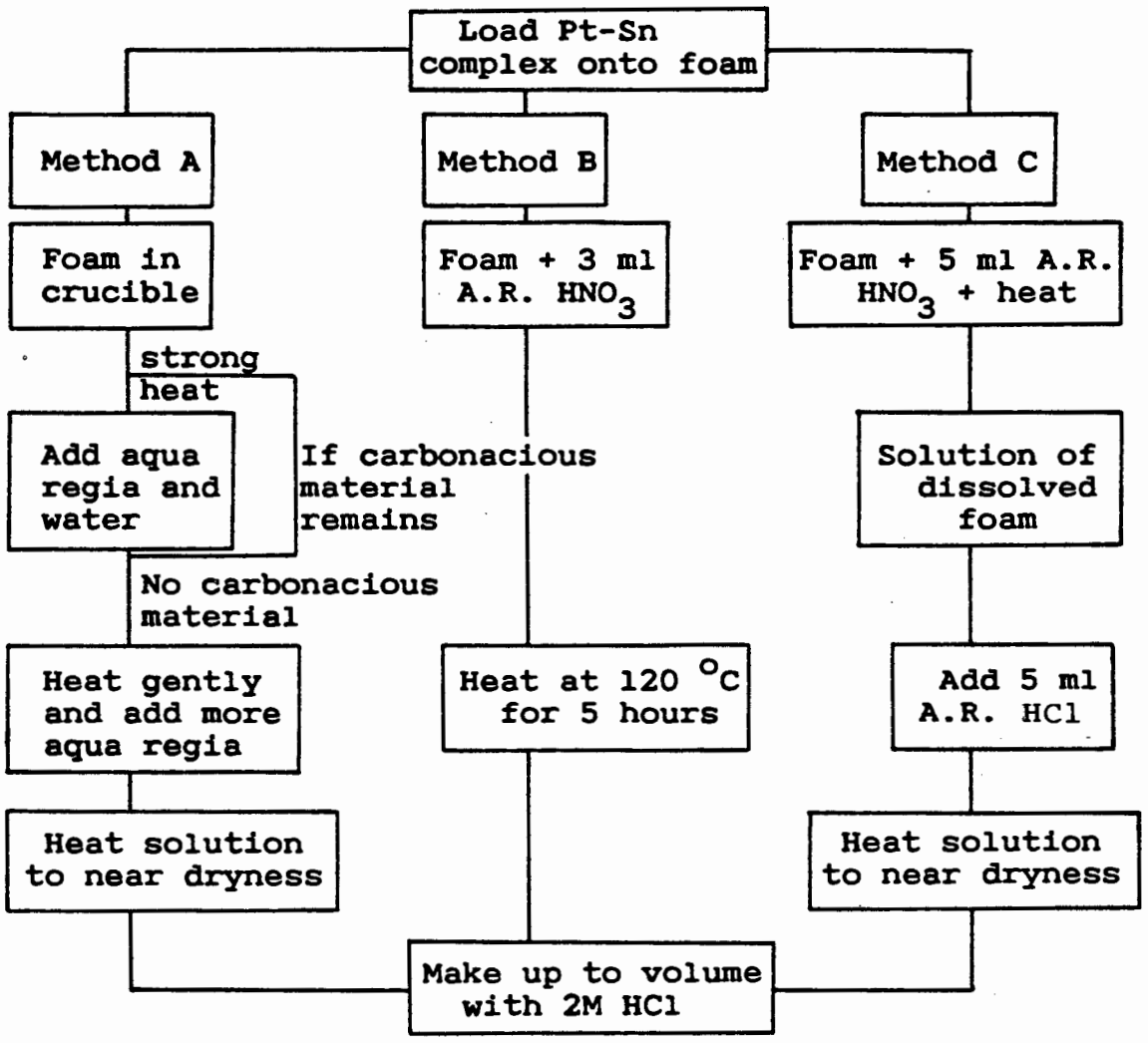


Figure 3.2 An outline of the experimental procedures employed for the degradation of loaded polyurethane foams.

The dry ashing technique employed (Method A) gave very poor and scattered results. A mean recovery of 64 ± 22% (11 samples), with a minimum recovery of 32% was obtained. The remaining platinum was unaccounted for. The sources of error contributing to the loss could be due to sputtering, incomplete degradation of the foam and incomplete dissolution of platinum from the ash.

Method B yielded complete recovery of the platinum (99,5 ± 4,6% for 27 samples). No solution can be lost during this degradation procedure as the digestion bombs are sealed. However, this method is very time consuming as a minimum period of 4,5 hours is required to completely destroy the foams at 120 ^{o}C. In order that a number of foams may be degraded at one time, a minimum of 8 digestion bombs are required. The use of polyurethane foam as an extractant for platinum becomes less economical due to the high cost of this equipment. It was also considered worthwhile to find a simpler method.

The third method employed (Method C) yielded encouraging results of 97,0 ± 6,0% for 8 samples. This method has subsequently been modified by using Kjeldahl flasks instead of small conical flasks heated over a flame. The stricter heat control and the the long necked flasks prevent the loss of material through sputtering. Details of the degradation procedure used throughout this study are given in Section 8.6.

3.2 THE EXTRACTION OF PLATINUM BY POLYURETHANE FOAMS.

The above preliminary studies have shown that quantitative recovery of platinum is possible; hence we chose to study the following experimental conditions based on the results of this work and others [205-207]. The effect of variable hydrochloric acid concentrations and Sn:Pt mole ratios on the quantitative recovery of platinum was investigated. It was hoped that these experiments would demonstrate the versatility of the use of polyurethane foams for the extraction of platinum.

3.2.1 *The Effect of Hydrochloric Acid on the Recovery of Platinum.*

Solutions containing the desired amounts of hydrochloric acid, platinum, tin(II) chloride and foam were shaken at room temperature for 90 minutes. The foams were then degraded prior to analysis of platinum by AAS.

[HCl]/M	Platinum found[a] mg	% [b]	95% confidence limits
0,5(3)[c]	4,74 ± 0,08	95	(4,54; 4,94)
1,5(4)	4,90 ± 0.06	98	(4,80; 5,00)
2,0(6)	4,89 ± 0,05	98	(4,81; 4,97)
2,5(4)	4,79 ± 0,05	96	(4,71; 4,87)
3,5(4)	4,82 ± 0,06	97	(4,72; 4,92)

(a) Found by AAS after decomposition of loaded foam with nitric acid.
(b) Mass of Pt found / Mass of Pt taken.
(c) Number of determinations in parenthesis

Conditions (a)-(c) apply throughout this work unless otherwise stated.

Table 3.1 The effect of hydrochloric acid concentration on the extraction of platinum by polyurethane foam. Experimental Conditions: volume of solution = 200 ml, initial mass Pt = 5 mg, *Ra*(Pt) = 20, 400 mg foam block used, [HCl] is varied (Appendix 1a).

The relatively lower amount of platinum sorbed by the foam at 0,5M HCl (Table 3.1) may be caused by hydrolysis reactions involving the chloro-(trichlorostannato)-platinum(II) anions [207]. The solutions of platinum-tin(II) in 0,5M HCl were brown-orange in colour rather than the bright orange solutions found at stronger acid concentrations. The sorption of platinum by the foams does not appear to be affected at hydrochloric acid concentrations greater than 0,5M up to that of 3,5M. We chose to continue working with 2M HCl for all further platinum studies.

3.2.2 *The Effect of Sn:Pt ratio on the Recovery of Platinum.*

The effect of very large excesses of stannous chloride on the extraction of platinum by polyurethane foams were also studied. Any co-extraction of tin(II) which may take place [29] would not be expected to interfere with the uptake of platinum since such large excesses of foam were employed. Brackenbury [206] investigated the extraction of tin(II) chloride in the absence of platinum, and found that negligible amounts are in fact sorbed for HCl concentrations between 1M and 2M.

R_a(Pt)	Pt taken mg	Platinum found mg	%	95% confidence limits
10(4)	2,5	2,51 ± 0,04	100	(1,45; 2,57)
20(3)	2,5	2,50 ± 0,02	100	(2,45; 2,55)
(4)	5,0	4,83 ± 0,12	97	(4,64; 5,02)
30(3)	2,5	2,45 ± 0,02	98	(2,40; 2,50)
(4)	5,0	5,02 ± 0,12	101	(4,83; 5,11)
40(4)	2,5	2,49 ± 0,03	100	(2,44; 2,54)
(4)	5,0	4,82 ± 0,10	97	(4,66; 4,98)

Table 3.2 The effect of Sn:Pt mole ratio on the extraction of platinum by polyurethane foam. Experimental Conditions: volume of solution = 200 ml, [HCl] = 2M, mass foam block = 400 mg, shaken at room temperature. R_a(Pt) varied (Appendix 1b)

It may be seen from Table 3.2 that the Sn(II):Pt mole ratio has no effect on the sorption of platinum by polyurethane foams.

3.2.3 *The Effect of Initial Platinum Concentration on the Recovery of Platinum.*

Quantitative extraction of platinum by polyurethane foams has been shown to occur from solutions containing

initial masses of platinum of 1,5 mg and 2,5 mg ([Pt] = 1,25 ppm and 2,5 ppm respectively). We chose to examine the effect of the initial platinum concentration on the sorption of platinum by polyurethane foams. Tables 3.3 and 3.4 show the results of some recovery experiments obtained for milligram and microgram quantities of platinum used in the aqueous phases.

Mass taken/mg	Pt/mg found	Conditions Mass foam/mg	$[Pt]_i$ [a]/ppm
5,00(8)	4,93 ± 0,15(99%)	400	25,0
2,50(10)	2,48 ± 0,03(100%)	400	12,5
1,00(8)	1,03 ± 0,01(103%)	200	5,0
0,50(11)	0,50 ± 0,01(99%)	200	2,5
0,25(10)	0,25 ± 0,004(100%)	100	1,25

(a) Initial concentration of Pt as $PtCl_4^{2-}$

Table 3.3 Recovery of milligram quantities of platinum from polyurethane foams following sorption from dilute hydrochloric acid solutions. Experimental Conditions: volume of solution = 200 ml, [HCl] = 2M, *Ra*(Pt) = 30, shaken at room temperature for 90 minutes (Appendix 1c).

It may be seen from Table 3.3 that satisfactory recoveries are achieved for 0,25-5,0 mg quantities of platinum. The recoveries are somewhat less than 100% for solutions containing 100 µg or less of platinum (Table 3.4). Brackenbury [206] observed the greater the solution concentration of platinum, the more rapid is the rate of sorption by the foam. These results suggest that 90 minutes of shaking may not be sufficient time for the quantitative sorption of platinum by polyurethane foams from solutions containing microamounts of platinum.

Mass taken/μg	Pt/μg found	Confidence limits	$[Pt]_i$/ppm
100(11)	83,8 ± 2,6(84%)	(82,0; 85,6)	0,50
50(9)	36,5 ± 2,7(73%)	(34,4; 38,6)	0,25
25(6)	16,5 ± 1,4(66%)	(15,0; 18,0)	0,125
10(7)	6,5 ± 1,3(65%)	(5,3; 7,7)	0,05

Table 3.4 Recovery of microgram quantities of platinum from polyurethane foams following sorption from dilute hydrochloric acid solutions. Experimental Conditions: volume of solution = 200 ml, [HCl] = 2M, *Ra*(Pt) = 100, mass foam blocks used = 100 mg, shaken at room temperature for 90 minutes (Appendix 1c)

However, preconcentration has been achieved. As an example, the original solution containing 1,25 ppm Pt(II) was concentrated onto a 200 mg foam block which was decomposed using hot nitric acid and allowed to boil until reduced to a volume of approximately 2 ml. This small volume contains *ca.* 125 ppm platinum which represents a 100-fold increase in concentration. Bearing in mind that large excesses of foam were used, one could expect an even greater concentration increase at the maximum capacity of the foam.

3.3 THE EXTRACTION OF PLATINUM BY POLYURETHANE FOAMS FROM SOLUTIONS CONTAINING BASE METALS.

The occurrence of large amounts of base metals in the majority of platinum metal ore bodies, led us to examine the feasibility of selectively extracting platinum as its stannous chloride complex from solutions containing a variety of base metals, using polyurethane foams.

Stannous chloride is generally known only to form stable complexes with the platinum metals and not with metals such as Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). Furthermore, the extraction of Co(II), Ni(II) and Cu(II) from dilute acid solutions has only been achieved using

treated polyurethane foams [13,21], or by the extraction of the metal thiocyanate complexes [23]. Iron(III) has been sorbed onto polyurethane foam as the $FeCl_4^-$ ion, provided that the hydrochloric acid concentration was sufficiently high [44].

To solutions containing the desired amounts of platinum(II) in 2M HCl, we added a 100-fold excess (mass ratio) of each of Co(II), Ni(II), Cu(II) and Zn(II) as their chlorides. In a further set of experiments, a 100-fold excess of Fe(III) was added to the platinum solutions. Attempts were made to reduce Fe(III) to Fe(II) prior to the addition of tin(II) chloride by purging the solutions with SO_2 and then N_2. However, the characteristic colour of chloro-(trichlorstannato)-platinum(II) complex anions did not develop when tin(II) chloride, representing a Sn:Pt mole ratio of 30, was added to the solutions. Presumably the SO_2 dissolving in the aqueous phase interfered with the Pt(II)-Sn(II) complex formation. No investigation as to the possible cause of this interference was undertaken. A large excess of stannous chloride was thus required to produce the characteristic orange-red platinum(II)-tin(II) solutions.

Results in Table 3.5 show that essentially all the platinum and less than 1% of the base metals Fe(III), Co(II), Ni(II) and Zn(II) are extracted from dilute solutions of hydrochloric acid. Copper(II), being the exception, extracts into the foam to a significant extent. The exact nature of the species being sorbed is unknown and no attempts were made to establish this. Copper(II) has been found not to sorb onto polyurethane foams [24], which indicates that the species may possibly be some Cu(II)-Sn(II) complex or possibly a Cu(I) species.

mass taken/mg	Found on foam mg	%	Confidence limits
2,5 mg Pt + 250 mg each of Co, Cu, Ni, Zn (n = 5)	Pt 2,48 ± 0,05	99	(2,42; 2,54)
	Co 0,43 ± 0,13	0,2	(0,27; 0,59)
	Ni 0,40 ± 0,20	0,2	(0,15; 0,60)
	Zn 1,00 ± 0,20	0,4	(0,80; 1,20)
	Cu 6,72 ± 0,58	2,7	(6,00; 7,44)
2,5 mg Pt + 250 mg Fe (n = 4)	Pt 2,47 ± 0,05	99	(2,39; 2,55)
	Fe 0,13 ± 0,04	0,05	(0,07; 0,19)

Table 3.5 The recovery of platinum from solutions containing base metals in 2M HCl, following sorption by polyurethane foams Experimental Conditions: volume of solution = 200 ml, 400 mg foam block used, shaken at room temperature for 90 minutes (Appendix 2)

3.4 THE SEPARATION OF PLATINUM FROM IRIDIUM USING POLYURETHANE FOAM.

At room temperature, dilute hydrochloric acid solutions containing iridium(IV) and tin(II) chloride do not form highly coloured solutions. Young *et al.* [103] observed that heating produced amber-coloured solutions. Pantani and Piccardi [120] noted that iridium(IV), unlike platinum, does not react with tin(II) bromide at room temperature. The authors [120] also found that the iridium from these solutions could not be extracted into isoamyl alcohol.

Solutions of $IrCl_6^{2-}$ are pale yellow-brown in colour for concentrations of 10-40 ppm. It was noted that on addition of stannous chloride, the solutions paled, becoming almost colourless with the addition of excess tin(II) chloride. This is probably due to the reduction of Ir(IV) to Ir(III), rather than to the formation of chloro-(trichlorostannato)-iridium complex anions.

However, we set out to establish whether iridium would be sorbed onto polyurethane foams from these solutions.

A preliminary solvent extraction experiment was performed to investigate the extraction of iridium(IV) in the presence of stannous chloride into methyl-isobutyl ketone (MIBK). The required amounts of iridium(IV) and tin(II) chloride giving mole ratios of Sn:Ir from 1 to 20 in 2M HCl were allowed to equilibrate for 2 hours. Sets of solutions were equilibrated at different temperatures, *viz.* room temperature, 50 ^{o}C and 75 ^{o}C. The solutions were cooled (if necessary) and shaken with equal volumes of degassed MIBK for 90 minutes. The aqueous phase was then analysed using AAS.

Less than 5% of iridium was found to extract into MIBK at room temperature and at 50 ^{o}C for Sn:Ir mole ratios, R_a(Ir), of 20. At 75 ^{o}C, however, approximately 3% and 13% iridium was extracted from the aqueous phases at R_a(Ir) of 10 and 20 respectively.

These results were very encouraging, especially as concentrated solutions of 500 ppm iridium had been used. The next objective was to separate platinum from iridium using polyurethane foams.

To the required amounts of platinum, iridium and tin(II) chloride, excess polyurethane foam was added and the solutions shaken at room temperature as outlined for platinum above. The foams were then degraded and solutions were analysed by AAS. The aqueous phase was retained, diluted to volume with 2M HCl and sufficient lanthanum nitrate to give a final $La(NO_3)_3$ concentration of 0,2% w/v.

Table 3.6 shows the results of platinum recovery experiments from a number of solutions containing iridium. It is clear that excellent separations are obtained. Only trace amounts of iridium ($\leq$ 0,5%) are detected on the foam at Ir:Pt mole ratios of 100.

Pt:Ir	mass taken/mg Pt	Ir	mass found/mg on foam	in solution
1:1(7)	2,50	2,46	Pt 2,52 ± 0,06(101%)	Ir 2,40 ± 0,08(98%)
(4)	1,50	1,48	Pt 1,48 ± 0,04(98%)	Ir 1,50 ± 0,03(101%)
1:10(5)	1,00	9,85	Pt 1,01 ± 0,01(101%)	Ir 9,55 ± 0,42(97%)
1:100(6)	0,50	24,63	Pt 0,51 ± 0,01(102%)	
			Ir 0,12 ± 0,01(0,5%)	Ir 24,47 ± 0,05(99%)
(5)	0,10	9,85	Pt 0,09 ± 0,005(94%)	
			Ir 0,04 ± 0,01(0,4%)	Ir 9,82 ± 0,29(100%)

Table 3.6 The recovery of platinum from solutions containing iridium in 2M HCl, following sorption by polyurethane foam. Experimental Conditions: volume of solution = 200 ml, R_a(Pt, Ir) = 30, (Pt, Ir) = sum of moles of metals taken), 400 mg foam bloc used, shaken at room temperature for 90 minutes (Appendix 3)

The relatively poor recovery of 94% platinum obtained for 0,1 mg Pt and Ir:Pt mole ratio of 100 may be a result of the extraction method which is not suitable for low platinum concentrations (initial platinum concentration of 0,05 ppm). When recovering small amounts of platinum (Table 3.4), it was also noted that solutions of 0,05 ppm Pt and less could not be quantitatively sorbed by polyurethane foams. However, considering the low concentration of platinum and high concentration of iridium present in the aqueous phases, the amount of platinum recovered is acceptable. The aqueous phases were analysed for both platinum and iridium. No platinum could be detected in these solutions (250 cm^3) as the AAS method is not sensitive enough to detect platinum at the 10^{-2} ppm level.

3.5 THE SEPARATION OF PLATINUM FROM RUTHENIUM BY POLYURETHANE FOAMS.

Ruthenium solutions containing tin(II) chloride tend to behave in a similar fashion to iridium-tin(II) solutions in that they do not form coloured species unless they are heated to some extent [103]. On addition of 20 molar excess of stannous chloride to hydrochloric acid solutions of ruthenium trichloride, the red-brown solutions rapidly became very pale yellow or colourless. This is followed by the development of a blue colour which is not associated with the formation of chloro-(trichlorostannato)-ruthenium(II) complex anions, but is generally thought to involve the reduction of Ru(III) to Ru(II) [209]. No ruthenium extracts into MIBK from these blue solutions [178].

On the basis of the results obtained from the separation of platinum from iridium, it was decided to investigate the feasibility of separating platinum from ruthenium. Experiments, similar to those in Section 3.4, were performed. Table 3.7 shows the results of the platinum recovery experiments from dilute acidic solutions containing ruthenium.

Quantitative separations have been achieved for Ru:Pt mole ratios of 1 and 10. Although only small amounts (*ca.* 0,1%) of ruthenium could be detected on the foam when in 100 times excess of platinum, only 86% of platinum was found to sorb onto the foam from these solutions. It appears that ruthenium, in such large quantities, inhibits the extraction of platinum onto the foam. The residual platinum which remained in the aqueous phase could not be detected by AAS as the solutions were too dilute.

Pt:Ru[a]	mass taken/mg Pt	Ru	mass found/mg on foam	in solution
1:1(6)	5,00	2,59	Pt 5,03 ± 0,07(101%)	Ru 2,62 ± 0,03(102%)
(6)	2,50	1,30	2,53 ± 0,03(101%)	1,29 ± 0,02(100%)
(6)	1,00	0,52	1,00 ± 0,01(100%)	0,51 ± 0,01(100%)
1:10(6)	2,50	12,95	Pt 2,50 ± 0,02(100%)	Ru 12,91 ± 0,09(100%)
(6)	1,00	5,18	1,02 ± 0,01(102%)	5,31 ± 0,11(103%)
1:100(6)	1,00	51,82	Pt 0,86 ± 0,10(86%)	Ru 51,88 ± 0,02(100%)
			Ru 0,06 ± 0,03(0,1%)	

(a) Number of determinations in parenthesis.

Table 3.7 The recovery of platinum from solutions containing ruthenium, following sorption by polyurethane foams. Experimental conditions: volume of solution = 200 ml, *Ra*(Pt, Ru) = 30, ((Pt, Ru) = sum of the moles of metals taken) 400 mg foam blocks used, shaken at room temperature for 90 minutes (Appendix 4)

3.6 THE RECOVERY OF PLATINUM FROM COMPLEX SYNTHETIC MIXTURES USING POLYURETHANE FOAMS.

The recovery of platinum from solutions containing base metals, iridium or ruthenium has been demonstrated with good results. It was thus decided to investigate the separation of platinum from complex synthetic mixtures containing these metals.

The required amounts of noble and base metals, known amounts of excess stannous chloride and foam in 2M HCl were shaken at room temperature for 90 minutes. The foams were decomposed in the usual manner and these

solutions, together with the aqueous phases were analysed by AAS for all the metals present. Results are shown in Table 3.8.

mass taken/mg[a]	mass found on foam and in solution/mg	
	foam	solution
1,0 mg Pt + 2,59 mg Ru + 4,93 mg Ir (n=7)	Pt 0,99 ± 0,02(99%)	Ru 2,64 ± 0,01(102%)
		Ir 4,90 ± 0,08(99%)
1,0 mg Pt + 2,59 mg Ru + 4,93 mg Ir + 1,68 mg Zn + 1,63 mg Cu + 1,51 mg Co + 1,51 mg Ni (n = 6)	Pt 1,00 ± 0,01(100%)	Ru 2,60 ± 0,02(101%)
	Zn 0,03 ± 0,01(1,6%)	Ir 4,98 ± 0,06(101%)
	Cu 0,03 ± 0,01(2,0%)	Zn 1,17 ± 0,002(105%)
	Ni 0,01 ± 0,04(0,8%)	Cu 1,60 ± 0,03(98%)
		Co 1,52 ± 0,01(100%)
		Ni 1,50 ± 0,02(99%)

(a) The masses of each metal (M) represents a M:Pt mole ratio of 5.

Table 3.8 The recovery of platinum from synthetic mixtures, following sorption by polyurethane foams. Experimental Conditions: volume of solution = 150 ml, Ra(Pt, Ir, Ru) = 50, 400 mg foam blocks used, shaken at room temperature for 90 minutes (Appendix 5)

Complete recovery of platinum from solutions containing ruthenium and iridium has been obtained. In the presence of base metals, platinum is quantitatively sorbed onto the foam together with trace amounts of Zn(II), Cu(II) and Ni(II). Mass balance was met for all the metals analysed except for zinc (total of 107%). The standard deviation for zinc is very small (0,002%), which suggests that a systematic (constant) bias may be present. The zinc standards and samples may not have been matrix matched.

CHAPTER 4

CHAPTER 4.

4. THE EXTRACTION, SEPARATION AND RECOVERY OF RHODIUM USING POLYURETHANE FOAMS.

The sorption of chloro-(trichlorostannato)- rhodium (III/I) complex anions from hydrochloric acid solutions using polyurethane foams as extractants was examined. The feasibility of the selective extraction, by this method, of rhodium from solutions containing other noble metals was also of great interest.

4.1 PRELIMINARY INVESTIGATIONS.

When rhodium(III) is treated with stannous chloride in a hydrochloric acid medium, anionic yellow and red complexes are formed. The predominant species in solution depend on the $SnCl_3^-$:Cl^- ratio. The ultraviolet-visible absorption spectra of freshly prepared aqueous solutions, containing Sn(II):Rh(III) mole ratios, R_a(Rh), of 1 to 12 in 1,5-3,5M HCl were determined as a function of time by Wyrley-Birch [178]. Steady state was reached in approximately 7 hours and 14 hours for solutions containing R_a(Rh) values of 1 to 3 and 12 respectively in 1,5-3,5M HCl. These results suggest that the formation of the rhodium-tin complex anions is a far slower process than the formation of platinum-tin complexes. A pre-equilibration period of 16 hours was necessary for maximum extraction of chloro-(trichlorostannato)-rhodium(III/I) complex anions into MIBK/hexane mixtures [178].

The amount of rhodium extracted into the organic phase was observed to increase as the R_a(Rh) value increased from 3 to 6. No significant increase was observed between R_a(Rh) values of 6 and 10. Saito *et al.* [127] have shown, by means of ^{119}Sn-NMR spectroscopy, that the species of type $[Rh(SnCl_3)_nCl_{6-n}]^{3-}$ (n = 1-5) exist in 3M HCl for R_a(Rh) values between 1 and 6. These authors demonstrated the redox process between rhodium(III) and tin(II) species to form the red-purple rhodium(I)

complex of probable composition $[Rh(SnCl_3)_5]^{4-}$ in the presence of excess tin(II) chloride ($R_a(Rh) \geq 6$). No information about the rate of reduction of rhodium(III) or its extent at room temperature is available.

The concentration of hydrochloric acid has been found to effect the amount of rhodium extracted both into MIBK/hexane mixtures [178] and by polyurethane foams [210]. After equilibration for 16 hours, aqueous solutions varied from bright yellow (3,5M HCl) to red-yellow at 0,5M HCl. The amount of rhodium extracted into MIBK/hexane mixtures from 3,5M HCl was greater than that extracted from 1,5M HCl [178]. It is thus clear that the HCl concentration affects not only the complex formation in the aqueous phase, but is also involved in the extraction process.

4.2 THE EXTRACTION OF RHODIUM BY POLYURETHANE FOAMS.

When solutions of $RhCl_3$ and $SnCl_2$ are mixed in hydrochloric acid, extractable species are formed. The rate of formation of these extractable chloro-(trichlorostannato)-rhodium(III/I) complexes is slower than the rate of formation of the extractable platinum(II)-tin(II) species.

We have shown that platinum can be quantitatively sorbed by polyurethane foam from dilute acidic solutions at room temperature within 90 minutes. Rhodium was not expected to be quantitatively sorbed by polyurethane foams within 90 minutes without a pre-equilibration period. To avoid the pre-equilibration period of 16 hours at room temperature suggested by Wyrley-Birch [178], we investigated the shaking time (time when the polyurethane foam blocks are in contact with the aqueous solutions) required for the quantitative extraction of rhodium. Table 4.1 shows the results of the sorption of rhodium by the foams for periods of 1,5 to 4,5 hours.

shaking time/ hours[a]	Rhodium found on foam/mg	%	in solution/mg	%
1,5(3)	3,33 ± 0,06	67	1,77 ± 0,06	35
2,5(3)	4,37 ± 0,10	87	0,62 ± 0,07	12
3,5(2)	4,58	92	0,37	7
4,5(3)	4,78 ± 0,03	96	0,32 ± 0,09	6

(a) = number of determinations in parenthesis

Table 4.1 The effect of shaking time on the extraction of rhodium by polyurethane foams. Experimental Conditions: volume of solution = 100 ml, [HCl] = 2M, initial mass of Rh = 5,00 mg, R_a(Rh) = 50, mass of foam blocks = 400 mg, shaken at room temperature (Appendix 6a).

The amount of rhodium sorbed by the polyurethane foams is increased from 67% to 96% as the contact time of the foams with the aqueous phases is increased from 90 to 270 minutes. By plotting these values, one could estimate that the shaking time required for the quantitative extraction of rhodium by polyurethane foam at room temperature would be in the region of 390 minutes (Figure 4.1).

It was decided that this method for the extraction of rhodium is too time consuming. A study was undertaken to determine whether heating the rhodium-tin(II) solutions would result in the quantitative extraction of rhodium in less time. An arbitrary temperature of 50 ^{o}C was chosen. Solutions containing the required amounts of rhodium trichloride and tin(II) chloride were heated in a waterbath set at this temperature for 1 to 3 hours prior to the addition of the foams. The foams were then shaken in contact with the solutions for a period of 90 minutes.

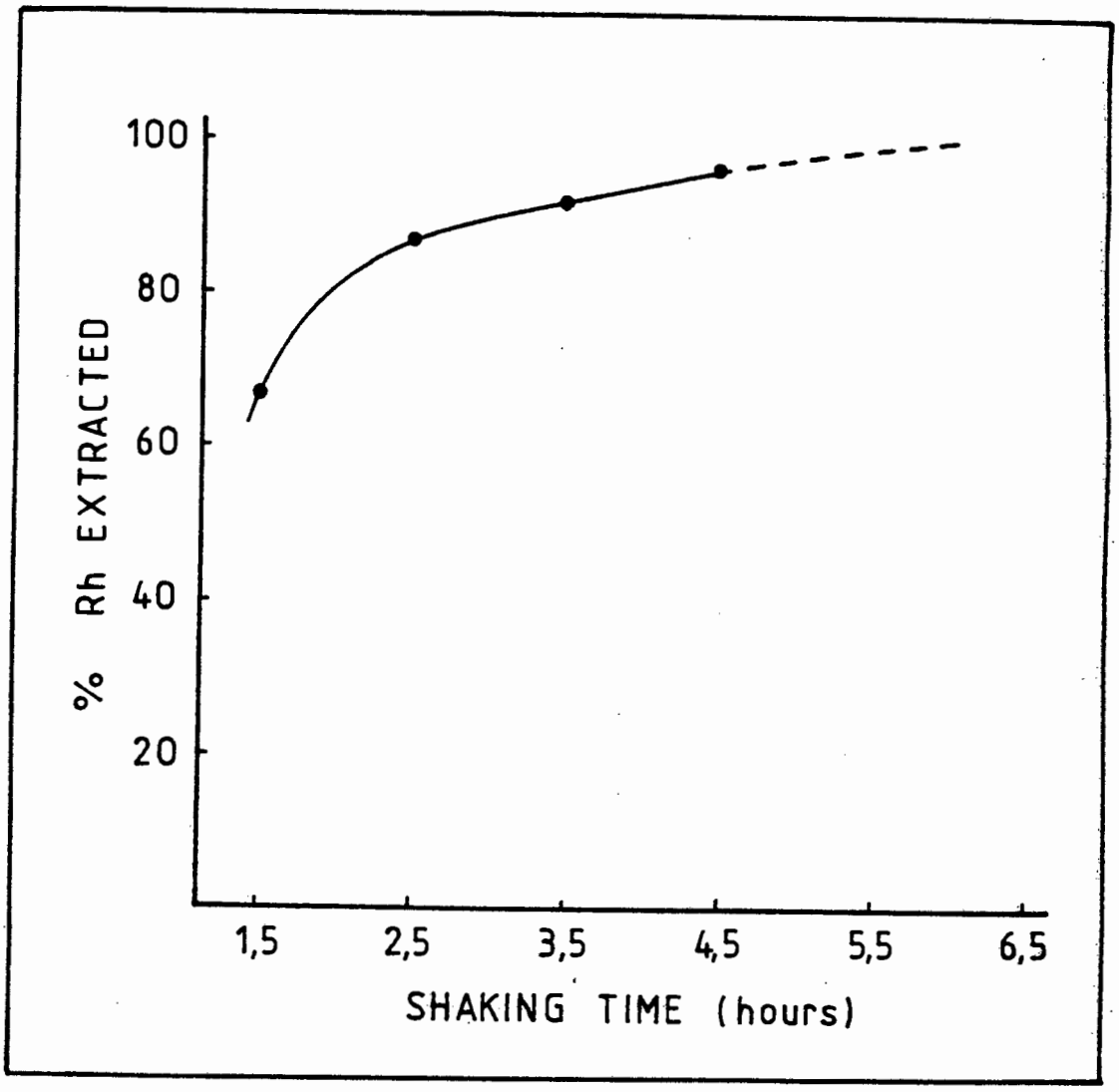


Figure 4.1 Variation of percentage extraction of rhodium from 2M HCl solutions as a function of shaking time at R_a(Rh) = 50.

The aqueous solutions which had been pre-equilibrated for 1 or 2 hours were pale yellow in colour on removal of the foam blocks, which suggested that incomplete extraction of rhodium by the polyurethane foams had taken place. No yellow tinge could be seen in the aqueous phases which had been pre-equilibrated for 3 hours at 50 ^{o}C. This lack of colour suggested that no rhodium remained in solution. The analysis of the degraded foams and aqueous solutions by AAS confirmed these assumptions. The results are shown in Table 4.2.

Equilibration time/ hours	Rhodium found on foam/mg	%	in solution/mg	%
1(4)	4,75 ± 0,11	95	0,17 ± 0,04	3,4
2(4)	4,84 ± 0,10	97	0,11 ± 0,03	2,3
3(4)	5,03 ± 0,13	101	not detected	

Table 4.2 The effect of pre-equilibration on the extraction of rhodium by polyurethane foams. Experimental Conditions: volume of solutions = 150 ml, initial mass Rh = 5,00 mg, R_a(Rh) = 50, mass foam blocks used = 400 mg, (Appendix 6b).

The rhodium-tin(II) solutions, for all further experimental work, were equilibrated for 3 hours at 50 °C prior to the addition of polyurethane foam blocks.

4.3 THE SEPARATION OF RHODIUM AND IRIDIUM USING POLYURETHANE FOAMS.

The ease with which platinum and iridium can be separated has been demonstrated in Section 3.3. However, the separation of rhodium and iridium is generally known to be difficult. Iridium in the form $IrCl_6^{3-}$ is strongly retained by anion exchange resins and is not quantitatively removed by either concentrated acids or bases [4]. Partial separation of rhodium and iridium is obtained by counter-current extraction using dilute HCl and TBP as the two phases [14]. Platinum is quantitatively separated from palladium and from rhodium using this method. Al-Bazi and Chow have achieved a number of noble metal separations using thiocyanate-polyurethane foam systems [69-72]. However, these authors could not quantitatively separate rhodium and iridium [67] without the addition of a large excess of lithium chloride [68].

Preliminary studies of the solvent extraction of iridium into MIBK indicated that 5% iridium, after 2 hours equilibration time with stannous chloride (R_a(Ir) = 20)

at 50 °C, was extracted into the organic phase. No iridium was extracted under the same conditions for solutions containing R_a(Ir) values of less than 20. A study of the separation of rhodium and iridium using polyurethane foams was undertaken. The effect of the R_a(Rh, Ir) (where (Rh,Ir) = sum of the moles of precious metals taken) on the separation of these metals was investigated.

Dilute hydrochloric acid solutions containing a Rh:Ir mole ratio of 1, and the desired amounts of stannous chloride were equilibrated for 3 hours at 50 °C. These solutions were each shaken with an excess of 400 mg of polyurethane foam. The digest foam solutions and aqueous phases were analysed for both metals by AAS. The results are shown in Table 4.3.

R_a(Rh, Ir)	Rhodium found/mg on foam	Rhodium found/mg in solution	Iridium found/mg in solution
10(4)	1,96 ± 0,07(78%)	0,48 ± 0,09(19%)	4,66 ± 0,07(100%)
15(3)	2,38 ± 0,03(95%)	0,03 ± 0,02(1,2%)	4,55 ± 0,10(97%)
20(4)	2,39 ± 0,07(96%)	0,03 ± 0,01(0,9%)	4,66 ± 0,07(100%)
25(4)	2,29 ± 0,07(92%)	0,06 ± 0,02(2,3%)	4,69 ± 0,10(101%)

Table 4.3 The effect of R_a(Rh, Ir) on the separation of rhodium and iridium using polyurethane foams. Experimental Conditions: volume of solutions = 100 ml, [HCl] = 2M, initial mass Rh = 2,5 mg, initial mass Ir = 4,67 mg, mass foam blocks = 400 mg, equilibration of 3 hours at 50 °C (Appendix 7a).

At R_a(Rh, Ir) = 10, only 78% rhodium was extracted onto the foam, whereas for R_a(Rh, Ir) values of 15 and 20, 96% rhodium was sorbed. The rate of formation of the chloro-(trichlorostannato)-rhodium(III/I) complexes and their subsequent sorption by polyurethane foams increases with increasing Sn:Rh mole ratios [210]. We

have shown that 3 hours equilibration at 50 °C is sufficient for the quantitative extraction of rhodium from solutions containing R_a(Rh) of 50. However, this equilibration period appears not to be sufficient for R_a(Rh, Ir) values of 10.

Essentially quantitative separation of rhodium and iridium has been achieved by selective sorption by the polyurethane foam of the chloro-(trichlorostannato) rhodium(III/I) complex anions for R_a(Rh, Ir) values greater than 10. Under these conditions of sorption, no iridium could be detected on the foam. Analysis of the aqueous phases for residual rhodium content showed that a mean of 38 µg Rh (n = 11) remained in solution; this amount accounts for 1,5% of the total mass of rhodium present.

The sums of the amounts of rhodium detected in the digest foam solutions and in the aqueous phases equalled at most 97% of the initial rhodium taken. Given the method of quantifying rhodium, as well as the possibilities of mechanical losses and other experimental errors, a relative standard deviation of 2,5% is estimated for the determination of rhodium. Within this experimental error, the recovery of rhodium is satisfactory.

The effect of shaking time on the recovery of rhodium from solutions containing iridium using polyurethane foams was also investigated. The rhodium-iridium-tin(II) solutions were pre-equilibrated for 3 hours at 50 °C prior to the addition of the polyurethane foam blocks. The shaking period was varied between 1,5 and 4,5 hours. Results are shown in Table 4.4

The period for which rhodium-iridium-tin(II) solutions are shaken in contact with the polyurethane foam blocks appears to have little effect on the extraction of rhodium by the foams. A mean of 3% Rh (n = 15) remained in the aqueous phases. The reason for this small amount of rhodium not being sorbed by polyurethane foams is

unknown. Possible reasons could be that the pre-equilibration period is not sufficient for R_a(Rh, Ir) of 20 or that iridium may inhibit the extraction of rhodium complex anions in some manner. A possible inhibition reaction may be due to the reduction of iridium(IV) to iridium(III) by Sn(II). A further possibility is that the overall thermodynamics of the sorption process of rhodium may be such that no more rhodium can be extracted, i.e. the rhodium-tin(II)-polyurethane foam system is at the limit of the overall thermodynamic distribution.

shaking time/ hours	Rhodium found/mg on foam	in solution	Iridium found/mg in solution
1,5(4)	2,36 ± 0,03(94%)	0,05 ± 0,04(2,1%)	4,48 ± 0,05(96%)
2,0(3)	2,34 ± 0,22(94%)	0,11 ± 0,07(4,3%)	4,48 ± 0,16(96%)
3,0(4)	2,47 ± 0,08(99%)	0,03 ± 0,06(1,2%)	4,64 ± 0,08(99%)
4,5(4)	2,35 ± 0,06(94%)	0,06 ± 0,04(3,9%)	4,50 ± 0,13(96%)

Table 4.4 The effect of shaking time on the extraction of rhodium from solutions containing iridium by polyurethane foams. Experimental Conditions: volume of solutions = 100 ml, initial mass Rh = 2,50 mg, initial mass Ir = 4,67 mg, R_a(Rh, Ir) = 20, mass of foam blocks = 400 mg, pre-equilibrated for 3 hours at 50 °C (Appendix 7b).

The separation of rhodium and iridium at an Ir:Rh mole ratio of 10 was attempted under similar conditions to those described above. One might expect that if iridium is inhibiting the sorption of rhodium by polyurethane foam, then a greater excess of iridium should further reduce the quantity of rhodium extracting onto the foams. The results of this experiment are given in Table 4.5.

	Rhodium	Iridium
mass taken/mg[a]	2,50	46,70
mass found (on foam/mg)	2,34 ± 0,04(94%)	N/D[b]
mass found (in solution/mg)	N/D	46,72 ± 1,21(100%)

(a) : Number of determinations = 8.
(b) : N/D = not detected.

Table 4.5 The separation of rhodium and iridium at Ir:Rh mole ratio of 10 by polyurethane foams. Experimental Conditions: volume of solution = 200 ml, [HCl] = 2M, R_a(Rh, Ir) = 20, mass of foam blocks = 400 mg, pre-equilibrated for 3 hours at 50 °C (Appendix 7c).

A mean recovery of 94% Rh (n = 8) is obtained in the extraction of rhodium from solutions containing a 10-fold molar excess of iridium. No residual rhodium could be detected in the aqueous phases by AAS as the solutions were too dilute. The results obtained correspond very closely to those obtained for Ir:Rh mole ratios of 1. This suggests that the presence of iridium may not be inhibiting the extraction of rhodium by the foams, but rather that the conditions for sorption do not allow the final residual 50 µg Rh onto the foam.

4.4 THE SEPARATION OF RHODIUM FROM RUTHENIUM BY POLYURETHANE FOAMS.

Wyrley-Birch [178] has studied the extraction of rhodium and ruthenium in the form of chloro-(trichlorostannato) complex anions from dilute acid solutions into MIBK/hexane mixtures. The best separation of rhodium from ruthenium occurred from aqueous phases consisting of 3,5M H^+ and 0,5M Cl^- (hydrochloric and perchloric acid mixtures).

The separation of rhodium and ruthenium by polyurethane foams was attempted. The desired amounts of rhodium and ruthenium trichlorides (for a Ru:Rh mole ratio of 1)

were equilibrated for 3 hours at 50 °C with tin(II) chloride in solutions containing various H^+ and Cl^- ion concentrations. The solutions were removed from the waterbath and polyurethane foam blocks were added. The foams were shaken in contact with these solutions for a period of 90 minutes. The foam digest solutions and the aqueous phases were analysed by AAS for rhodium and ruthenium. Typical results obtained for these experiments are given in Table 4.6.

[Acid]	Rhodium found[a] on foam/mg	Rhodium found in solution/mg	Ruthenium found on foam/mg	Ruthenium found in solution/mg
2M HCl(6)	1,37 ± 0,09(55%)	1,14 ± 0,08(46%)	N/D	2,44 ± 0,04(99%)
	2,36 (94%)	0,10 (4%)	N/D	2,40 (98%)
2M HCl(6)	1,15 ± 0,06(46%)	1,35 ± 0,10(54%)	N/D	2,47 ± 0,03(101%)
	2,32 (93%)	0,13 (5%)	N/D	2,43 (99%)
3,5M H^+, 0,5M Cl^- (4) ($HCl/HClO_4$)	1,95 ± 0,08(78%)	0,51 ± 0,08(20%)	0,04 ± 0,01(2%)	2,40 ± 0,06(98%)
	2,35 (94%)	0,14 (6%)		2,39 (97%)
3,5M H^+, 0,5M Cl^- (6) (HCl/H_2SO_4)	1,54 ± 0,03(62%)	0,95 ± 0,05(38%)	N/D	2,44 ± 0,05(99%)
	2,32 (93%)	0,22 (2%)	N/D	2,47 (101%)

(a) The figure below each mean mass of rhodium/ruthenium found represents a sample containing either rhodium or ruthenium only as a means of comparison.

Table 4.6 The effect of acid concentrations on the separation of rhodium and ruthenium using polyurethane foams. Experimental Conditions: volume of solutions = 150 ml, initial mass Rh = 2,50 mg, initial mass Ru = 2,46 mg, R_a(Rh, Ru) = 50, mass of foam blocks = 400 mg, pre-equilibrated for 3 hours at 50 °C (Appendix 8a).

Two identical sets of experiments were performed for the extraction of rhodium from 2M HCl solutions containing

ruthenium, on two different days. One set of samples yielded a mean recovery of 54,9 ± 3,7% Rh (n = 6) from the digested foam solutions while the other yielded a mean recovery of 45,9 ± 2,2% Rh (n = 6). The cause of the different results obtained is not known. Various causes for the discrepancies are possible.

The ambient temperature may have differed so that the rate of cooling of the two sets of solutions would differ. Although this temperature range could be slight, it is possible that this could have affected the amount of rhodium extracted by the polyurethane foams.

As two different tin(II) solutions were used, it is possible that one solution may have been inadvertently exposed to air for a short time, resulting in a decrease in the concentration of Sn(II). It has been shown that the rate of formation of extractable chloro-(trichlorostannato)-rhodium(III/I) complex anions is dependent on the concentration of tin(II) [178].

Ruthenium(III) is reduced to ruthenium(II) by tin(II) [209]. Under slightly varying conditions, this reduction may occur to different extents, resulting in different amounts of tin(II) available to react with rhodium to form extractable complex anions.

A further reason could be that, although fresh rhodium trichloride stock solutions were prepared each week, rhodium may still age sufficiently in this period to affect the rate of formation of the chloro-(trichlorostannato)-rhodium(III/I) complex anions and hence the subsequent sorption of these anions by polyurethane foams.

Raising the H^+ ion concentration to 3,5M and lowering the Cl^- ion concentration to 0,5M results in an increase in the amount of rhodium sorbed by the foams. Mean recoveries of 78 ± 3% and 62 ± 1% of the total rhodium content were achieved from mixtures of $HCl/HClO_4$ and mixtures of HCl/H_2SO_4 respectively. The presence of sulphate ions, however, appears to inhibit the sorption

of rhodium as compared with the extraction of rhodium from solutions containing ClO_4^- ions. Rhodium(III) is thought to form complex sulphates [211], although no species have been identified. Analogous iridium complexes have been isolated and identified as $[Ir_3O(SO_4)_9]^{10-}$ [212]. The sulphate ions present in solution may also slow the rate of formation of extractable chloro-(trichlorostannato)-rhodium(III/I) complex anions.

No ruthenium could be detected on the foams except from the solutions containing perchloric acid. Under these conditions, 2% Ru was extracted onto the foam. Within experimental error, satisfactory mass balance for rhodium and ruthenium was achieved for all conditions.

The effect of sulphate ions on the extraction of rhodium in the presence of ruthenium by polyurethane foams was further investigated. Solutions containing the desired amounts of rhodium, ruthenium, tin(II) chloride, HCl and H_2SO_4 were equilibrated for 16 hours at 50 ^oC prior to the addition of polyurethane foams. Results of this experiment are given in Table 4.7.

	Rhodium	Ruthenium
Mass taken/mg[a]	2,50	2,46
Mass found (on foam/mg)	2,29 ± 0,04(91%)	2,47 ± 0,03(100%)
Mass found (in solution/mg)	0,15 ± 0,03(6%)	N/D

(a) Number of determinations = 6

Table 4.7 The separation of rhodium and ruthenium by polyurethane foams from solutions containing mixtures of HCl and H_2SO_4 to give a H^+ and Cl^- ion concentration of 3,5M and 0,5M respectively. Experimental Conditions: volume of solutions = 150 ml, R_a(Rh, Ru) = 50, mass of foam blocks = 400 mg, pre-equilibrated for 16 hours at 50 ^oC. (Appendix 8b).

Under these conditions, 91% of Rh is sorbed by polyurethane foams from solutions containing ruthenium. An average of 6% Rh was retained in the aqueous phases together with the total amount of ruthenium.

4.5 THE RECOVERY OF RHODIUM FROM SOLUTIONS CONTAINING IRIDIUM AND RUTHENIUM USING POLYURETHANE FOAMS.

The recovery of rhodium from solutions containing iridium or ruthenium has been demonstrated with good results. It was thus decided to investigate the separation of rhodium from synthetic mixtures containing both ruthenium and iridium.

The required amounts of noble metals representing a Rh:Ru:Ir mole ratio of 1 and known amounts of excess stannous chloride were added to solutions containing mixtures of hydrochloric and sulphuric acids to give a final H^+ ion concentration of 3,5M and a final Cl^- ion concentration of 0,5M. These solutions were then pre-equilibrated at 50 °C for 16 hours. Results are shown in Table 4.8

Mass taken	Mass found on foam/mg	Mass found in solution/mg
2,5mg Rh + 2,46mg Ru + 4,67mg Ir (8)	Rh 2,29 ± 0,05(92%)	Rh 0,03 ± 0,007(1,3%)
		Ru 2,45 ± 0,04(98%)
		Ir 5,65 ± 0,08(121%)

Table 4.8 The recovery of rhodium from synthetic mixtures containing ruthenium and iridium following sorption by polyurethane foams. Experimental Conditions: volume of solutions = 150 ml, R_a(Rh, Ru, Ir) = 50, 400 mg foam blocks used, HCl/H_2SO_4 mixtures to give $[H^+]$ = 3,5M, $[Cl^-]$ = 0,5M, pre-equilibrated for 16 hours at 50 °C. (Appendix 9).

The mean recovery of 92% rhodium obtained for this experiment, results of which are shown in Table 4.8, is very similar to the mean recovery of 91% Rh obtained from extracting rhodium by polyurethane foams from

solutions containing ruthenium (Table 4.7). Less than 2% Rh could be detected in the aqueous phases. If one considers the mean recovery of 2,29 mg Rh from the foams to be correct, then the aqueous solutions contained at most 0,31mg or 1,5ppm rhodium. The sensitivity of rhodium in this concentration range is poor and hence the means of quantification of rhodium in this work may not be sufficiently sensitive to detect these small amounts of rhodium.

Under the above conditions of sorption, no ruthenium or iridium could be detected on the foams. A mean recovery of 121 $\pm$ 2% iridium was obtained from the aqueous solutions. The absorbance of iridium in 3,5M H^+ and 0,5M Cl^- solutions was found to be approximately half as sensitive, and the signal:noise ratio greater than for solutions of iridium in 2M HCl (Figure 2.7). The presence of ruthenium in these solutions causes a further depressive effect on the absorbance of iridium (Table 2.13). The blank absorbance value (solution containing 3,5M H^+ and 0,5M Cl^-, added as an HCl/H_2SO_4 mixture, and 0,2% w/v $La(NO_3)_3$) obtained for iridium was 0,015 as compared to a maximum value of 0,002 obtained for solutions containing 2M HCl. Blank absorbance values for Rh, Ru and Pt in any of the media used throughout this work, i.e. 2M HCl, 3,5M H^+ and 0,5M Cl^-, or mixtures of HCl and ethanol, had maximum values of 0,002. These observations suggest that AAS is not a good method of analysis for iridium in solutions containing high H^+ ion and low Cl^- ion concentrations.

CHAPTER 5

CHAPTER 5

5. THE EXTRACTION/SEPARATION OF PLATINUM AND RHODIUM USING POLYURETHANE FOAMS.

The sorption of chloro-(trichlorostannato)-platinum(II) and -rhodium(III/I) complex anions from dilute hydrochloric acid solutions using polyurethane foams as extractants has been achieved. The feasibility of the selective extraction of one of these metals by polyurethane foams from solutions containing both platinum and rhodium was of great interest.

5.1 THE SORPTION OF PLATINUM AND RHODIUM BY POLYURETHANE FOAMS.

The rate of formation of the extractable chloro-(trichlorostannato)-platinum(II) complex anions at room temperature in 2M HCl is relatively rapid, provided that an excess of tin(II) chloride is present (R_a(Pt) > 10). Under these conditions, no pre-equilibration of the platinum-tin solutions is required prior to the addition of the polyurethane foams. On the other hand, the rate of formation of extractable chloro-(trichlorostannato)-rhodium(III/I) complex anions, under the same conditions, is somewhat slower. Rhodium-tin(II) solutions require a pre-equilibration period of either 16 hours at room temperature [178] or 3 hours at 50 ^{o}C for the complete extraction of rhodium.

It was decided to investigate whether this difference in the rates of formation of the extractable species could be used to obtain quantitative separations of platinum and rhodium using polyurethane foams.

Dilute hydrochloric acid solutions containing the desired amounts of platinum, rhodium, stannous chloride and foam were shaken for 90 minutes at room temperature. It was hoped that the selective sorption of platinum onto the polyurethane foam blocks would take place under these conditions. Table 5.1 shows the results of the

recoveries of platinum and rhodium extracted by the foams and the amounts retained in the aqueous phases.

Mass taken	Mass found[a] on foam/mg	%	in solution/mg	%
4,74 mg Pt + 2,50 mg Rh(6)	Pt 4,58 ± 0,05	97	N/D	
	Rh 1,71 ± 0,28	68	Rh 0,76 ± 0,25	30
4,74 mg Pt(1)	Pt 4,65	98	N/D	
2,50 mg Rh(1)	Rh 1,62	65	Rh 0,92	37

(a) N/D = not detected.

Table 5.1 The recovery of platinum and rhodium, following sorption by polyurethane foams at room temperature. Experimental Conditions: volume of solutions = 200 ml, Pt:Rh mole ratio = 1, R_a(Pt, Rh) = 30, [HCl] = 2M, mass of foam blocks = 400 mg, shaken at room temperature for 90 minutes (Appendix 10a).

Under optimum conditions for the quantitative sorption of chloro-(trichlorostannato)-platinum(II) complex anions, 97 ± 1% Pt and 68 ± 11% Rh were found to extract onto the polyurethane foams (Table 5.1). A single element control for each metal was loaded onto a polyurethane foam block under identical conditions. Each control falls within the 99% confidence interval calculated for the recoveries obtained from the foam digest solutions containing both rhodium and platinum. These results suggest that there is no significant difference in the amounts of platinum and rhodium sorbed by polyurethane foam, either from mixed solutions or from solutions containing only one noble metal. A separate study of the sorption of rhodium by polyurethane foams yielded a mean recovery of 67 ± 2,5% Rh (n = 3) extracted by the foams from dilute hydrochloric acid solutions under identical conditions (Table 4.1). This is further evidence that the sorption of rhodium is not inhibited or enhanced by the presence of platinum.

The quantitative extraction of both the chloro-(trichlorostannato)-platinum(II) and -rhodium(III/I) complex anions was subsequently investigated. The optimum conditions for quantitative sorption of rhodium were employed, i.e. the Pt-Rh-Sn(II) solutions were pre-equilibrated for 3 hours at 50 °C prior to the addition of polyurethane foams. Table 5.2 shows the results obtained under these conditions.

Mass taken	Mass found on the foam			
	Platinum/mg	%	Rhodium/mg	%
4,74 mg Pt + 2,5 mg Rh(6)	4,77 ±0,08	101	2,38 ± 0,02	95
4,74 mg Pt(1)	4,85	102		
2,5 mg Rh(1)			2,49	100

Table 5.2 The recoveries of platinum and rhodium, following sorption by polyurethane foams after a pre-equilibration period of 3 hours at 50 °C. Experimental Conditions: volume of solutions = 200 ml, Pt:Rh mole ratio = 1, R_a(Pt, Rh) = 50, [HCl] = 2M, mass of foam used = 500 mg, pre-equilibrated at 50 °C for 3 hours (Appendix 10b).

Under the optimum conditions found for the extraction of rhodium, 101 ± 2% Pt and 95 ± 1% Rh were found to extract onto polyurethane foams (Table 5.2). Single element controls for each metal were loaded onto polyurethane foam blocks under identical conditions. A slightly higher recovery (100%) was obtained for rhodium sorbed by polyurethane foams in the absence of platinum. However, this value does fall within the 99% confidence interval calculated for the recoveries of rhodium obtained from the foam digest solutions containing platinum. Under these conditions of sorption, no rhodium or platinum could be detected in the aqueous solutions.

5.2 THE SEPARATION OF PLATINUM AND RHODIUM FROM IRIDIUM USING POLYURETHANE FOAMS.

Iridium is not co-sorbed by polyurethane foams under either the optimum conditions for the extraction of platinum (Section 3.4) or for the extraction of rhodium (Section 4.3). Nor does its presence in solution interfere with the quantitative extraction of these metals. Hence, it is reasonable to expect the quantitative extraction of platinum, partial sorption of rhodium (*ca.* 65%) and no extraction of iridium by polyurethane foams from solutions containing all 3 metals which are not pre-equilibrated prior to the addition of the foams, to be analogous to the "extraction" of each metal separately. Furthermore one could expect quantitative extraction of platinum and rhodium and no sorption of iridium from solutions which are pre-equilibrated for 3 hours at 50 ^{o}C prior to the addition of polyurethane foams. A study of the latter expectation was undertaken. Results are shown in Table 5.3.

It may be seen from Table 5.3 that within experimental error, quantitative extraction of the chloro-(trichlorostannato)-platinum(II) and -rhodium(III/I) complex anions by polyurethane foams have been achieved from solutions containing iridium. Under these conditions, no rhodium or platinum could be detected in the aqueous solutions while no iridium was detected in the foam digest solutions.

	Platinum mg	%	Rhodium mg	%	Iridium mg	%
Mass taken[a]	4,74		2,50		4,67	
Mass found on foam	4,66 ± 0,06	98	2,44 ± 0,05	98	N/D	
Mass found in solution	N/D		N/D		4,63 ± 0,08	99

a *Number of determinations = 6.*

Table 5.3 The recoveries of platinum and rhodium, following sorption by polyurethane foams from solutions containing iridium. Experimental Conditions: volume of solutions = 200 ml, Pt:Rh:Ir mole ratio = 1, R_a(Pt, Rh, Ir) = 50, [HCl] = 2M, mass of foam used = 500 mg, pre-equilibrated at 50 °C for 3 hours (Appendix 11).

5.3 THE EXTRACTION OF PLATINUM BY POLYURETHANE FOAMS FROM SOLUTIONS CONTAINING RHODIUM AND RUTHENIUM.

The complex formation of ruthenium-tin(II) species is incomplete and/or very slow at room temperature, and prolonged heating at 100 °C is required to produce extractable chloro-(trichlorostannato)-ruthenium(II) complex anions [178]. This difference in the behaviour of platinum and ruthenium can conveniently be exploited to achieve excellent separation of these metals (Section 3.5). However, ruthenium appears to inhibit the formation and/or sorption of chloro-(trichlorostannato)-rhodium(III/I) complex anions. Under optimum conditions for the extraction of rhodium by polyurethane foams, only approximately 50% Rh was sorbed from solutions containing ruthenium (Section 4.4).

It was thus decided to investigate the possible selective sorption of platinum by the polyurethane foams from solutions containing both rhodium and ruthenium.

The required amount of noble metals to give a Pt:Rh:Ru mole ratio of 1, tin(II) chloride and polyurethane foams were mechanically shaken in 2M HCl at room temperature for 90 minutes. The loaded foams were then decomposed with hot nitric acid. The foam digest solutions and aqueous phases were analysed by AAS for all three metals. The results of this experiment are shown in Table 5.4.

	Platinum		Rhodium		Ruthenium	
	mg	%	mg	%	mg	%
Mass taken[a]	4,74		2,50		2,46	
Mass found on foam	4,55 ± 0,05	95	0,28 ± 0,02	11	N/D	
Mass found in solution	N/D		2,12 ± 0,08	85	2,48 ± 0,08	101

(a) Number of determinations = 8.

Table 5.4 The separation of platinum from ruthenium and rhodium, using polyurethane foams. Experimental Conditions: volume of solution = 200 ml, Pt:Rh:Ru mole ratio = 1, R_a(Pt, Rh, Ru) = 50, [HCl] = 2M, mass foam used = 400 mg, shaken at room temperature for 90 minutes (Appendix 12).

It may be seen from Table 5.4 that the presence of ruthenium does inhibit the sorption of the chloro-(trichlorostannato)-rhodium(III/I) complex anions. Only 11 ± 1% Rh co-extracted onto the foam with 96 ± 1% Pt. Under these conditions of sorption, no platinum was detected in the aqueous solutions and no ruthenium was found in the foam digest solutions. A total of 96 ± 4% of all the rhodium in the system was detected, which is satisfactory given the method of quantifying rhodium as well as the possibilities of mechanical losses and other experimental errors. The relatively low platinum recovery of 96 ± 1% may be due to mechanical losses rather than platinum left in solution and not being

detected although a similar inhibition of the extraction of platinum by ruthenium cannot be ruled out.

5.4 THE EXTRACTION OF PLATINUM FROM COMPLEX NOBLE METAL MIXTURES BY POLYURETHANE FOAMS.

The final separation attempted was that of platinum from solutions containing rhodium, ruthenium and iridium. Solutions of 2M HCl containing the desired amounts of each metal, to give a Pt:Rh:Ru:Ir mole ratio of 1, stannous chloride and polyurethane foams were shaken at room temperature for 90 minutes. The solutions were not pre-equilibrated for any period of time to allow as little rhodium as possible to co-extract onto the foams. Results are given in Table 5.5

Mass taken	Mass found on foam/mg	%	Mass found in solution/mg	%
5,00 mg Pt + 2,64 mg Rh + 2,51 mg Ru + 4,93 mg Ir(8)	Pt 4,95 ± 0,10	99	N/D	
	Rh 0,21 ± 0,03	8	2,33 ± 0,03	88
	Ru N/D		2,57 ± 0,08	102
	Ir N/D		4,97 ± 0,08	101
4,74 mg Pt + 2,50 mg Rh + 2,46 mg Ru + 4,67 mg Ir(8)	Pt 4,63 ± 0,02	98	N/D	
	Rh 0,06 ± 0,02	2	2,38 ± 0,08	95
	Ru N/D		2,62 ± 0,07	107
	Ir N/D		4,59 ± 0,09	98

Table 5.5 The extraction of platinum from complex mixtures of noble metals. Experimental Conditions: volume of solutions = 200 ml, Pt:Rh:Ru:Ir mole ratio = 1, R_a(Pt, Rh, Ru, Ir) = 50, [HCl] = 2M, mass foam used = 400 mg, shaken at room temperature for 90 minutes. (Appendix 13).

The near quantitative extraction of platinum by polyurethane foams has been achieved; small amounts of rhodium are co-extracted onto the foams, but complete

separation of platinum from iridium and ruthenium has been achieved.

The experimental conditions employed for both sets of experiments given in Table 5.5 were identical, although one batch yielded a mean recovery of 8 ± 1% Rh and the other yielded a mean recovery of 2 ± 0,8% Rh. The cause of the difference of results obtained is not known. The two sets of experiments were performed on different days. The ambient temperatures may have differed which could affect the rate of formation of extractable rhodium-tin(II) chloride complex anions.

Ruthenium(III) is reduced to ruthenium(II) by tin(II) [209]. Under slightly varying conditions, this reduction may occur to different extents, resulting in different amount of tin(II) available to react with rhodium to form extractable complex anions. A further explanation could be that, although fresh rhodium trichloride stock solutions were prepared each week, rhodium may still age sufficiently in this period to affect the rate of formation of chloro-(trichlorostannato)-rhodium(III/I) complex anions and hence the subsequent sorption of these anions by polyurethane foams.

A high yield of 107 ± 3% Ru was obtained for one set of aqueous solutions. This may be due to standards and samples not being quite matrix matched.

CHAPTER 6

CHAPTER 6

6. THE STRIPPING OF LOADED POLYURETHANE FOAMS AND A PLATINUM APPLICATION USING POLYURETHANE FOAMS.

In order to avoid the time-consuming decomposition of the loaded foams, attempts were made to strip the chloro-(trichlorostannato)-platinum(II) and -rhodium (III/I) complex anions from intact polyurethane foams.

The possible use of polyurethane foams for the collection of small amounts of cisplatin ($PtCl_2(NH_3)_2$), a well established drug used in cancer chemotherapy, from artificial urine samples was also investigated.

6.1 PRELIMINARY FOAM STRIPPING INVESTIGATIONS.

Preliminary foam stripping experiments were performed on platinum-loaded foams to establish whether platinum could in fact be quantitatively desorbed from the polyurethane foams. Several eluents were tested by allowing the solution to pass through a small column filled with loaded polyurethane foam. The foam was manually squeezed using a glass rod.

The eluents tested include mixtures of hydrogen peroxide and dilute HCl; hydrogen peroxide and ethanol; as well as mixtures of concentrated HCl and acetone or ethanol, with and without H_2O_2. Figures 6.1 and 6.2 show the results obtained for these experiments.

The boiling H_2O_2/2M HCl mixture is not a very effective stripping reagent, as only 56% Pt is desorbed from the loaded polyurethane foam. Wetting the loaded foam with ethanol just prior to elution with the H_2O_2/2M HCl mixture improved the amounts of platinum recovered to 68% (Figure 6.1).

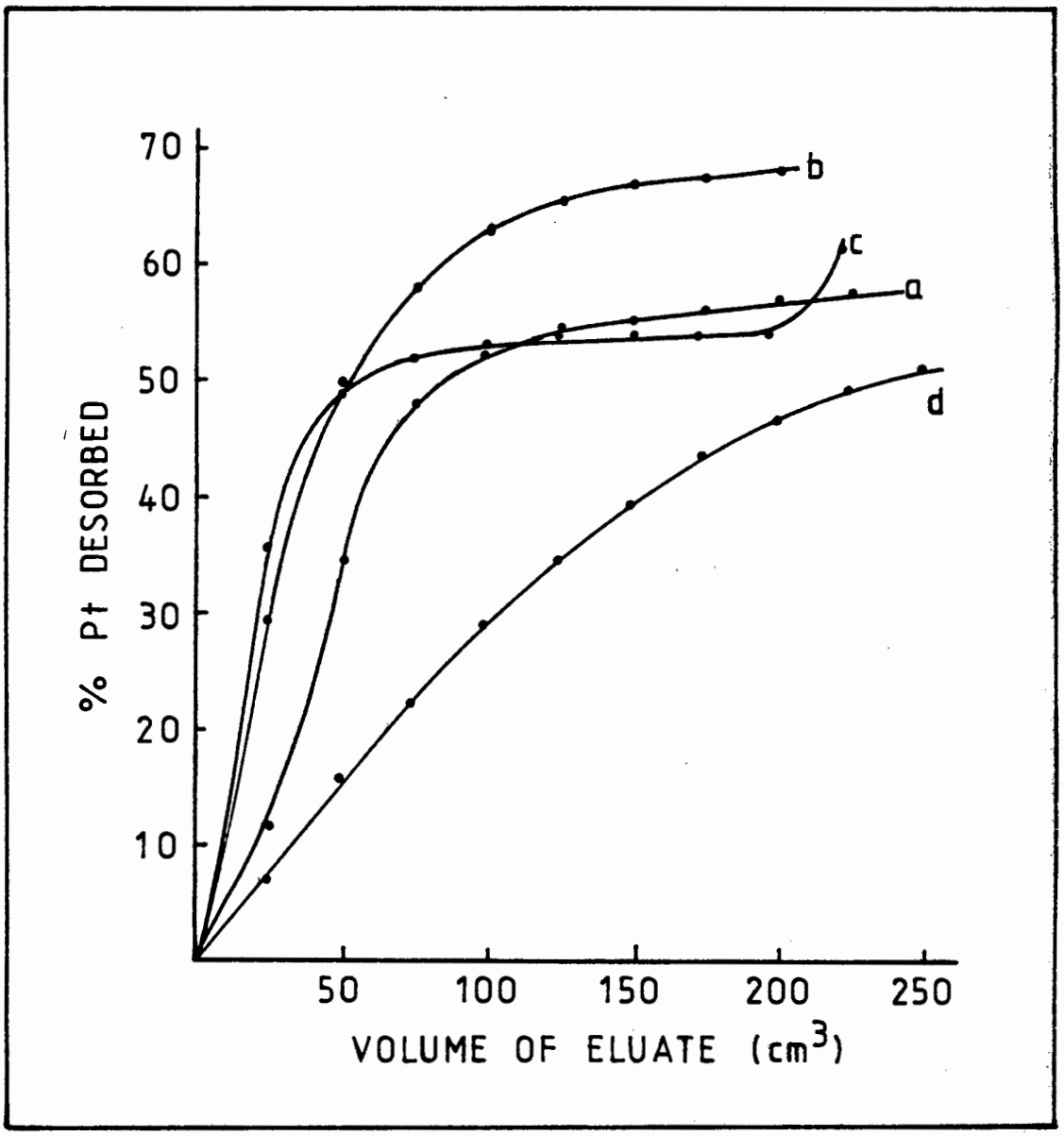


Figure 6.1 Stripping of Pt from loaded foams using: (a) boiling 5% v/v H_2O_2/2MHCl, (b) boiling 5% v/v H_2O_2/2M HCl (foam wetted with ethanol), (c) 5% v/v H_2O_2/ethanol, and (d) 5% v/v H_2O_2 + 5% v/v HCl in ethanol as eluents. (Appendix 14).

The overall stripping of platinum from the loaded polyurethane foams at room temperature is low. Atmost 70% of platinum was recoverable in a reasonable volume of eluent (Figure 6.1 and 6.2 curves a and b). A considerably better recovery of 91% was obtained using a hot (50 ^{o}C) mixture of concentrated 5% v/v HCl and ethanol as the eluent (Figure 6.2 curve c).

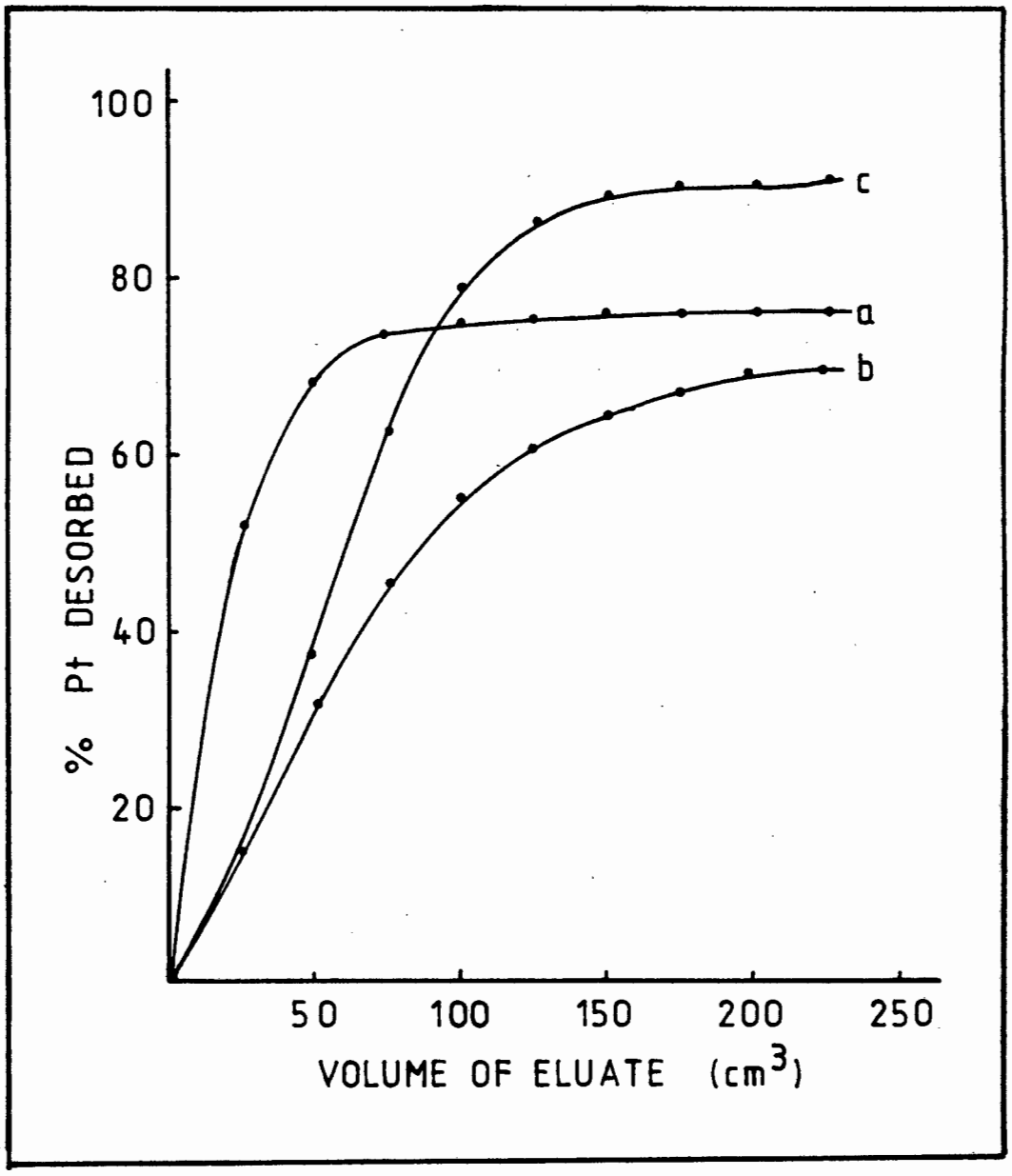


Figure 6.2 Stripping of Pt from loaded foams using (a) 5% v/v HCl/acetone, (b) 5% v/v HCl/ethanol, and (c) 5% v/v HCl/ethanol (50 °C) as eluents. (Appendix 14).

Mass balance for platinum was checked by dissolution of the stripped foam blocks, followed by analysis by AAS with matrix matched standards. Results can be seen in Table 6.1.

Stripping solution	Mass platinum found: volume /ml[a]	total in eluate/mg	%	on foam /mg	%	Total % Pt recovered
5% v/v H_2O_2 in 2M HCl	> 200	2,83	56	1,68	34	90
5% v/v H_2O_2 in 2M HCl (foam wetted with ethanol)	> 200	3,39	68	1,45	29	97
5% v/v H_2O_2 in ethanol	100	3,10	62	1,65	33	95
5% v/v H_2O_2 + 5% v/v HCl in ethanol	> 250	1,27	51	1,13	45	96
5% v/v HCl in acetone	75	3,80	76	0,99	20	96
5% v/v HCl in ethanol	> 200	3,47	69	1,08	25	94
5% v/v HCl in ethanol (50 °C)	175	2,28	91	0,02	1	92

(a) *Minimum volume eluate required for the bulk of platinum to be removed for a given eluent.*

Table 6.1 The recovery of platinum by foam stripping using various eluents, followed by foam degradation (Appendix 14)

Satisfactory mass balance of platinum was obtained if one considers the crudity of the method employed.

6.2 THE RECOVERY OF PLATINUM BY MEANS OF FOAM STRIPPING.

Preliminary studies have shown that essentially quantitative recovery of platinum can be achieved using hot mixtures of concentrated HCl and ethanol. In order to obviate mechanical loss of solution, a closed column with a pump system was employed. Details of the apparatus and method are given in Section 8.7.

Various mixtures of HCl and ethanol preheated to 70 ^{o}C, were tested. Results are shown in Figure 6.3.

The lowest recovery of 75% Pt was obtained by stripping the foam with hot ethanol solutions (70 ^{o}C) containing no hydrochloric acid. As the HCl content was increased, so the amount of platinum desorbed from the foam increased, reaching a maximum of approximately 95% Pt for 5% v/v HCl in ethanol. Increasing the HCl content to 10% v/v in ethanol had no significant effect on the amount of platinum stripped from the polyurethane foam.

It was noted that less eluent (25% of the volume of the other mixtures tested) was required to achieve near-quantitative desorption of platinum. Satisfactory mass balance of platinum was obtained by dissolution of the stripped foams, followed by analysis by AAS in the usual manner. See Table 6.2.

It is noteworthy that although stripping with hot ethanol/HCl mixtures results in elution of $\geq$ 95% of the total platinum, completely quantitative elution of platinum was not achieved. Small quantities of platinum (<5%) were always found to remain on the foam.

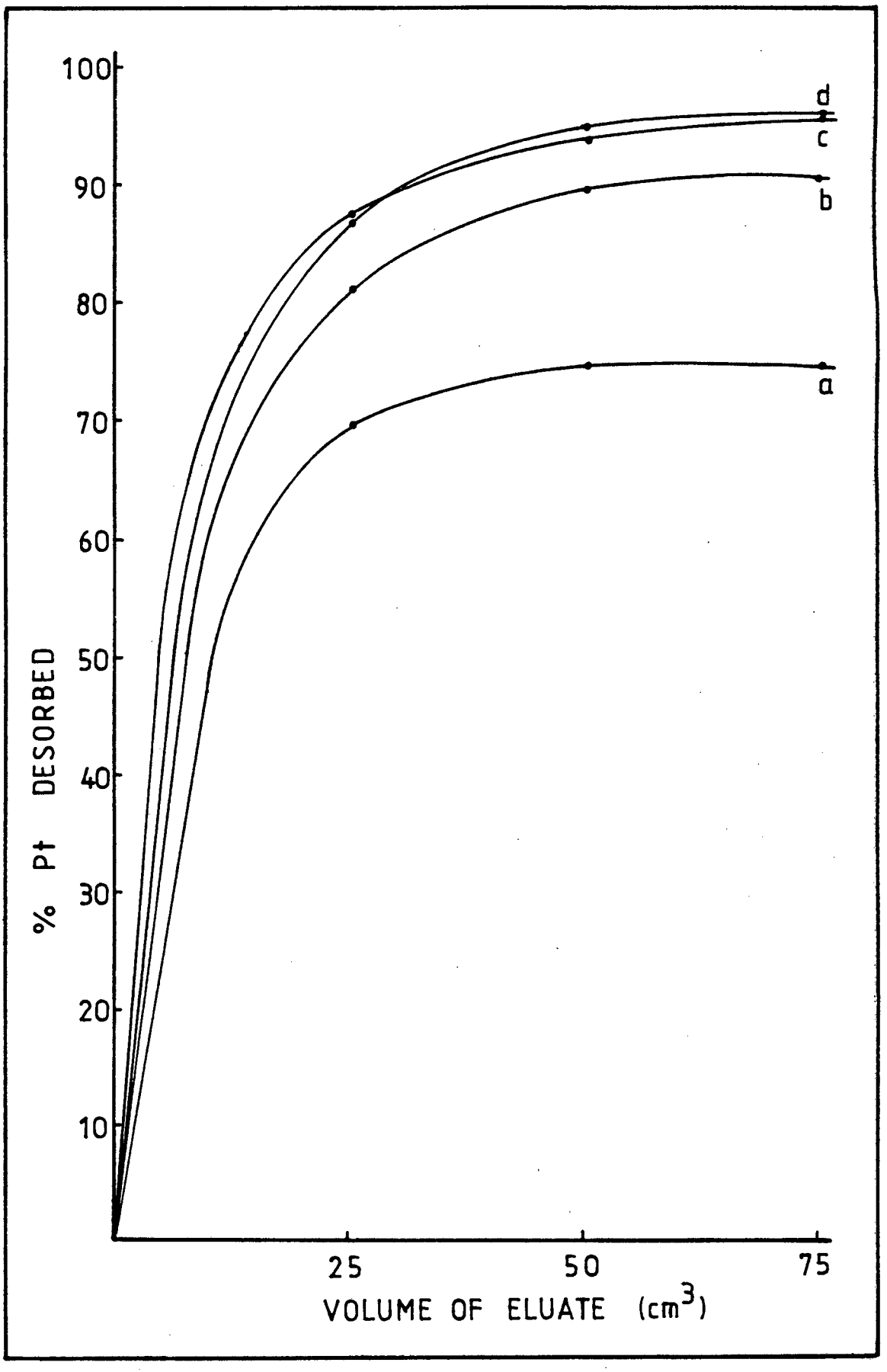


Figure 6.3 Stripping of Pt from loaded foams using the heated (70 °C) eluents: (a) ethanol, (b) 2,5% v/v HCl/ethanol, (c) 5% v/v HCl/ethanol, and (d) 10% v/v HCl/ethanol. (Appendix 15).

Stripping solution at 70 °C	Mass platinum found volume /ml[a]	total in eluate/mg	%	on foam /mg	%	Total % Pt recovered
ethanol	50	1,87	75	0,56	22	97
2,5% v/v HCl in ethanol	50	2,26	90	0,17	7	97
5% v/v HCl in ethanol	50	2,37	95	0,06	2	97
10% v/v HCl in ethanol	50	2,40	96	0,08	3	99

(a) Minimum volume required for the bulk of platinum to be removed for a given eluent

Table 6.2 The recoveries of platinum by foam stripping using various HCl/ethanol mixtures, followed by foam degradation (Appendix 15).

6.3 THE RECOVERY OF RHODIUM BY MEANS OF FOAM STRIPPING.

The possible stripping of rhodium-loaded polyurethane foams was also investigated. Mixtures of concentrated hydrochloric acid and ethanol were tested as eluents. Results are shown in Figure 6.4.

At room temperature (Figure 6.4 curve a) the rate of stripping of rhodium from the loaded foam is low, with atmost 87% of rhodium being recoverable in a relatively large volume of eluent (175 ml). However, for the same volume of the identical eluent, only approximately 62% of platinum was removed from the polyurethane foam by means of foam stripping (Figure 6.2 curve b). These results suggest that the platinum may be more strongly bonded to the foam phase than rhodium. The rate of rhodium stripped from polyurethane foams is increased with the use of hot ethanol (70 °C), although only 80% of rhodium appears to be removable from the foam using this eluent (Figure 6.4 curve b).

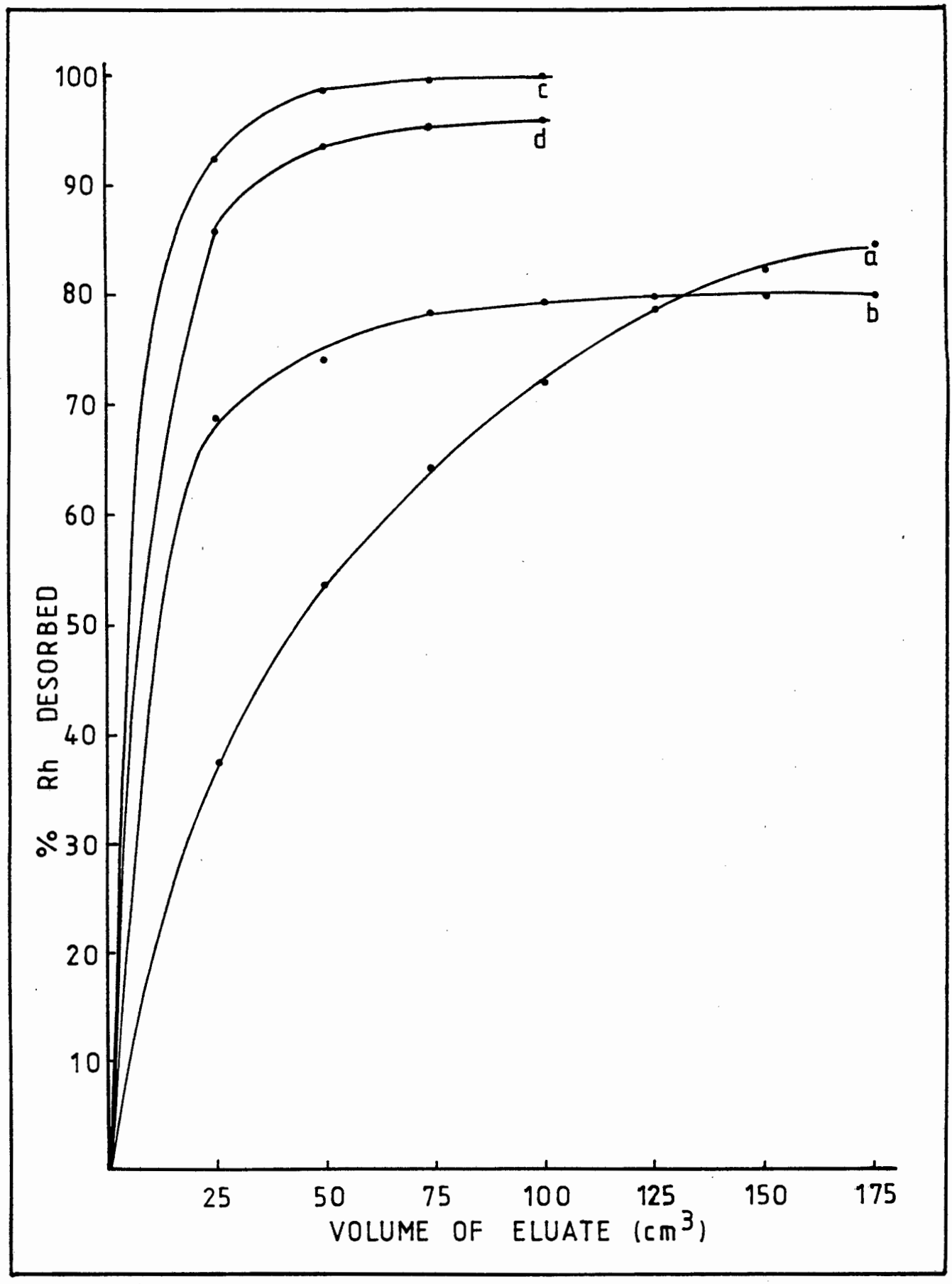


Figure 6.4 Stripping of Rh from loaded foams using (a) 5% v/v HCl/ethanol, (b) ethanol (70 °C), (c) 2% v/v and 10% v.v HCl/ethanol (70 °C) and (d) 5% v/v HCl/ethanol (70 °C) as eluents. (Appendix 16).

The addition of small volumes of concentrated HCl (2,5 - 10% v/v) to the hot ethanol solutions, further increases both the rate of removal of rhodium and the amount of rhodium stripped from the foams. The eluents containing 2,5% and 10% v/v HCl in ethanol yielded recoveries of >99% Rh, while the eluent containing 5% v/v HCl/ethanol yielded a recovery of 95% Rh. However, less than 1% Rh was detected in this foam solution (Table 6.3) which suggests that possible mechanical losses occurred. It can thus be concluded that there is no significant difference in the percentage of rhodium stripped from the loaded foam by mixtures of HCl and ethanol with HCl concentrations between 2,5 and 10% v/v.

Stripping solution	Mass volume /ml[a]	Rhodium found total in eluate/mg	%	on foam /mg	%	Total % Rh recovered
5% v/v HCl/ ethanol	> 175	2,16	86	0,40	16	102
Ethanol (70 °C)	75	1,99	80	0,49	19	99
2,5% v/v HCl/ ethanol (70 °C)	50	2,49	100	< 0,01	< 1	100
5% v/v HCl/ ethanol (70 °C)	50	2,39	96	0,02	< 1	96
10% v/v HCl/ ethanol (70 °C)	50	2,49	100	0,01	< 1	100

(a) Minimum volume required for the bulk of rhodium to be removed for a given eluent.

Table 6.3 The recoveries of rhodium by foam stripping using various HCl/ethanol mixtures, followed by foam degradation (Appendix 16).

It may be seen from Table 6.3 that satisfactory mass balance of rhodium has been achieved by dissolution of the stripped foams, followed by AAS analysis.

6.4 THE SEPARATION OF PLATINUM AND RHODIUM BY MEANS OF FOAM STRIPPING.

It has been shown that more than 95% Pt and 99% Rh can be removed from polyurethane foams loaded with platinum or rhodium respectively by means of foam stripping using hot (70 ^{o}C) mixtures of HCl and ethanol. One could predict that similar recoveries would be obtained by stripping polyurethane foam blocks loaded with both platinum and rhodium. This was investigated using a 10% v/v HCl/ethanol mixture. The effect of stannous chloride in the stripping solution on the amounts of platinum and rhodium removed from the loaded foams was also studied, in the hope of separating the two metals by this method. Results are shown in Figure 6.5.

It may be seen from Figure 6.5 curves Pt(a) and Rh(a) that essentially quantitative recoveries of both platinum and rhodium are achieved by eluting these metals from polyurethane foams using a mixture of 5% v/v HCl/ethanol preheated to 70 ^{o}C. The presence of excess stannous chloride in the eluent, calculated to give an approximate R_a(Pt, Rh) = 50, appears to slow down the removal of the metals from the loaded foam, as would be expected (curves Pt(b) and Rh(b)). It did not, however, cause one metal to be retained by the foam more strongly than the other.

Satisfactory mass balance of platinum and rhodium was obtained by dissolution of the stripped foams, followed by AAS analysis using matrix matched standards (Table 6.4).

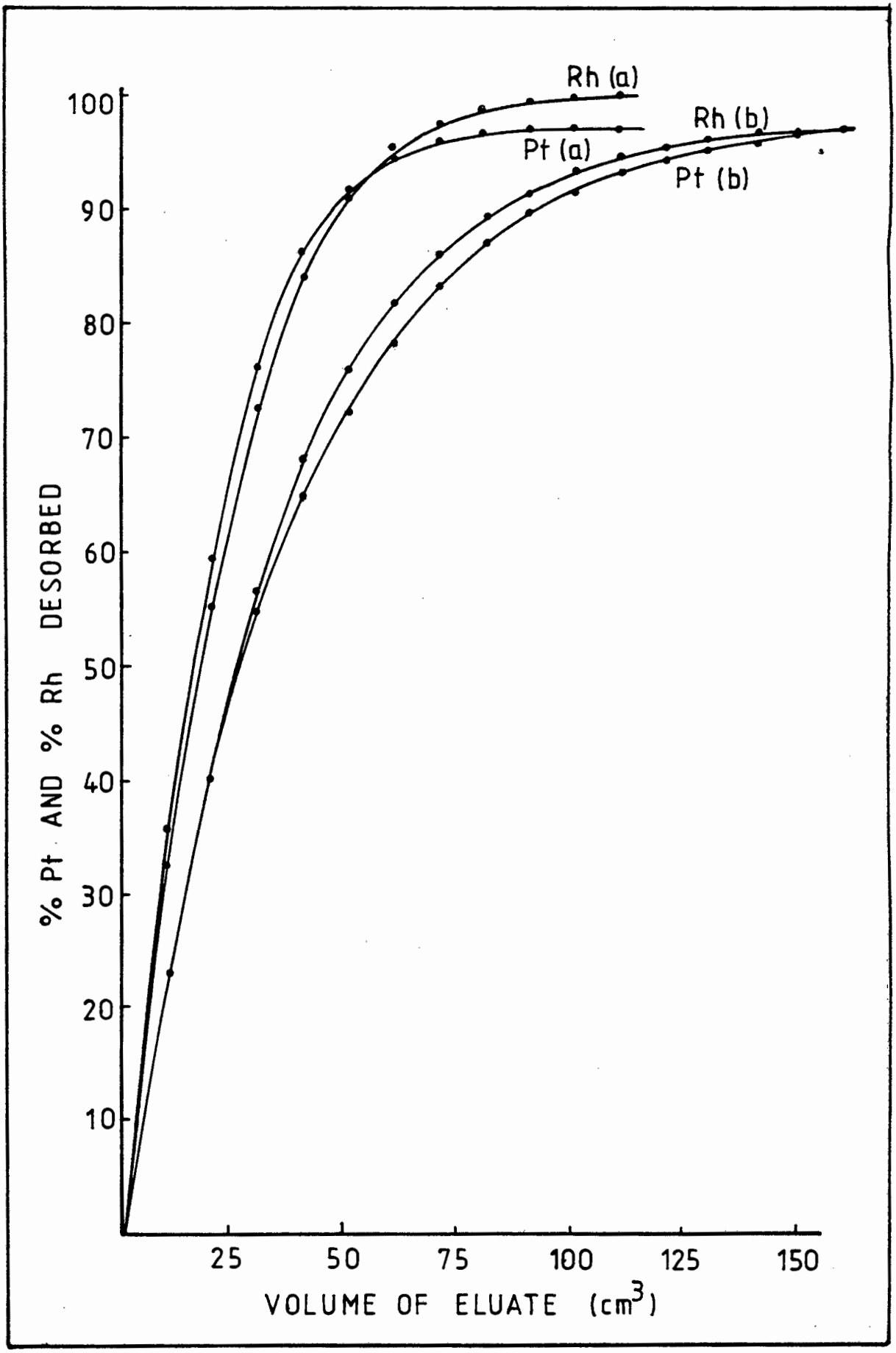


Figure 6.5 Striping of Pt-Rh-loaded foams using the heated (70 °C) eluents, (a) 5% v/v HCl/ethanol and (b) 5% v/v HCL/ethanol + $SnCl_2$. (Appendix 17a).

Stripping solution (70 °C)	Volume/ml[a]		Mass found total eluate/mg	%	on foam /mg	%	Total % recovered
5% v/v HCl/ ethanol	100	Pt	4,64	98	0,03	0,6	99
	100	Rh	2,52	101	N/D		101
5% v/v HCl/ ethanol + $SnCl_2$	200	Pt	4,65	98	0,02	0,4	98
	150	Rh	2,43	97	N/D		77

(a) *Minimum volume required for the bulk of platinum/ rhodium to be removed for a given eluent.*

Table 6.4 The recoveries of platinum and rhodium by foam stripping in the absence and presence of excess stannous chloride (R_a(Pt, Rh) = 50) (Appendix 17a).

A separation of platinum and rhodium was attempted following the quantitative sorption of both metals by polyurethane foams. Clean polyurethane blocks, representing double the mass of loaded foam (*ca.* 800 mg), were placed on top of the loaded foam blocks in the stripping apparatus. A mixture of 10% v/v HCl and ethanol, heated to 70 °C was passed through the foam in the usual manner. The effect of stannous chloride in the eluent was also investigated for this system. Results are shown in Figure 6.6

The presence of excess clean foam does not appear to retain one platinum metal more strongly than the other, either in the presence or absence of stannous chloride (Figure 6.6). The excess foam slowed the rate of desorption of both metals slightly, as did the presence of stannous chloride in the absence of excess foam (Figure 6.5). There does not appear to be any significant difference in the amounts of platinum and rhodium desorbed in the presence or absence of stannous chloride when using excess clean polyurethane foams.

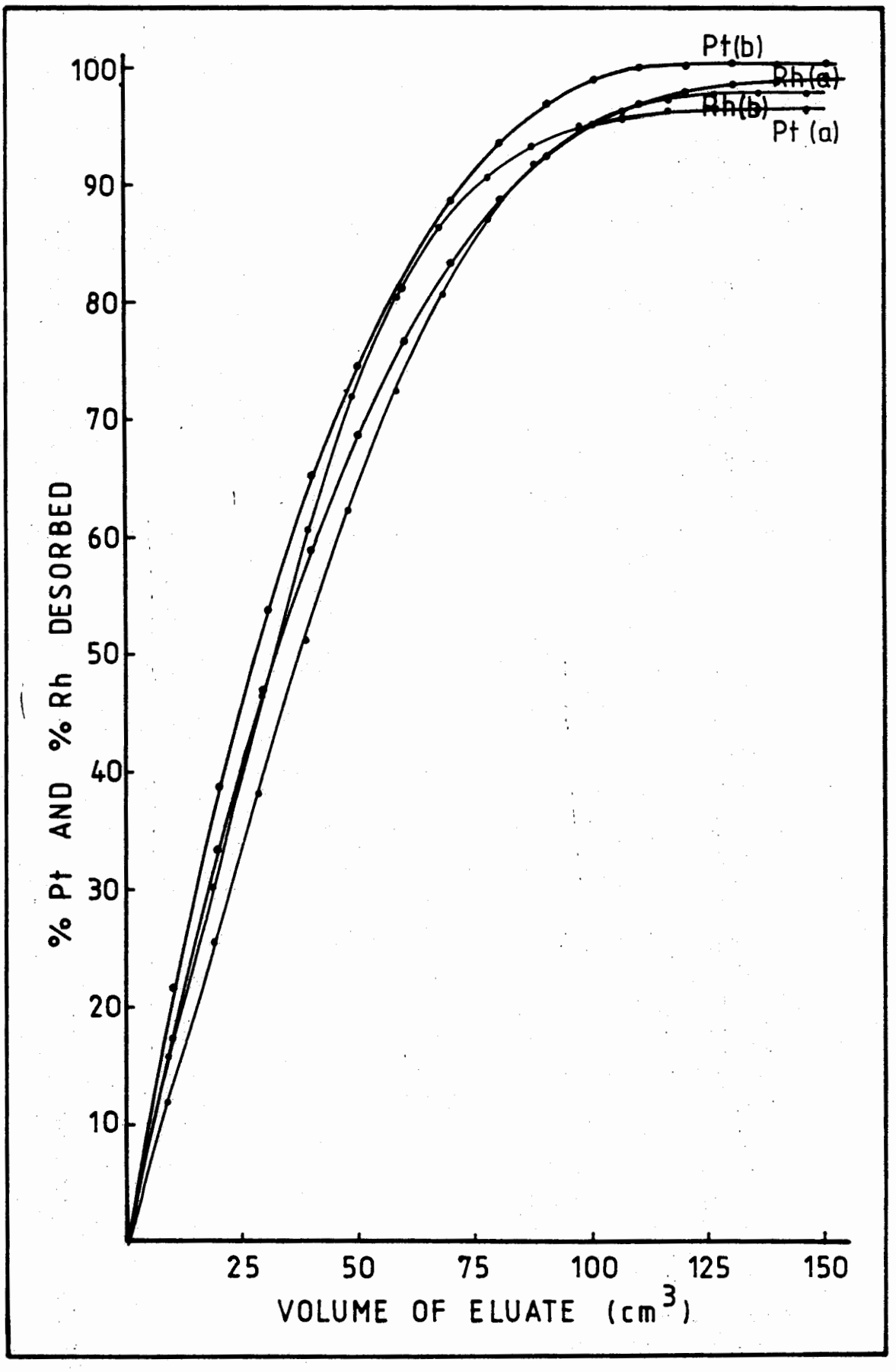


Figure 6.6 Stripping of Pt-Rh-loaded foams in a system containing excess (800 mg) clean polyurethane foams using (a) 5% v/v HCl/ethanol and (b) 5% v/v HCl/ethanol + $SnCl_2$. (Appendix 17b).

Stripping solution (70 °C)	Volume/ml[a]		Mass found total eluate/mg	%	on foam /mg	%	Total % recovered
5% v/v HCl/ ethanol	120	Pt	4,67	99	0,10	2	101
	140	Rh	2,49	100	< 0,01	< 0,1	100
5% v/v HCl/ ethanol + $SnCl_2$	120	Pt	4,81	101	< 0,01	< 0,1	101
	150	Rh	2,49	100	N/D		100

(a) Minimum volume required for the bulk of platinum/ rhodium to be removed by a given eluent

Table 6.5 The recoveries of platinum and rhodium by foam stripping in the absence and presence of stannous chloride (R_a(Pt, Rh) = 50), using excess clean polyurethane foam (Appendix 17b).

It appears that the separation of platinum and rhodium is not possible by means of foam stripping. The two metals follow similar desorption trends under identical conditions. It was noted that slightly more platinum (± 4%) was desorbed from loaded foams containing rhodium and platinum than from Pt-loaded foams alone. However, small amounts of platinum still remain on the foam.

6.5 AN APPLICATION - THE COLLECTION OF CISPLATIN USING POLYURETHANE FOAM.

The discovery of the antitumor activity of cisplatin, cis-$[PtCl_2(NH_3)_2]$ in 1969 generated considerable interest in the pharmacology of metal complexes, especially in the platinum systems [213]. More than 30 000 cancer patients in the United States of America are now being treated each year with a combination of drugs which includes cisplatin [214].

Low doses of 20 $mg.m^{-2}$-body surface area are administered to patients [211]. A quantity of the drug passes through the body and is excreted in the patients

urine. The feasibility of converting cisplatin to the tetrachloroplatinate anion, followed by the extraction of platinum in the presence of stannous chloride by polyurethane foams was studied.

Initially, we attempted to optimise the sorption of cisplatin, otherwise known as platinol, without adding artificial urine. The first experiment was carried out using the optimum conditions found for $PtCl_4^{2-}$ (2M HCl, R_a(Pt) = 40). The solutions containing platinol were equilibrated at room temperature for 20 minutes prior to the addition of polyurethane foams. The foams were then shaken in contact with the solutions for 2 hours. The loaded foams were decomposed using hot nitric acid and yielded a mean recovery of 10,6 $\pm$ 3,5% Pt (7 samples).

The effect of varying the HCl concentrations up to 6M, and increasing the Sn:Pt mole ratio to 100 was investigated. Results are shown in Figure 6.7.

The amount of platinum sorbed by polyurethane foam increases from approximately 10% to about 30% by altering the R_a(Pt) value from 40 to 100. Increasing the HCl concentration does not appear to affect the sorption of the platinum-tin(II) complex anions significantly (Figure 6.7).

The aqueous solutions were retained and analysed for the remaining platinum by AAS with matrix matched standards. Satisfactory mass balance was obtained as shown in Table 6.6.

An attempt to convert platinol into $PtCl_4^{2-}$ was made by boiling the cisplatin solutions with concentrated HCl to give a final HCl concentration of 3,5M, for 20 minutes prior to the addition of 2M HCl and tin(II) chloride (R_a(Pt) = 50). A mean recovery of 56 $\pm$ 4% Pt (n = 7) was achieved. A further attempt to quantitatively sorb platinum onto polyurethane foams was undertaken by heating the cisplatin solutions with HCl (to give a final [HCl] of 5M) for varying periods of time prior to the addition of excess tin(II) chloride

(R_a(Pt) = 100 or 10^3) and polyurethane foams. Results are shown in Table 6.7.

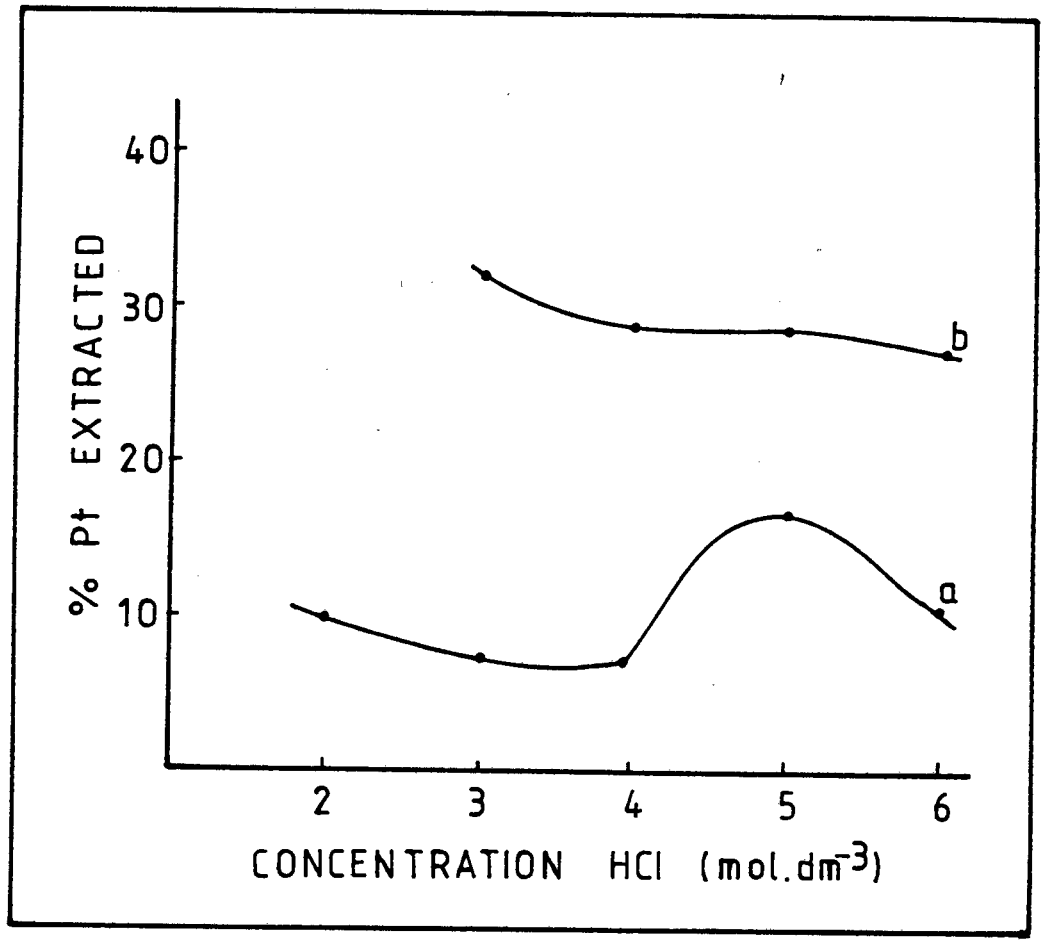


Figure 6.7 The effect of HCl concentration on amounts of Pt, added as $Pt(NH_3)_2Cl_2$ with (a) R_a(Pt) = 40 and (b) R_a(Pt) = 100, extracted by polyurethane foams.

[HCl]/M	R_a(Pt)	Platinum found on foam	%	in solution	%	Total % Pt recovered
2(7)	40	0,11 ± 0,03	11	0,90 ± 0,07	90	101
3	40	0,08	8	0,96	96	104
4	40	0,06	6	0,92	92	98
5	40	0,18	18	0,84	84	102
6	40	0,11	11	0,85	85	96
3	100	0,32	32	0,69	69	101
4	100	0,29	29	0,71	71	100
5	100	0,29	29	0,69	69	98
6	100	0,27	27	0,74	74	101

Table 6.6 The recoveries of platinum from foam digest and aqueous solutions. Experimental Conditions: volume of solutions = 200 ml, initial [Pt] = 1 mg, added as $PtCl_2(NH_3)_2$, mass of foam used 400 mg, equilibrated for 20 minutes at room temperature prior to foam addition, shaken for 2 hours.

The extraction of platinum (added as platinol) onto the polyurethane foams is increased as the heating period is increased. Essentially quantitative extraction occurs after preheating the solutions for 5 hours prior to the addition of tin(II) chloride (R_a(Pt) = 100) and polyurethane foams. Shorter periods of heating are required for solutions containing R_a(Pt) = 1000. As an example, after 30 minutes pre-equilibration 87% Pt was sorbed by the foams from solutions with R_a(Pt) = 100, whereas 95% Pt was sorbed from solutions with R_a(Pt) = 1000. Since the stannous chloride was added after heating, these results suggest that the presence of increasing amounts of excess tin(II) chloride promotes the formation of extractable platinum-tin(II) complex anions.

Heating period/hours	R_a(Pt)	Pt found on foam mg	%
0,5	100	0,43	87
1,5	100	0,44	88
2,0	100	0,45	90
5,0(6)	100	0,50 ± 0,01	100
0,5	1000	0,47	95
1,0	1000	0,49	98

Table 6.7 The extraction of platinol by polyurethane foams, following the heating of the solutions for varying periods of time. Experimental Conditions: initial mass Pt = 0,5 mg, added as $PtCl_2(NH_3)_2$, mass foam used = 400 mg, preheated in glycerol bath.

It was hoped, on the basis of these results, that the presence of excess tin(II) chloride in the platinol-HCl solutions would reduce the pre-treatment time required, prior to the addition of polyurethane foams, for the quantitative extraction of platinum-tin(II) complexes. Solutions containing the required amounts of platinol, HCl and stannous chloride (R_a(Pt) = 50) were boiled for 15 minutes. Further quantities of excess tin(II) chloride and a polyurethane foam block were added. The foams were then shaken in contact with the solutions for 90 minutes, followed by foam degradation in the usual manner.

It may be seen from Table 6.8 that essentially quantitative extraction of platinum, added as platinol, has been achieved by preheating the platinol-HCl solutions in the presence of $SnCl_2$, followed by further additions of $SnCl_2$ (R_a(Pt) $\geq$ 500).

R_a(Pt)	Pt found on foam mg	%
100(1)	0,46	92
500(2)	0,50	99
1000(2)	0,51	103

Table 6.8 The extraction of platinol by polyurethane foams following the heating of the solutions with tin(II) chloride for 15 minutes. Experimental Conditions: initial mass Pt = 0,5 mg, added as $Pt(NH_3)_2Cl_2$, mass foam used = 400 mg.

Artificial urine was prepared according to the method suggested by Burns and Finlayson [215]. The mixture consists of the following compounds: Na_2SO_4, KCl, NH_4Cl, NH_4OH, $MgSO_4.7H_2O$, Na_2HPO_4, $NaH_2PO_4.2H_2O$, NaCl, $Na_3C_6H_5O_7.2H_2O$ and urea. Small aliquots (15 ml) were added to a number of flasks containing platinol, HCl and stannous chloride. The above experimental conditions were used. Results are shown in Table 6.9.

R_a(Pt)	Platinum found on foam mg	%
200(2)	0,39	78
500(2)	0,40	81
1000(2)	0,46	92

Table 6.9 The extraction of platinol by polyurethane foams following the heating of the platinol-urine-tin(II) solutions for 15 minutes. Experimental Conditions: initial mass Pt = 0,5 mg, added as $Pt(NH_3)_2Cl_2$, mass foam used = 400 mg, volume urine = 15 ml.

The presence of artificial urine appears to inhibit the sorption of platinum by polyurethane foams. There is a strong possibility that complex formations of platinum with other constituents present in the urine takes

place. These species are unlikely to be extractable by the organic polymer, and may react more slowly with tin(II) chloride than $Pt(NH_3)_2Cl_2$ to form the extractable chloro-(trichlorostannato)-platinum(II) complex anions. A further explanation for this effect, is that the urine dilutes the initial HCl-platinol solution, giving a hydrochloric acid concentration of approximately 50% of those solutions containing no artificial urine. Two possible means of overcoming this effect could be to either increase the volume of HCl added, or to reduce the volume of platinol-urine samples prior to the addition of HCl.

Time did not permit further study of the sorption of platinum, added as platinol, by polyurethane foams. However, from the results thus far obtained, we have shown that the extraction of platinum complexes, such as platinol is not as readily achieved as that of tetrachloroplatinate from synthetic mixtures containing tin(II) chloride. The platinum complexes that exist in the artificial urine are not readily converted to the extractable chloro-(trichlorostannato)-platinum(II) complex anions.

CHAPTER 7

CHAPTER 7

7 - DISCUSSION AND CONCLUSIONS.

The reaction of tin(II) chloride with the platinum metals to form intensely coloured solutions has been known for over a century [81,82]. At the turn of the century, it was reported that the blood-red colour of platinum-tin(II) solutions was extractable into ether [86].

A number of platinum species exist in dilute hydrochloric acid solutions of K_2PtCl_4. The major anion found in these solutions is $[PtCl_4]^{2-}$, although small amounts of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ are also known to exist [167]. It is known that a number of species are formed when stannous chloride is prepared in HCl medium. The tin(II) species present in solution include $[SnCl]^+$, $[SnCl_2]$, $[SnCl_3]^-$ and $[SnCl_4]^{2-}$. The trichlorostannato anion is the major tin(II) chloro species known to form complexes with the platinum metals.

It is obvious that, due to the number of different complexes formed in acid platinum and tin(II) solutions, on mixing, an extremely complicated series of reactions will occur. Examples of some of the species which are likely to be formed in equilibrium with each other are:

$$SnCl_4^{2-} \longrightarrow SnCl_3^- + Cl^-$$

$$SnCl_2 + Cl^- \longrightarrow SnCl_3^-$$

$$[PtCl_4]^{2-} + SnCl_3^- \longrightarrow [Pt(SnCl_3)Cl_3]^{2-} + Cl^-$$

$$[Pt(SnCl_3)Cl_3]^{2-} + SnCl_3^- \longrightarrow t/c\text{-}[Pt(SnCl_3)_2Cl_2]^{2-} + Cl^-$$

$$t/c\text{-}[Pt(SnCl_3)_2Cl_2]^{2-} + SnCl_3^- \longrightarrow [Pt(SnCl_3)_3Cl]^{2-} + Cl^-$$

$$t/c\text{-}[Pt(SnCl_3)_2Cl_2]^{2-} + 3SnCl_3^- \longrightarrow [Pt(SnCl_3)_5]^{3-} + 2Cl^-$$

where t/c = trans- or cis-

The platinum group metals are all known to form complex anions with tin(II) chloride [103] and hence similar

processes could be expected to occur for rhodium, ruthenium and iridium. The rates of formation of the chloro-(trichlorostannato)-rhodium(III/I),-ruthenium(II) and -iridium(III) complex anions are slow compared to the formation of similar platinum complexes. However, the rate of formation of the rhodium-tin complexes is very much more rapid than in the case of ruthenium and iridium. This difference in the behaviour of the platinum group metals with tin(II) chloride may be conveniently exploited to achieve separations of these noble metals.

Essentially quantitative separations of rhodium and ruthenium [178] and platinum and palladium [205] by solvent extraction have been achieved by utilizing the variation in the relative rates of platinum metal-tin(II) complex formation.

Polyurethane foams behave in a manner analogous to organic solvents in the extraction of metal anion complexes from aqueous solutions. The use of a solid organic polymer has a number of advantages over an organic solvent. The foams are inexpensive, readily available from numerous commercial outlets and have the capacity to hold large quantities of metals. As an example, 250 μg platinum may readily be sorbed from a 250 cm^3 solution by 100 mg block of foam, representing a concentration factor of approximately $2,5 \times 10^3$. Furthermore, polyurethane foam is relatively inert and the open physical structure of the foam permits rapid sorption of the complex anions.

There are a number of problems associated with the direct analysis of the organic phases by AAS in the solvent extraction methods for the separation of noble metals [178]. For example, the air/acetylene ratio is critical when determining the noble metals by AAS, as small variations in the fuel/oxidant ratio result in large fluctuations in the absorbance measured. Since organic solvents act as a fuel when aspirated into the burner, the acetylene fuel flow has to be adjusted and

strictly monitored in order to compensate for the organic solvent present in solution and to maintain reproducible flame conditions.

However, polyurethane foams may be solubilized by hot nitric acid. The resultant digest solutions do not appear to alter the flame stoichiometry significantly and can easily be analysed for their metal content by AAS.

The use of polyurethane foams to extract and separate the platinum metals as their thiocyanate complexes has been studied in recent years [67-72]. The use of thiocyanate as the ligand to convey the precious metal into an extractable complex anion has some limitations. Firstly, a thiocyanate-based extraction from highly acidic solutions is compromised to some extent by the formation of interfering thiocyanic acid and 5-amino-1,2,4-dithiazole-3-thione [70]. Secondly, the method is not selective toward the platinum group metals because various transition metals such as Co [43], Zn, Hg and In [45] are also extracted efficiently from the thiocyanate medium [216].

On the other hand, stannous chloride is known only to form relatively stable complex anions with the noble metals. Furthermore, the strongly "π acid" nature of the $SnCl_3^-$ ligand [217] labilizes the kinetically inert complexes of the platinum group metals to ligand substitution.

The tin chloride species present in solution, *viz.* $SnCl^{2-}$, $SnCl_3^-$, $SnCl_2$ and $SnCl^+$ are not co-extracted by polyurethane foams to a significant extent at low HCl concentrations, although at high acid concentrations ($\geq$ 3M) some tin is claimed to be extractable [206]. Thus a reasonable excess of stannous chloride may be used to increase the rate of formation of extractable chloro-(trichlorostannato)-platinum(II) and -rhodium (III/I) complex anions.

Tin(II) is easily oxidized to tin(IV) in the presence of traces of oxygen and hence strict measures are required to exclude as much air as possible in order to use the minimum practical amount of tin(II). The analyte solutions must be purged of oxygen prior to the addition of stannous chloride and well stoppered vessels are essential. A further disadvantage in the use of tin(II) chloride is that the overall cost of the method employed is increased due to the high cost of tin(II) chloride. Brackenbury [206] has however devised a method for the recovery of tin from the loaded polyurethane foams. The foam may be solubilized with warm nitric acid, followed by the separation of tin from the platinum metal(s) present by distilling the tin over as a volatile bromide ($SnBr_4$).

7.1 THE EXTRACTION AND SEPARATION OF THE PLATINUM GROUP METALS.

The experimental conditions required for the quantitative immobilisation of the complex chloro-(trichlorostannato)-platinum(II) anions onto polyurethane foams appear to be reasonably flexible. Hydrochloric acid concentrations between 1M and 3,5M appear to have no significant effect on the sorption process (Section 3.2.1). Polyurethane foams are mostly unaltered, apart from reversible swelling by HCl up to 6M [24]. However, a decrease in the amount of chloro-(trichlorostannato)- platinum(II) sorbed by the foam may occur from solutions with hydrochloric acid concentrations greater than 3,5M. At high chloride ion concentrations, the equilibrium of the two tin species,

$$SnCl_4^{2-} \longrightarrow SnCl_3^- + Cl^-$$

would be shifted to the left, favouring the formation of the $SnCl_4^{2-}$ species which is not known to form complexes with $PtCl_4^{2-}$. Equally, the equilibria in the following equations would be expected to shift to the left at high chloride ion concentrations.

$$[PtCl_4]^{2-} + nSnCl_3^- \longrightarrow [Pt(SnCl_3)_nCl_{4-n}]^{2-} + nCl^-$$

(where n = 1-4)

$$[PtCl_4]^{2-} + 5SnCl_3^- \longrightarrow [Pt(SnCl_3)_5]^{3-} + 4Cl^-.$$

Platinum, as $PtCl_4^{2-}$ is not extractable by polyurethane foams [206]. Hence a decrease in the sorption of platinum may be expected at high acid concentrations.

In the presence of sufficient tin(II) chloride, platinum may be quantitatively and selectively sorbed by polyurethane foams from dilute hydrochloric acid solutions containing up to a 100-fold molar excess of iridium(IV). (Section 3.4).

The presence of ruthenium appears to have no significant effect on the extraction of platinum by polyurethane foams from solutions containing Ru:Pt mole ratios of 1 and 10. Ruthenium, however, appears to inhibit the sorption of platinum when Ru is in 100-fold excess of Pt. A mean extraction of 86 $\pm$ 10% Pt (n = 6) was obtained from these solutions (Table 3.7). Ruthenium does not appear to be co-extracted by the polyurethane foams under the experimental conditions employed.

Under the solution conditions used, the $SnCl_3^-$ ligand only forms stable complexes with platinum and not with base metals. Polyurethane foams extract platinum in this form, but generally do not sorb the base metal chloro complexes, except for $GaCl_4^{2-}$ [73] and $FeCl_4^-$ [74]. Results in Table 3.5 demonstrate the selectivity of this method for the extraction of platinum. Small amounts of copper, however, have been found to be co-extracted by the organic polymer.

It has been shown that copper in its bivalent state is not extractable by polyurethane foam from HCl media [33]. There are two possible explanations for the co-extraction of copper by polyurethane foams. Firstly, in the presence of stannous chloride, bivalent copper may form complexes of type $[Cu(SnCl_3)_nCl_{4-n}]^{2-}$ which are

extractable by polyurethane foam, although these species have not been demonstrated previously. An alternative is that Cu(II) is reduced to its univalent state as shown below,

$$2Cu(II) + Sn(II) \longrightarrow 2Cu(I) + Sn(IV)$$

and copper(I) as its chloride may be extractable into the foam. No attempts were made to establish the form in which copper extracts.

Iron(III) is known to extract into polyurethane foam as its $FeCl_4^-$ complex [74]. However, the Fe(III) was not sorbed by the foams under the experimental conditions employed in this work. As the solutions contained tin(II) in excess, most of the Fe(III) should have been reduced to its bivalent state as shown below,

$$2Fe(III)Cl_4^- + Sn(II) \longrightarrow 2Fe(II)Cl_4^{2-} + Sn(IV)$$

Iron in its bivalent state, does not appear to be extracted by polyurethane foams.

In the study of the antitumor drug, cis-$Pt(NH_3)_2Cl_2$, attempts to convert platinol into $PtCl_4^{2-}$ were initially made by boiling the solutions with concentrated hydrochloric acid, prior to the addition of tin(II) chloride. Essentially quantitative extraction was found to occur after a preheating period of 5 hours. Furthermore, it was noted that shorter periods of heating were required for solutions containing a further 10-fold excess of stannous chloride added after the pretreatment step (Table 6.7).

These results led to an investigation of the effect of adding excess tin(II) chloride (R_a(Pt) = 50) prior to heating, on the extraction of platinum (added as platinol). Essentially quantitative sorption of platinum was obtained after boiling the platinol-tin(II)-HCl solutions for 15 minutes.

The above results suggest that the $SnCl_3^-$ ligand is effective at labilizing the kinetically inert $Pt(NH_3)_2Cl_2$ so that in the presence of concentrated HCl, $Pt(NH_3)_2Cl_2$ is converted to $PtCl_4^{2-}$ more readily. However, large quantities of stannous chloride (R_a(Pt) $\geq$ 500) were required for the conversion of platinol into extractable chloro-(trichlorostannato)-platinum(II) complex anions.

Rhodium(III)-tin(II) solutions require a pre-extraction treatment step in order to achieve the quantitative sorption of rhodium by polyurethane foams. Heating the rhodium solutions in the presence of excess stannous chloride to 50 ^{o}C for 3 hours was found to be sufficient for the quantitative extraction of the chloro-(trichlorostannato)-rhodium(III/I) complex anions.

The quantitative and selective extraction of rhodium by polyurethane foams from dilute hydrochloric acid solutions containing iridium has easily been achieved. On the other hand the presence of ruthenium in the aqueous phase was found to severely retard the sorption of the chloro-(trichlorostannato)-rhodium(III/I) complex anions.

The red-brown ruthenium trichloride solutions in hydrochloric acid medium rapidly become pale yellow or colourless on the addition of stannous chloride. This is followed by the development of a blue colour which is generally thought to involve the reduction of ruthenium(III/IV) to ruthenium(II) [209]. The simultaneous oxidation of tin(II) to tin(IV) results in a decrease in the effective concentration of $SnCl_3^-$ anions. The total concentration of tin(II) species determines the overall rate of formation of extractable chloro-(trichlorostannato)-rhodium(III/I) complex anions and hence the amount of rhodium sorbed by polyurethane foams. The reduction of ruthenium cannot however, account solely for the incomplete extraction of rhodium (approximately 50% Rh) by the organic polymer from

solutions containing ruthenium (Section 4.4) for the following reasons:

Firstly, an excess of stannous chloride was added to the rhodium-ruthenium solutions, resulting in a Sn:Rh+Ru mole ratio of 50. Between 0,5 and 1 mole of tin(II) per mole of ruthenium is consumed in the reduction of ruthenium(III/IV) to ruthenium(II). This small decrease in the tin(II) concentration should not significantly affect the rate of formation of the extractable chloro-(trichlorostannato)-rhodium(III/I) complex anions.

Secondly, tetrachloroiridate anions in solution undergo a similar reduction from Ir(IV) to Ir(III) with the simultaneous oxidation of Sn(II) to Sn(IV). The presence of iridium in dilute acid solutions of rhodium and tin appears to have no effect on the extraction of chloro-(trichlorostannato)-rhodium(III/I) complex anions (Section 4.3).

Thirdly, the presence of ruthenium trichloride at Ru:Pt mole ratios of 1 and 10 does not appear to significantly affect the extraction of chloro-(trichlorostannato)-platinum(II) complex anions from dilute hydrochloric acid solutions (Section 3.5).

It thus appears that ruthenium inhibits the rate of the rhodium(III/I)-tin(II) complex formation in some more complicated manner than a simple decrease in the tin(II) concentration.

The effect of ruthenium on the sorption of chloro-(trichlorostannato)-rhodium(III/I) by polyurethane foams, using this method of separation is not understood and it was beyond the scope of this work to establish the cause of the results obtained.

In his critical review of methods of isolating and separating the six platinum metals, Beamish [2] remarked: "One cannot overemphasize the fact that even today too few authors have recognised the potential complexity of equilibria in platinum metal solutions,

the character of which may well affect the methods of separation, as well as the methods of determination".

The inhibition of the extraction of rhodium by ruthenium can however be overcome to some extent by altering the experimental conditions. Almost quantitative separation of Rh and Ru was achieved on the extraction of rhodium by polyurethane foams from solutions of low Cl^- ion concentration (0,5M) and high H^+ ion concentration (3,5M) following 16 hours equilibration at 50 ^oC. The increase in the amount of rhodium sorbed by the polyurethane foams can be explained as follows. The concentration of $SnCl_3^-$, the only tin(II) chloro species which is known to form complexes with the platinum metal species in solution, varies with hydrochloric acid.

It has been suggested [178] that the variation in the distribution, and hence the concentration, of the reacting tin(II) species may influence (*i*) the rate of chloro-(trichlorostannato)-rhodium(III/I) complex anion formation and (*ii*) the nature and distribution of these complexes formed in the aqueous phase at different HCl concentrations. For example, a decrease in the Cl^- ion concentration is expected to shift the equilibrium

$$SnCl_4^{2-} \longrightarrow SnCl_3^- + Cl^-$$

to the right, favouring the formation of $SnCl_3^-$. Furthermore, a decrease in Cl^- ion concentration is expected to shift the equilibria

$$[RhCl_n(H_2O)_{6-n}]^{3-n} + mSnCl_3^- \longrightarrow [Rh(SnCl_3)_mCl_{6-m}]^{3-} + xCl^- + yH_2O$$

$$[RhCl_n(H_2O)_{6-n}]^{3-n} + 5SnCl_3^- \longrightarrow [Rh(SnCl_3)_5]^{4-} + nCl^- + 6-nH_2O$$

where m,n,x,y = 1 to 5.

to the right, favouring the formation of the extractable chloro-(trichlorostannato)-rhodium(III/I) complexes.

On the other hand, the effect of ruthenium on the sorption of rhodium by polyurethane foams can be conveniently exploited to achieve the near separation of platinum and rhodium. In the absence of ruthenium, approximately 65% of the rhodium is co-extracted together with the quantitative sorption of platinum by polyurethane foams (Table 5.1). However, in the presence of ruthenium, the quantitative extraction of platinum is still achieved, but only 2-10% of rhodium is co-extracted (Tables 5.4 and 5.5).

7.2 THE RECOVERY OF THE PLATINUM METALS IMMOBILISED ON POLYURETHANE FOAMS.

Decomposing the loaded polyurethane foams with hot nitric acid appears to be the most convenient and efficient method of recovering platinum and/or rhodium from the foams. Polyurethane foam blocks weighing up to 600 mg are completely degraded by small volumes of hot nitric acid (approximately 10 cm^3) in *ca.* 5 minutes. Once the foam has been completely solubilized, the HNO_3 can be boiled off and concentrated HCl added to dissolve the probable tin nitrate as a chloride. This method retains the concentration step achieved by immobilising the metal(s) onto polyurethane foams.

Solubilizing the loaded polyurethane foams has a further advantage in that the resultant solutions can be analysed for their metal content by atomic absorption spectroscopy, provided that the matrices of the samples and standards are matched.

A second method of recovering platinum and rhodium from loaded polyurethane foams has been achieved. The foams may be stripped with hot (70 ^{o}C) mixtures of concentrated hydrochloric acid and ethanol.

Stripping platinum-loaded foams with 5-10% HCl/ethanol mixtures resulted in the elution of $\geq$ 95% of the total platinum, although complete quantitative elution was not achieved (Section 6.2). Small quantities of platinum (< 5%) were found to remain on the foam. This suggests

that some of the platinum may be more strongly bonded to the foam phase than would be expected on the basis of an ion exchange type mechanism [24] alone.

Near quantitative recoveries of platinum ($\geq$ 99%) were however achieved by stripping foams loaded with both platinum and rhodium (Section 6.4). These results suggest that less platinum is strongly bonded to the polyurethane foams when co-extracted with rhodium. The procedure for the sorption of platinum varied from that of mixtures of platinum and rhodium. The presence of rhodium necessitated the pre-equilibration of the Pt-Rh-Sn(II) solutions for 3 hours at 50 ^{o}C prior to the addition of polyurethane foams. This pretreatment may well alter the concentrations of the various platinum-tin(II) species present in solution, and hence the amount of each $[Pt(SnCl_3)_nCl_{4-n}]^{2-}$ (n = 1-4) and $[Pt(SnCl_3)_5]^{3-}$ complex anion sorbed by the polyurethane foams.

The chloro-(trichlorostannato)-rhodium(III/I) complex anions do not appear to be as strongly bonded to the polyurethane foam phase as is some of the platinum. Near-quantitative recoveries of rhodium from Rh- and Pt-Rh-loaded foams were achieved (Section 6.3 and 6.4).

The separation of platinum and rhodium by means of foam stripping was not achieved. Both metals were found to elute from the loaded foams at approximately the same rates for all the eluents tested, both in the absence and presence of excess clean polyurethane foam (Figures 6.5 and 6.6).

The disadvantage of using stripping agents such as mixtures of concentrated hydrochloric acid and ethanol is that pure aliquots must be continuously passed through the foam until the platinum and/or rhodium have been quantitatively eluted. This results in a significant dilution of the metal concentrate. Furthermore, small amounts of platinum (0,5-5%) were always found to remain on the foam. For quantitative

recovery studies, therefore, dissolution of the loaded foams appears to be necessary.

The solubilized polyurethane foam solutions and the aqueous solutions were analysed by AAS for the presence of noble metals. The demonstration of mass balance for the platinum metals showed that quantitative recovery of platinum and rhodium is readily achieved.

7.3 THE DETERMINATION OF THE PLATINUM GROUP METALS.

There are a number of problems associated with the use of AAS as a method of analysis. Firstly, the platinum metals are subject to a number of interelement interferences, both from other noble metals and from base metals which may be present in solution. The use of a suitable releasing agent, such as lanthanum nitrate, which was used throughout this experimental work, can however overcome these effects.

Secondly, the absorbance values obtained for each metal vary according to the matrix of the solution being analysed. It is thus imperative to matrix match the standards and samples as closely as possible in order to allow for the accurate determination of the metals.

Thirdly, the calibration curves of the platinum metals deviate from Beer's Law at higher metal concentrations. This effect was particularly noticeable in the determination of ruthenium and iridium from solutions containing an H^+ ion concentration of 3,5M and a Cl^- ion concentration of 0,5M (Figures 2.6 and 2.7). It was thus necessary to adjust the sample concentrations by dilution of the solutions, in order to fall within the linear portion of the calibration curves.

Fourthly, although AAS is a relatively rapid method of analysis, the determination of the platinum metals was time-consuming when two or more metals were present in solution. The inability of the instrument to perform multi-element analyses necessitated the separate

determination of each metal in both the foam digest and the aqueous solutions.

A more convenient method of analysis could be achieved by the simultaneous determination of the platinum group metals by inductively coupled plasma emission spectroscopy (ICP). A further advantage of the use of ICP in the analysis of the platinum metals is that the calibration curves for each metal is linear over a concentration range of 3 to 4 orders of magnitude [219].

With one exception, no significant mutual interference effects have been observed for the presence of 1000 ppm of each of the other platinum metals on the determination of 10 ppm of the analyte platinum metal in aqueous solutions [220]. A significant enhancement of the platinum signal using the Pt 265,95 nm line was observed when ruthenium was in-100 fold excess of platinum. However, no interference of ruthenium on platinum was observed for the determination when the Pt 299,79 nm line was used [220].

The interference effects using ICP of the base metals Cu, Ni and Fe have been found to be negligible for solutions containing low and comparable concentrations of platinum and base metals. [221].

Preliminary investigations using ICP as a method of analysis were undertaken. However, due to the unavailability of the instrument, this line of work had to be discontinued.

An alternative method of analysis of the loaded polyurethane foams is that of X-ray fluorescence (XRF). A major advantage of this method is that the solid foams can be analysed *per se*. The time-consuming degradation procedure and the associated experimental errors due to mechanical losses would be eliminated using XRF. Other advantages of XRF are the speed and convenience of the procedure, which permits multi-element analyses to be completed in a few minutes. The spectra are relatively simple; spectral line interferences are thus unlikely.

Furthermore, the accuracy and precision of XRF methods often equal or exceed those of other methods.

Preliminary qualitative studies using XRF as a means of analysing the loaded polyurethane foams were undertaken. Various masses of between 10 μg and 250 μg of platinum or rhodium were loaded onto polyurethane foams and qualitatively analysed by XRF. The RhK_{α} and PtL_{β} lines appeared on the spectra for foam samples containing 20 μg metal but not for those containing 10 μg of the platinum metal. One must, however, bear in mind that these small masses of platinum and rhodium are not quantitatively sorbed from dilute acidic solutions by polyurethane foams (Table 3.4). Better-defined spectra were obtained from foam samples containing masses $\geq$ 50 μg Pt or Rh.

The analysis of the polyurethane foams by XRF was complicated by the open structure of the polymer. The use of polyurethane films for loading and subsequent analysis by XRF may eliminate this problem. However, XRF appears to have potential in the analysis of the platinum metals sorbed by polyurethane foams and deserves further research.

7.4 CONCLUSIONS.

The research objectives of this work have essentially been met. It has been found that chloro-(trichlorostannato)-platinum(II) and -rhodium(III/I) complex anions may be quantitatively sorbed by polyurethane foams from dilute acidic solutions. Complete separations of platinum or rhodium from iridium and ruthenium using this method have also been achieved.

The near-separation of platinum and rhodium has been obtained by the extraction of platinum from solutions containing rhodium and ruthenium by polyurethane foams.

The rate of formation of chloro-(trichlorostannato)-platinum(II) complex anions is rapid when platinum, added as $PtCl_4^{2-}$, is reacted with an excess of stannous

chloride (R_a(Pt) $\geq$ 10) at room temperature. However, the reaction of platinol, cis-$Pt(NH_3)_2Cl_2$ with tin(II) chloride is very slow and forcing experimental conditions are required for the complete formation of the extractable chloro-(trichlorostannato)-platinum(II) complex anions.

Loaded polyurethane foams may be conveniently decomposed using hot nitric acid for the recovery and determination of the platinum metal content sorbed by the polymer. AAS provided a means of quantitatively determining the platinum metals present both in the solubilized foam solutions and in the aqueous phases.

The research findings of certain portions of this work have contributed to the following papers:

L. Jones, I. Nel and K.R. Koch. **Polyurethane Foams as Selective Sorbents for Noble Metals. Quantitative Extraction and Separation of Rhodium from Iridium in Hydrochloric Acid Containing Tin(II) Chloride.**, *Anal. Chim. Acta*, 182, 1986, 61.

K.F.G. Brackenbury, L. Jones, I. Nel, K.R. Koch and J.M. Wyrley-Birch. **Tin(II) Chloride in the Analytical Chemistry of the Platinum Metals: From the "Purple of Cassius" to Polyurethane Foams.**, *Polyhedron*, 6(1), 1987, 71.

K.F.G. Brackenbury, L. Jones and K.R. Koch. **Polyurethane Foams as Sorbents for the Noble Metals. Selective Preconcentration of Small Amounts of Platinum from Hydrochloric Acid Containing Tin(II) Chloride Followed by Flame Atomic Absorptiron Analysis.**, *The Analyst*, 1987, (in press).

CHAPTER 8

CHAPTER 8

8. EXPERIMENTAL.

8.1 CHEMICALS, REAGENTS AND GLASSWARE.

All the chemicals and reagents used for this work were analytically pure and were obtained from various suppliers. The K_2PtCl_4, $RuCl_3.nH_2O$ (n = 3 or 4) and K_2IrCl_6 used were produced by Johnson Matthey Chemicals Limited, England. Aldrich Chemical Company, U.S.A. supplied the $RhCl_3.3H_2O$. E. Merck, Darmstadt supplied the $La(NO_3)_3.6H_2O$, $SnCl_2.2H_2O$, $CoCl_2.6H_2O$, $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $ZnCl_2$ and zinc metal.

The HNO_3 and H_2SO_4 were obtained from BDH Chemicals, England. HCl and $HClO_4$ were produced by Holpro Analytics, South Africa and E.Merck, Darmstadt respectively.

Commercial grade nitrogen was used throughout the course of this work. The gas was purged of residual oxygen by passing it through a chromous chloride solution and distilled water before use [222].

Polyether type polyurethane foam of high density (0,031217 g/cm^3), obtained from Flexaire Foams, South Africa, was used throughout. The sheets of foam were cut into small cubes, each weighing roughly 0,4 grams. The cleaning procedure used was adapted from that recommended by Al-Bazi and Chow [223]. The foam cubes were first washed with Tepol detergent and thoroughly rinsed. They were then soaked in 0,75M HCl for 72 hours, followed by thorough rinsing with deionized water until the rinsing water was approximately neutral to pH indicator paper. Finally, the foam cubes were allowed to stand overnight in acetone, and then dried in an oven at 50 ^{o}C. They were stored in the dark until use.

A mixture of A and B grade glassware was used. For accurate volume measurements of 5ml or less Gilson

pipettes were used (models p1000 and p5000). The accuracy and precision of the Gilson pipettes were determined prior to use (Appendix 18). Grade A pipettes were used for greater volume transfers. All glassware was soaked in 5% Contrad overnight, where possible, followed by a number of hours in 10% nitric acid. Finally the glassware was rinsed with double distilled water several times.

Mettler and Sartorius four decimal place balances were used for all weighings.

8.2 ATOMIC ABSORPTION OF THE PLATINUM METALS.

Stock solutions of 1000 ppm platinum(II), rhodium(III), ruthenium(III) and iridium(IV) in 2M HCl were prepared from the analytical grade salts, K_2PtCl_4, $RhCl_3.3H_2O$, $RuCl_3.nH_2O$ (n = 3 or 4) and K_2IrCl_6. A fresh stock solution of rhodium was made up for each experiment.

Tin(II) chloride solutions were freshly prepared from analytical grade $SnCl_2.2H_2O$ by dissolving an accurately weighed amount of salt first in the appropriate amount of degassed concentrated HCl, followed by dilution with degassed water.

Stock solutions of the releasing agent lanthanum nitrate, $La(NO_3)_3.6H_2O$ were made up in 2M HCl and diluted ten times on addition to standards and samples, to give a final La^{3+} concentration of 0,2% w/v.

The standards were prepared in the same medium as the samples in order to matrix match them as closely as possible. Quantities of foam decomposed by nitric acid, corresponding to the amount added to the samples, were added to the standard matrix when analysing the degraded foam solutions (Section 8.6). Additions of tin(II) chloride were also made so as to match the ratio of platinum:tin in the standard matrix to the expected ratio in the samples. Standards were prepared in ethanol with 10% HCl (v/v) for use with the foam-stripped samples (Section 8.7). Standards were also

prepared in either 2M HCl or in a H_2SO_4/HCl mixture to give a final H^+ ion concentration of 3,5M and a Cl^- ion concentration of 0,5M. These were used when analysing the solutions retained after separation had been achieved. The platinum metal content of all solutions was measured using a Varian Model AA6 atomic absorption spectrophotometer. Air-acetylene flames optimised for maximum sensitivity of each metal were used at the spectrophotometer settings listed in Table 8.1.

Noble metal	Pt	Rh	Ru	Ir
Lamp current/mA	10	5	10	20
Wavelength/nm	265,9	345,5	349,9	264,0
Slitwidth/nm	0,2	0,5	0,2	0,1
Flame conditions	oxidizing	oxidizing	reducing	stoichiometric
Burner head configurations	normal	45°	normal	normal

Table 8.1 The spectrophotometer settings used during the analysis of the platinum metals.

The high absorbance values obtained for rhodium (absorbance value of $\pm$ 3,6 for 40 ppm Rh) necessitated the rotation of the burner head by 45°. This resulted in a lower noise level at the higher rhodium concentrations.

The emission spectra of iridium were determined for wavelengths in the regions of 208,9 nm and 264,0 nm (Figure 8.1).

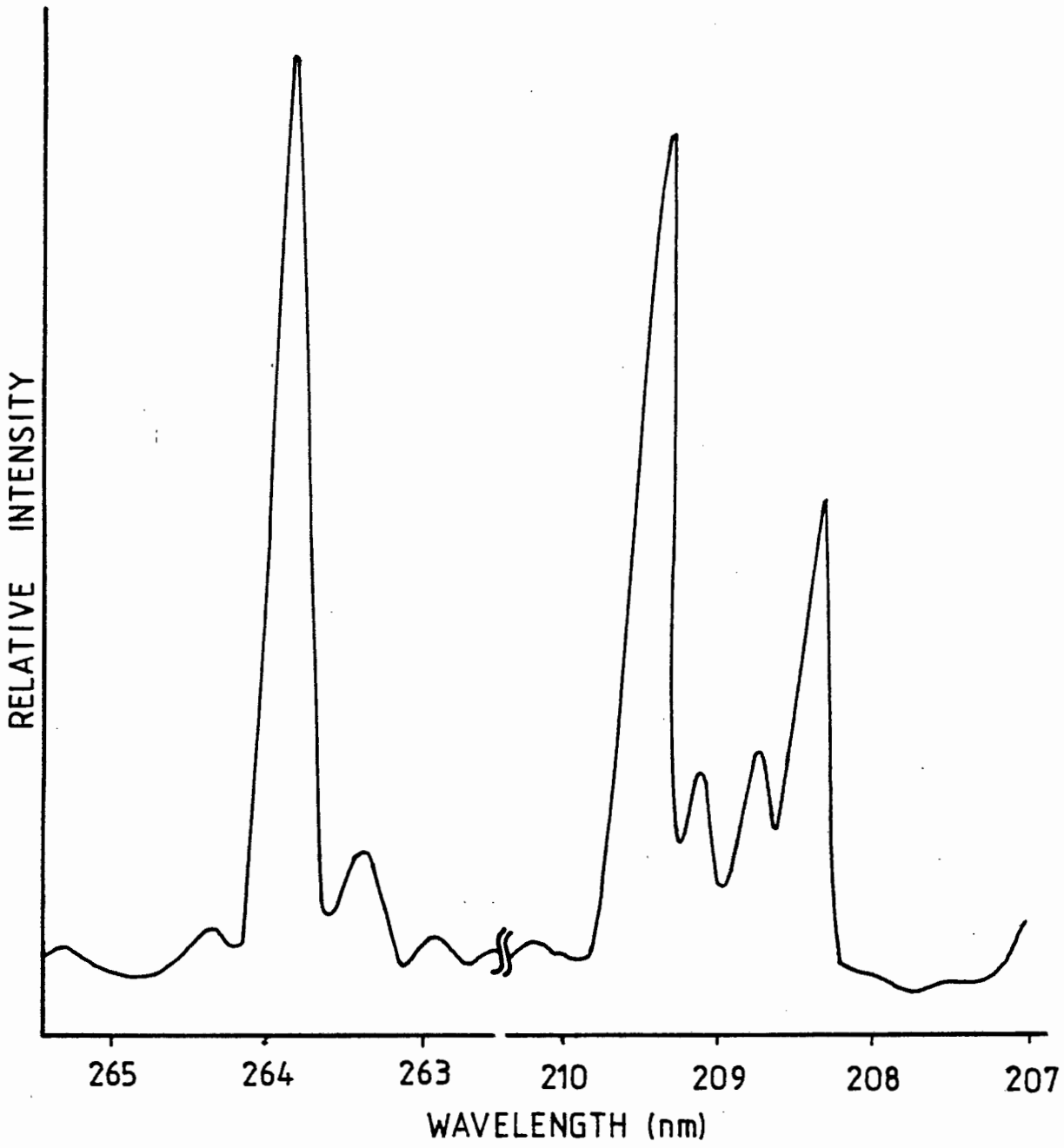


Figure 8.1 The emission spectra of iridium.

The recommended wavelength for iridium, 208,9 nm, while the most sensitive for atomic absorption, has complex iridium spectra comprising nearly forty lines, 1 nm each side of this line. This causes difficulty in setting the wavelength. The signal strength of the line may also cause too much noise. To avoid the above, a wavelength of 264,0 nm was used, as this line is both

cleaner and more intense. The slight decrease in sensitivity is offset by the improvement in signal to noise ratio.

Linear relationships between absorbance and concentration have been shown to exist for the noble metals in the concentration range 0 - 40 ppm (Figure 2.2 to Figure 2.7). A slight deviation of Beer's Law is observed for the analysis of ruthenium (Figure 2.6) and iridium (Figure 2.7) in the H_2SO_4/HCl matrix. However, the samples in this matrix were adjusted in such a way that their absorbance values fell within the linear part of the calibration curve.

Typical calibration curves for the noble metals showing the variation in the absorbance values obtained are shown in Figure 8.2.

8.3 ATOMIC ABSORBANCE OF THE BASE METALS.

Stock solutions of cobalt, zinc, nickel, copper and iron were prepared from analytical grade chloride salts of these metals by dissolving them in 2M HCl. The concentrations of these solutions were accurately determined by atomic absorption using BDH spectrosol standards.

A series of base metal standards were prepared in the range 0 - 30 ppm in 2M HCl. Lanthanum nitrate stock solution was added to both samples and standards to give a final La^{3+} concentration of 0,2% w/v.

A Varian Model AA6 atomic absorption spectrophotometer was used in the analysis of the base metals. Air-acetylene flames optimised for maximum sensitivity of each base metal were used at the spectrophotometer settings listed in Table 8.2.

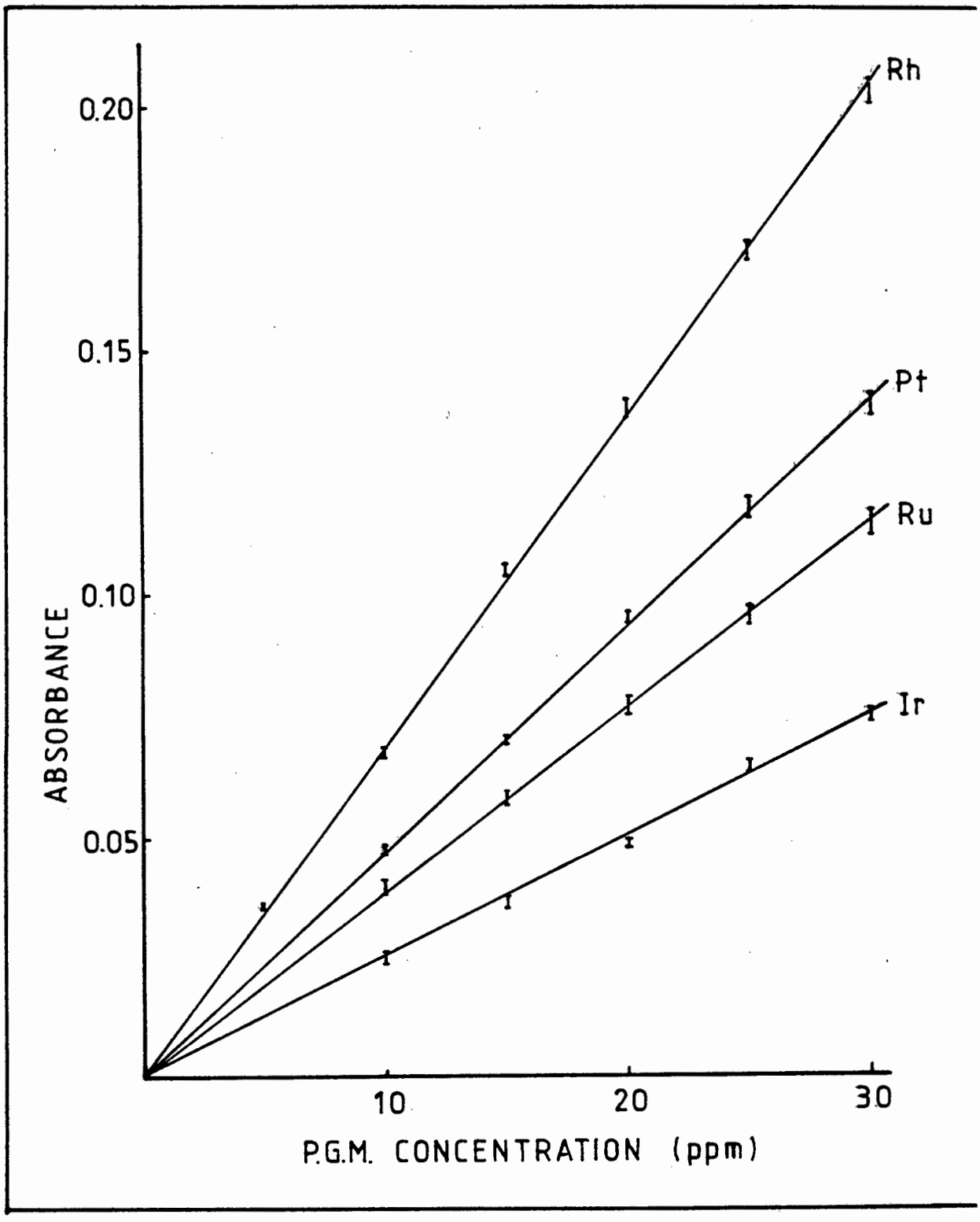


Figure 8.2 Typical calibration curves of the noble metals showing the variations in the absorbance values.

Base Metal	Fe	Cu	Ni	Co	Zn
Lamp current/mA	5	3	5	5	5
Wavelength/nm	372,0	327,4	341,5	304,4	213,9
Slitwidth/nm	0,2	0,2	0,2	0,2	0,2
Burner head configuration	normal	45°	90°	normal	90°

Table 8.2 The spectrophotometer settings used during the analysis of the base metals.

The high absorbance values obtained for Cu, Ni and Zn necessitated the rotation of the burner head. This resulted in a lower noise level at the higher metal concentrations.

The quantities of base metals extracted by the foam was calculated by comparing the sample absorbance values to those of the standards. The quantities of base metals in the aqueous solutions were determined in the same manner, to ensure that mass balance was obtained.

8.4 THE APPARATUS AND PROCEDURE FOR THE CONTINUOUS MEASUREMENT OF PLATINUM SORPTION.

The sorption of the chloro-(trichlorostannato)-platinum(II) complex anions by polyurethane foams was monitored continuously using a Varian Superscan 3 Spectrophotometer.

The apparatus used to conduct the experiments had to fulfil certain criteria. Firstly, the solution had to be pumped through the system in order to ensure that it was brought into contact with the foam and reached the quartz cell continuously. Secondly, because tin(II) is easily oxidized to tin(IV), the experiment had to be conducted under nitrogen.

Figure 8.3 illustrates the apparatus used in the determination of the time required for the quantitative extraction of the chloro-(trichlorostannato)-platinum(II) complex anions by polyurethane foams.

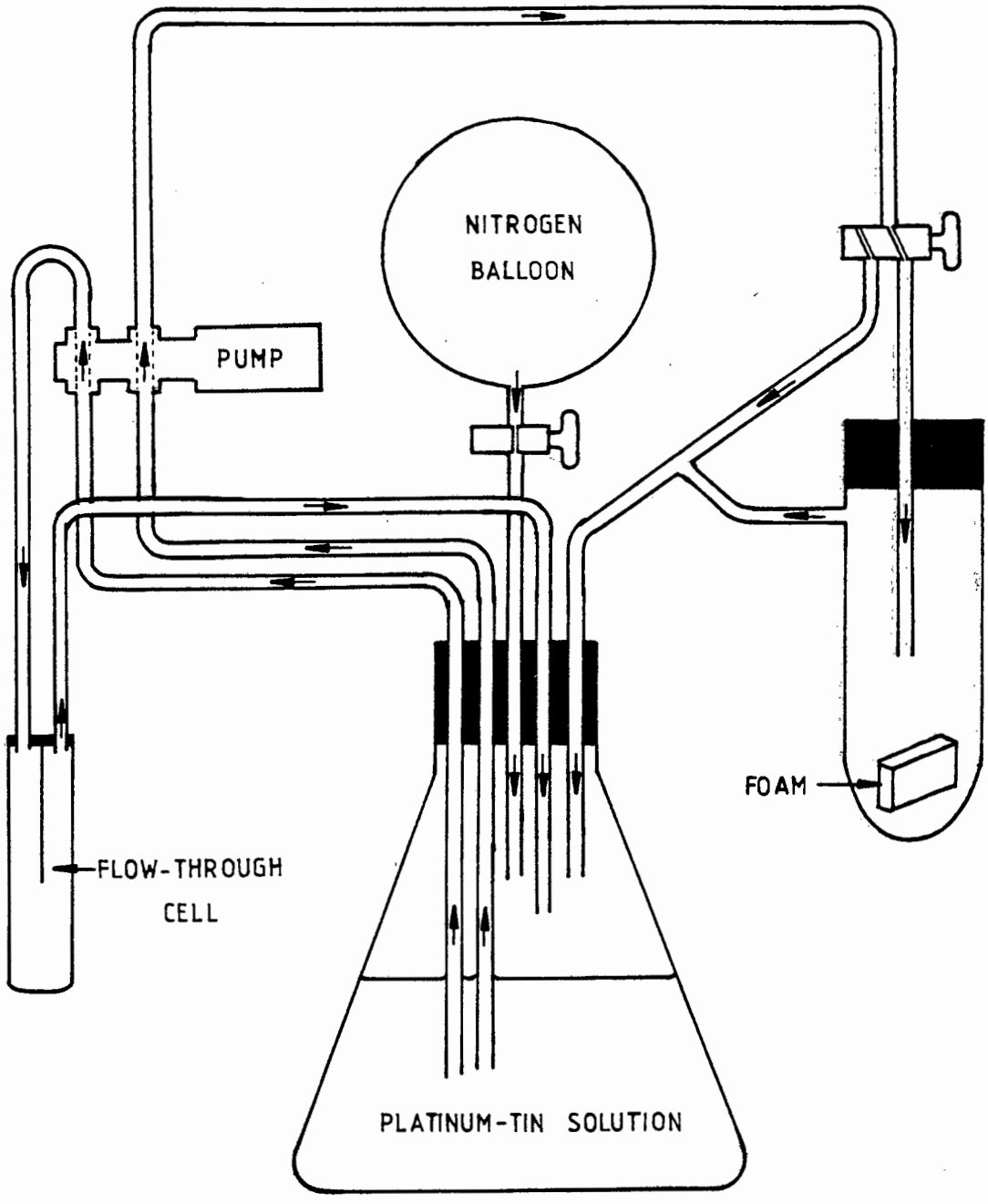


Figure 8.3 The experimental apparatus used for the continuous measurement of platinum sorption.

An electronic variable speed drill-driven penstaltic pump circulated the solution from the conical flask through to the test tube containing a polyurethane foam block. The solution was simultaneously pumped through a flow-through cell in the spectrophotometer. A two-way tap allowed the solution to bypass the foam when required.

The conical flask contained the desired amounts of platinum, tin(II) and 600 cm^3 deoxygenated 2M HCl. The foam block, wet slightly with acetone, was placed in the test-tube. The solution was pumped through the system, initially bypassing the foam to obtain a wavelength scan between 650 and 250 nm (Figure 3.1(a)). The instrument was then set at a chosen fixed wavelength of 400 nm. The solution was diverted to flow over the foam, and the change in absorption was continuously monitored.

8.5 FOAM - LOADING PROCEDURE.

The required volumes of stock metal solutions were dispensed with Gilson pipettes into graduated polypropylene flasks. The appropriate acid medium was added to the required mark on the flasks (100-200 ml). These media were:

(a) 2M hydrochloric acid for most extraction procedures.

(b) A mixture of hydrochloric and sulphuric acids to give a final H^+ concentration of 3,5M and a final Cl^- concentration of 0,5M. This medium was used for the extraction of rhodium in the presence of ruthenium.

Nitrogen was then bubbled through the solutions for 20 minutes to exclude as much oxygen as possible. A solution of stannous chloride was added to give the required metal(s):Sn mole ratios. Fresh tin(II) chloride solutions were prepared for each experiment. The flasks were then securely stoppered and the solutions allowed to equilibrate for:

(a) 15 minutes at room temperature for solutions containing no rhodium;

(b) 3 hours in a water bath set at 50 ^{o}C for solutions containing rhodium but no ruthenium;

(c) 16 hours in a waterbath set at 50 ^{o}C for solutions containing both rhodium and ruthenium.

A cube of foam, of known mass, was wetted with ethanol and briefly dried between two sheets of filter paper, just prior to addition to the aqueous solution. This ensured rapid, uniform contact between the foam and the aqueous phase. Care again was taken to exclude oxygen. The solutions were allowed to shake on an automatic Griffin flask shaker for 90 minutes.

The foams were removed from the solutions, squeezed to allow the excess solution to run back into the flask, and dried between 2 sheets of filter paper. They were then either degraded or used in foam stripping experiments. The residue solutions were retained and analysed to ensure mass balance was achieved.

8.6 FOAM DEGRADATION PROCEDURE.

The loaded blocks of foam were placed in Kjeldahl flasks with 8 - 10 ml concentrated nitric acid. These were gently heated until the foam dissolved and the volume was reduced to about 2 ml. An 8 - 10 ml aliquot of concentrated hydrochloric acid was added and the heating procedure repeated to dissolve any precipitate.

On cooling, the foam digests were diluted to the required volume with 2M HCl, after sufficient lanthanum nitrate was added to give a final La^{3+} concentration of 0,2% w/v. This procedure ensured the complete digestion of the loaded foams for subsequent AAS.

Standards were prepared in a similar way, except that stock metal solutions were pipetted directly into a Kjeldahl flask, together with a clean block of foam, followed by digestion with concentrated nitric and hydrochloric acids. In this way, the matrix of the analyte and standard solutions were satisfactorily matched. In order to check for mass balance, the aqueous phase was made up to volume containing 0,2% w/v lanthanum nitrate. These solutions were analysed by AAS by comparing them to matrix matched standards.

8.7 FOAM STRIPPING APPARATUS AND PROCEDURE.

Preliminary foam stripping experiments were performed on platinum-loaded foams using a small column filled with loaded polyurethane foam. The foams were manually squeezed using a glass rod. The stripping solution was poured over the foam and collected in small aliquots.

A more sophisticated system was employed once it was established that platinum could in fact be stripped from foam.

The stripping apparatus is shown in Figure 8.4. The vessels containing the solvent and the loaded foam were placed in a thermostated water bath as the stripping solvent, an HCl/ethanol mixture, had to be heated to 70 ^{o}C for the removal of platinum or rhodium from the foam. The solvent was pumped through the foams from below to avoid air bubbles forming in the column containing the foam discs. Small aliquots of the eluent were collected. When no further metal was eluted, the foam was dried and degraded using the method described in Section 8.6. The eluent samples, together with the degraded foam solution, were analysed by comparing them to matrix matched standards using atomic absorption spectroscopy.

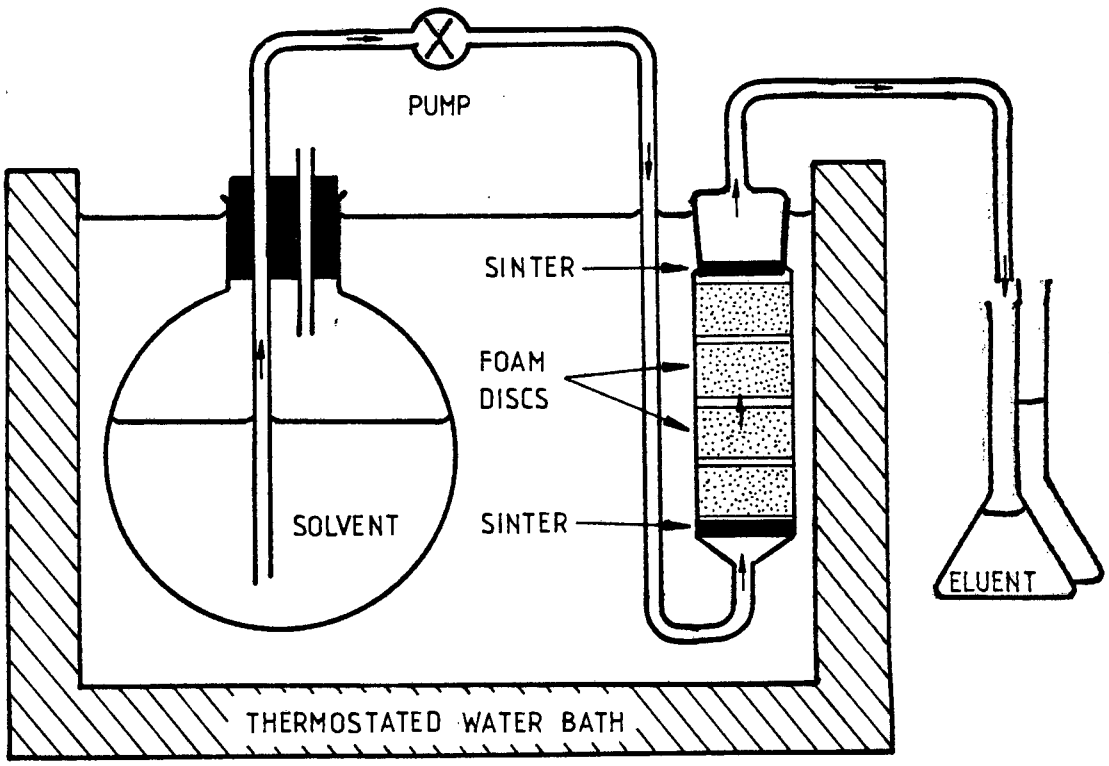


Figure 8.4 The experimental apparatus used for the stripping of loaded polyurethane foams.

APPENDICES

Appendix 1

Appendix 1a

The effect of [HCl] on the sorption of Pt onto polyurethane foam.

[HCl]/M	Pt found/mg	%[a]
0,5	4,66	93,2
	4,83	96,6
	4,74	94,8
1,5	4,95	99,0
	4,83	96,6
	4,95	99,0
	4,88	97,6
2,0	4,83	96,6
	4,95	99,0
	4,83	96,6
	4,88	97,6
	4,95	99,0
	4,88	97,6
2,5	4,83	96,6
	4,83	96,6
	4,74	94,8
	4,77	95,4
3,5	4,88	97,6
	4,83	96,6
	4,83	96,6
	4,74	94,8

(a) Pt found/Pt taken

Appendix 1b

The effect of Ra(Pt) on the sorption of Pt onto polyurethane foams.

Ra	Pt taken	Pt found	%
10	2,5	2,53	101,0
		2,56	102,2
		2,49	99,8
		2,46	98,5
20	25	2,53	101,0
		2,49	99,8
		2,49	99,8
	50	4,82	96,4
		4,70	94,0
		4,82	96,4
		5,00	100,0
30	25	2,43	97,3
		2,46	98,5
		2,46	98,0
	50	5,05	101,0
		5,18	103,6
		5,00	100,0
		4,88	97,6
40	25	2,53	101,0
		2,46	98,5
		2,46	98,5
		2,49	99,8
	50	4,83	96,6
		4,83	96,6
		4,70	94,0
		4,95	99,0

(a) Pt found/Pt taken

Appendix 1c

Recovery of Pt from polyurethane foam. Initial mass Pt taken : A = 5,0 mg, B = 2,5 mg, C = 1,0 mg, D = 0,50 mg, E = 0,25 mg, F = 100 ug, G = 50 ug, H = 20 ug, I = 10 ug.

Pt found/mg	%[a]	Pt found/mg	%	Pt found/mg	%
A		B		C	
5,00	100,0	2,53	101,0	1,00	100,4
4,88	97,6	2,46	98,5	1,01	101,3
4,83	96,6	2,49	99,8	1,00	100,4
4,70	94,0	2,46	98,5	1,00	100,4
4,95	99,0	2,46	98,5	0,99	99,4
5,18	103,6	2,46	98,5	1,00	100,2
5,05	101,0	2.43	97,3	1,01	101,1
4,83	96,6	2,53	101,0	0,99	99,4
		2,49	99,8		
		2,49	99,8		
D		E		F	
0,50	99,2	0,25	99,2	84,0	84,0
0,51	101,6	0,25	100,7	85,9	85,9
0,50	100,0	0,25	99,2	80,3	80,3
0,49	98,4	0,26	102,2	85,9	85,9
0,51	101,6	0,25	99,2	86,9	86,9
0,50	100,8	0,25	99,2	85,6	85,6
0,50	99,2	0,25	100,7	84,3	84,3
0,49	98,5	0,25	98,8	85,6	85,6
0,49	97,6	0,26	104,4	83,1	83,1
0,49	98,5			79,3	79,3
0,49	98,5			80,6	80,6
G		H		I	
34,1	68,2	15,0	60,0	5,2	51,9
39,0	78,0	16,8	67,2	6,7	66,9
37,8	75,6	18,6	74,4	6,7	66,9
36,0	72,0	15,0	60,0	5,2	51,9
32,3	64,6	16,8	67,2	8,1	81,3
34,1	68,2	16,8	67,2	5,2	51,9
39,9	79,2			8,1	81,3
36,0	72,0				
39,6	79,2				

(a) *The % Pt is calculated using mass Pt found/mass Pt taken, where mass Pt found was taken to 3 decimal places. This gives rise to different percentage values for the same mass Pt found as shown in the table.*

Appendix 2

The extraction of Pt from solutions containing base metals

A. Initial solutions contain 2,5 mg Pt + 250 mg each of Co, Cu, Ni and Zn.

Pt/mg	%	Mass found on foam Co/mg	%	Cu/mg	%	Ni/mg	%	Zn/mg	%
2,50	100	0,66	0,26	6,91	2,76	0,74	0,30	1,36	0,54
2,43	97	0,33	0,13	7,25	2,90	0,19	0,08	0,89	0,36
2,50	100	0,33	0,13	5,96	2,38	0,36	0,14	0,85	0,34
2,43	97	0,39	0,16	7,23	2,89	0,30	0,12	0,89	0,36
2,53	101	0,46	0,18	6,26	2,50	0,41	0,16	1,03	0,41

B. Initial solutions contain 2,5 mg Pt + 250 mg Fe

Mass found on foam Pt/mg	%Pt	Fe/mg	%Fe
2,43	97,2	0.09	0.03
2,53	101,2	0,13	0,05
2,48	99,2	0,11	0,05
2,43	97,2	0,18	0,07

Appendix 3

The separation of Pt from Ir

Initial mass Pt taken (mg): initial mass Ir taken (mg):
A = 2,5:2,46, B = 1,50:1,48, C = 1,00:9,85, D = 0,50:24,63,
E = 0,10:9,85.

	Platinum found on foam/mg	%	Iridium found in solution/mg	%	on foam/mg	%
A.	2,58	103,4	2,38	96,7	N/D	
	2,61	104,4	2,42	98,3		
	2,57	100,6	2,46	100,0		
	2,57	100,6	2,46	100.0		
	2,49	99,6	2,31	93,8		
	2,42	96,8	2,31	93,8		
	2,54	101,5	2,50	101,6		
B.	1,49	99,1	15,38	104,1	N/D	
	1,45	96,6	14,97	101,3		
	1,44	96,0	14,57	93,6		
	1,52	101,0	14,97	101,3		
C.	1,01	100,8	8,96	91,1	N/D	
	1,01	100,8	9,33	94,7		
	1.02	101,8	9,70	98,5		
	1,00	99,8	9,70	98,5		
	1,00	99,8	10,07	102,2		
D.	0,51	101,4	24,30	98,7	0,12	0,50
	0,52	103,4	24,80	100,1	0,12	0,50
	0,50	100,4	24,30	98,7	0,12	0,50
	0,51	101,4	23,79	66,6	0,13	0,50
	0,53	105,4	24,30	98,7	0,13	0,50
	0,50	100,4	25,31	102,8	0,12	0,50
E.	0,09	90,1	10,18	103,4	0,02	0,20
	0,09	92,1	9,78	99,1	0,04	0,40
	0,09	92,1	9,62	97,7	0,04	0,40
	0,10	104,0	10,04	101,9	0,04	0,40
	0,10	98,0	9,48	96,2	0,06	0,60

Appendix 4

The separation of Pt and Ru.

Initial mass Pt taken(mg): initial mass Ru taken (mg);
A = 5,00:2,59, B = 2,50:1,30. C = 1,00:0,52, D = 2,50:12,95,
E = 1,00:5,18, F = 1,00:51,82.

	Platinum found on foam/mg	%	Ruthenium found in solution/mg	%	Ruthenium found on foam/mg	%
A.	5,09	101,8	2,64	101,8	N/D	
	5,09	101,8	2,64	101,8		
	4,91	98,1	2,61	100,8		
	5,02	100,5	2,58	99,7		
	5,03	100,7	2,66	102,8		
	5,03	100,7	2,61	100,8		
B.	2,54	101,8	1,30	100,1	N/D	
	2,54	101,8	1,32	102,2		
	2,57	102,9	1,27	98,0		
	2,52	100,7	1,30	100,1		
	2,52	100,7	1,27	98,0		
	2,49	99,5	1,30	100,1		
C.	1,00	100,5	0,51	98,3	N/D	
	1,00	100,5	0,52	99,4		
	0,99	99,3	0,51	98,3		
	1,02	101,6	0,51	98,3		
	1,00	100,5	0,50	97,1		
	0,99	99,3	0,51	98,3		
D.	2,49	99,8	12,80	98,8	N/D	
	2,52	100,9	12,93	99,8		
	2,49	99,8	12,80	98,8		
	2,49	99,8	13,05	100,7		
	2,52	100,9	12,93	99,8		
	2,49	99,8	12,93	99,8		
E.	1,01	101,4	5,20	100,3	N/D	
	1,00	100,2	5,45	105,3		
	1,01	101,4	5,32	102,8		
	1,02	102,5	5,20	100,3		
	1,01	101,4	5,39	104,0		
	1,04	103,6	5,26	101,5		
F.	0,80	80,4	51,70	99,8	0,09	0,11
	0,79	79,2	52,08	100,5	0,10	0,19
	0,77	77,0	51,70	99,8	0,06	0,12
	0,89	89,5	51,80	100,0	0,05	0,10
	1,05	105,5	51,80	100,0	0,30	0,06
	0,83	82,7	52,20	100,7	0,01	0,02

Appendix 5

The recovery of platinum from synthetic mixtures

A. Initial solutions contain 1,0 mg Pt + 2,59 mg Ru and 4,93 mg Ir.

Platinum found on foam/mg	%	Iridium found in solution/mg	%	Ruthenium found in solution/mg	%
1,02	102,0	4,97	100,9	2,64	101,8
1,00	99,9	4,80	97,4	2,64	101,8
0,99	98,5	4,97	100,9	2,66	102,5
1,00	99,9	4,97	100,9	2,64	101,8
0,96	96,4	4,88	99,2	2,62	101,0
0,99	99,2	4,88	99,2	2,62	101,0
0,99	99,9	4,80	97,4	2,64	101,8

B. Initial solutions contain 1,0 mg Pt + 2,59 mg Ru + 4,93 mg Ir + 1,68 mg Zn + 1,63 mg Cu + 1,51 mg Co + 1,51 mg Ni.

mass found/mg						
Pt	Ru	Ir	Zn	Cu	Co	Ni
			in solution			
N/D[a]	2,57	4,92	1,77	1,59	1,50	1,48
	2,60	4,98	1,77	1,58	1,52	1,49
	2,60	4,98	1,80	1,65	1,52	1,51
	2,59	4,92	1,77	1,59	1,50	1,49
	2,63	5,05	1,73	1,61	1,52	1,54
	2,63	5,05	1,78	1,59	1,53	1,49
			on foam			
1,01	N/D	N/D	0,03	0,03	N/D	0,01
1,00			0,02	0,04		0,01
0,99			0,02	0,02		0,01
1,01			0,02	0,04		0,02
1,01			0,03	0,04		0,01
0,99			0,04	0,03		0,01

a N/D = not detected by AAS.

Appendix 6

Appendix 6a

The effect of shaking time on the extraction of rhodium by polyurethane foams.

Shaking time/ hours	Rhodium found on foam/mg	%	in solution/mg	%
1,5	3,19	63,8	1,74	34,8
	3,38	67,6	1,69	33,8
	3,42	68,4	1,88	37,6
2,5	4,45	89,0	0,67	13,4
	4,40	88,0	0,64	12,8
	4,25	85,0	0,54	10,8
3,5	4,55	91,0	0,31	6,2
	4,61	92,2	0,42	8,4
4,5	4,75	95,0	0,34	6,8
	4,80	96,0	0,39	7,8
	4,80	96,0	0,22	4,4

Appendix 6b

The effect of pre-equilibration on the extraction of rhodium by polyurethane foams.

Equilibration time/ hours	Rhodium found on foam/mg	%	in solution/mg	%
1	4,69	93,8	0,22	4,4
	4,88	97,6	0,15	3,0
	4,72	94,4	0,19	3,8
	4,80	96,0	0,13	2,6
2	4,87	97,4	0,15	3,0
	4,73	94,6	0,13	2,6
	4,80	96,0	0,09	1,8
	4,91	98,2	0,09	1,8
3	4,90	98,0	N/D	
	4,95	99,0		
	5,10	102,0		
	5,05	101,0		

Appendix 7

Appendix 7a

The effect of R_a(Rh, Ir) on the separation of rhodium and iridium using polyurethane foams

R_a(Rh, Ir)	Rhodium found on foam/mg	%	in solution/mg	%	Iridium found in solution/mg	%
10	1,87	74,7	0,58	23,2	4,56	97,6
	1,94	77,7	0,50	20,1	4,69	100,5
	2,02	80,8	0,46	18,5	4,69	100,5
	1,99	79,8	0,36	14,4	4,69	100,5
15	2,40	96,0	0,05	2,0	4,61	98,7
	2,40	96,0	0,01	0,6	4,43	94,9
	2,40	96,0	0,03	1,3	4,61	98,7
20	2,40	96,0	0,02	0,7	4,69	100,5
	2,37	94,9	0,02	0,7	4,69	100,5
	2,30	91,9	0,03	1,3	4,69	100,5
	2,49	99,0	0,02	0,7	4,56	97,6
25	2,35	93,9	0,05	2,0	4,61	98,7
	2,30	91,9	0,05	2,0	4,78	102,4
	2,20	87,9	0,05	2,0	4,78	102,4
	2,32	92,9	0,08	3,0	4,61	98,7

Appendix 7b

The effect of shaking time on the extraction of rhodium from solutions containing iridium by polyurethane foams

Shaking time/ hours	Rhodium found/mg on foam	%	Rhodium found/mg in solution	%	Iridium found/mg in solution	%
1,5	2,37	94,9	0,04	1,7	4,46	95,5
	2,40	96,0	0,06	2,5	4,46	95,4
	2,33	93,4	0,01	0,4	4,44	95,0
	2,33	93,4	0,09	3,8	4,57	97,8
2,0	2,10	83,9	0,19	7,6	4,57	97,8
	2,53	101,3	0,09	3,8	4,57	97,8
	2,40	96,1	0,04	1,7	4,30	92,1
3,0	2,37	94,8	0,12	4,9	4,57	97,8
	2,49	99,4	N/D	0,0	4,70	100,6
	2,55	102,1	N/D	0,0	4,57	97,8
	2,46	98,4	N/D	0,0	4,70	100,6
4,5	2,29	91,8	0,09	3,8	4,57	97,8
	2,34	93,8	0,09	3,8	4,30	92,1
	2,43	97,2	0,04	1,7	4,57	97,8
	2,34	93,8	0,09	3,8	4,57	97,8

Appendix 7c

The separation of rhodium and iridium at Ir:Rh mole ratios of 10 by polyurethane foams.

Rhodium found on foam/mg	%	Iridium found in solution/mg	%
2,28	91,3	46,72	100,0
2,34	93,7	45,71	97,9
2,37	94,6	45,71	97,9
2,39	95,4	48,74	104,4
2,39	95,4	45,71	97,9
2,34	93,7	45,71	97,9
2,34	93,7	47,73	102,2
2,30	92,1	47,73	102,2

Appendix 8

Appendix 8a

The effect of acid concentrations on the separation of rhodium and ruthenium using polyurethane foams

[Acid]	Rhodium found/mg on foam	%	in solution	%	Ruthenium found/mg on foam	%	in solution	%
2M HCl	1,35	54,0	1,18	47,4	N/D		2,43	98,9
	1,21	48,4	1,28	51,1			2,49	101,3
	1,48	59,1	1,03	41,1			2,40	97,8
	1,36	54,6	1,15	46,1			2,49	101,3
	1,39	55,7	1,09	43,6			2,43	99,0
	1,45	57,9	1,12	44,9			2,40	97,8
2M HCl	1,13	45,2	1,40	56,1	N/D		2,49	101,3
	1,13	45,2	1,35	53,9			2,49	101,3
	1,13	45,2	1,44	57,6			2,51	102,0
	1,11	44,4	1,35	53,9			2,43	99,0
	1,13	45,2	1,40	56,1			2,45	100,0
	1,26	50,4	1,17	46,9			2,45	100,0
3,5M H^+	2,03	81,3	0,45	18,0	0,03	1,2	2,47	100,7
0,5M Cl^-	1,84	73,4	0,61	24,3	0,06	2,5	2,33	95,0
(HCl/	1.92	76,6	0,51	20,4	0,03	1,4	2,42	98,4
$HClO_4$)	1,99	79,5	0,45	18,0	0,04	1,7	2,38	96,8
3,5M H^+	1,56	62,5	0,91	36,6	N/D		2,43	98,7
0,5M Cl^-	1,52	61,0	0,98	39,2			2,38	96,8
(HCl/	1,58	63,2	0,89	35,7			2,43	98,7
H_2SO_4)	1,50	60,2	1,01	40,1			2,38	96,8
	1,56	62,5	0,91	36,6			2,52	102,7
	1,50	60,2	1,01	40,1			2,47	100,7

Appendix 8b

The separation of rhodium and ruthenium by polyurethane foams from solutions containing 3,5M H^+ and 0,5M Cl^- concentrations

Rhodium found on foam/mg	%	Rhodium found in solution	%	Ruthenium found in solution	%
2,30	92,0	0,10	4,1	2,43	98,7
2,32	92,7	0,15	5,9	2,43	98,7
2,30	92,0	0,17	6,7	2,47	100,7
2,26	90,5	0,17	6,7	2,52	102,7
2,32	92,7	0,15	5,9	2,47	100,7
2,21	88,3	0,15	5,9	2,47	100,7

Appendix 9

The recovery of rhodium from synthetic mixtures containing ruthenium and iridium

Mass found on foam/mg (%) Rh	Mass found in solution/mg (%) Rh	Ru	Ir
2,30 (92,0)	0,03 (1,2)	2,47 (100,4)	5,80 (124,3)
2,22 (88,9)	0,03 (1,2)	2,47 (100,4)	5,69 (121,8)
2,26 (90,5)	0,05 (2,1)	2,47 (100,4)	5,58 (119,4)
2,26 (90,5)	0,03 (1,2)	2,35 (95,7)	5,58 (119,4)
2,38 (95,0)	0,03 (1,2)	2,47 (100,4)	5,69 (121,8)
2,32 (92,7)	0,03 (1,2)	2,47 (100,4)	5,58 (119,4)
2,26 (90,5)	0,03 (1,2)	2,47 (100,4)	5,69 (121,8)
2,30 (92,0)	0,03 (1,2)	2,41 (98,0)	5,58 (119,4)

Appendix 10

Appendix 10a
The recoveries of platinum and rhodium, following sorption by polyurethane foams at room temperature

Platinum on foam/mg	%	Rhodium on foam/mg	%	Rhodium in solution/mg	%
4,54	95,8	1,28	51,2	1,22	48,8
4,60	97,0	1,68	67,2	0,84	33,6
4,54	95,8	1,49	59,6	0,55	22,0
4,60	97,0	1,95	78,0	0,55	22,0
4,54	95,8	1,98	79,2	0,66	26,4
4,65	98,2	1,66	74,4	0,75	30,0

Appendix 10b
The recoveries of platinum and rhodium, following sorption by polyurethane foams after a pre-equilibration period of 3 hours at 50 ^{o}C

Mass found on foam			
Platinum/mg	%	Rhodium/mg	%
4,69	99,0	2,38	95,3
4,75	100,1	2,38	95,3
4,75	100,1	2,38	95,3
4,75	100,1	2,38	95,3
4,75	100,1	2,35	93,9
4,90	103,5	2,42	96,7
4,85	102,4	2,49	99,5

Appendix 11

The recoveries of platinum and rhodium, following sorption by polyurethane foams from solutions containing iridium

Mass found on foam				Mass found in solution	
Platinum/mg	%	Rhodium/mg	%	Iridium/mg	%
4,63	97,7	2,41	96,4	4,67	100,0
4,69	98,9	2,48	99,2	4,55	97,4
4,58	96,6	2,37	94,8	4,62	98,9
4,63	97,7	2,45	98,0	4,55	97,4
4,69	98,9	2,41	96,4	4,76	101,9
4,75	100,2	2,52	100,8	4,62	98,9

Appendix 12

The separation of platinum from ruthenium and rhodium using polyurethane foams

Platinum found/mg		Rhodium found/mg			Ruthenium found/mg		
on foam	%	on foam	%	in solution	%	in solution	%
4,48	94,5	0,26	10,6	2,13	85,3	2,52	100,6
4,53	95,5	0,24	9,7	2,17	86,8	2,41	96,3
4,63	97,6	0,26	10,6	2,10	83,8	2,41	96,3
4,58	96,6	0,29	11,4	2,19	87,5	2,41	96,3
4,58	96,6	0,29	11,4	2,10	83,8	2,63	105,0
4,53	95,5	0,29	11,4	2,19	87,5	2,52	100,6
4,53	95,5	0,29	11,4	2,13	85,3	2,52	100,6
4,53	95,5	0,31	12,2	1,95	78,0	2,41	96,3

Appendix 13

The extraction of platinum from complex mixtures of noble metals. Initial mass taken/mg:
A: Pt = 5,00; Rh = 2,63; Ru = 2,59; Ir = 4,93
B: Pt = 4,74; Rh = 2,50; Ru = 2,46; Ir = 4,46

	Mass found on foam/mg				Mass found in solution/mg					
	Pt	%	Rh	%	Rh	%	Ru	%	Ir	%
A.	5,16	103,2	0,23	8,7	2,37	91,6	2,64	102,0	5,11	103,7
	4,91	98,1	0,26	9,9	2,35	90,6	2,56	99,0	5,01	101,6
	4,83	96,7	0.19	7,2	2,32	89,5	2,53	97,6	5,01	101,6
	4,94	98,9	0,17	6,4	2,35	90,6	2,38	91,7	4,90	99,5
	4,91	98,1	0,19	7,2	2,35	90,6	2,60	100,5	5,01	101,6
	4,94	98,9	0,21	8,0	2,29	88,4	2,64	102,0	4,90	99,5
	4,91	98,1	0,19	2,7	2,29	88,4	2,57	99,0	4,90	99,5
	5,01	100,3	0,23	8,7	2,32	89,5	2,60	100,5	4,90	99,5
B.	4,66	98,3	0,04	1,8	2,42	97,0	2,74	111,7	4,66	99,9
	4,62	97,6	0,04	1,8	2,36	94,3	2,62	106,8	4,57	98,0
	4,62	97,6	0,07	2,6	2,30	92,2	2,56	104,3	4,57	98,0
	4,60	97,0	0,09	3,4	2,30	92,2	2,56	104,3	4,66	99,9
	4,62	97,6	0.07	2,6	2,52	100,7	2,56	104,3	4,75	101,8
	4,66	98,3	0,07	2,6	2,45	98,1	2,56	104,3	4,48	96,1
	4,66	98,3	0,02	0,9	2,33	93,3	2,68	109,3	4,57	98,0
	4,60	97,0	0,04	1,8	2,33	93,3	2,68	109,3	4,48	96,1

Appendix 14

The recoveries of platinum by foam stripping. Eluents used: A,B = Boiling 5% v/v H_2O_2/2M HCl, B = foam wetted with ethanol prior to stripping; C = 5% v/v H_2O_2/ ethanol; D = 5% v/v H_2O_2 + 5% v/v HCl/ethanol; E = 5% v/v HCl/acetone; F = 5% v/v HCl/ethanol; G = 5% v/v HCl/ethanol, pre-heated to 50 ^{o}C.

	Volume eluate/ml	Mass found mg	%	Total Mass found mg	%
A.	25	0,58	11,6	0,58	11,6
	50	1,15	23,0	1,73	34,6
	75	0,66	13,2	2,39	47,8
	100	0,25	5,0	2,64	52,8
	125	0,07	1,4	2,71	54,2
	150	0,05	1,0	2,76	55,2
	175	0,04	0,8	2,80	56,0
	200	0,04	0,8	2,84	56,8
B.	25	1,49	29,8	1,49	29,8
	50	1,01	20,2	2,50	50,0
	75	0,38	7,6	2,88	57,6
	100	0,26	5,2	3,14	62,8
	125	0,12	2,4	3,26	65,2
	150	0,07	1,4	3,32	66,6
	175	0,03	0,6	3,35	67,2
	200	0,03	0,6	3,38	67,8
C.	25	1,80	36,0	1,80	36,0
	50	0,65	13,0	2,45	49,0
	75	0,15	3,0	2,60	52,0
	100	0,06	1,4	2,66	53,4
	125	0,02	0,4	2,68	53,8
	150	0,02	0,4	2,70	54,2
	175	0,01	0,2	2,71	54,4
	200	0,01	0,2	2,72	54,6
	225	0,37	7,4	3,09	62,0
D.	25	0,17	6,8	0,17	6,8
	50	0,22	8,8	0,39	15,6
	75	0,17	6,8	0,56	22,4
	100	0,17	6,8	0,73	29,2
	125	0,13	5,2	0,86	34,4
	150	0,12	4,8	0,98	39,2
	175	0,11	4,4	1,09	43,6
	200	0,07	2,8	1,16	46,4
	225	0,06	2,4	1,22	48,8
	250	0,05	2,0	1,27	50,8

	Volume eluate/ml	Mass found mg	%	Total Mass found mg	%
E.	25	2,63	52,6	2,63	52,6
	50	0,85	17,0	3,48	69,6
	75	0,21	4,2	3,69	73,8
	100	0,06	1,2	3,75	75,0
	125	0,02	0,4	3,77	75,4
	150	0,01	0,2	3,78	75,6
	175	<0,01	0,2	3,79	75,8
	200	<0,01	0,2	3,79	76,0
F.	25	0,83	16,6	0,83	16,6
	50	0,80	16,0	1,63	32,6
	75	0,68	13,6	2,31	46,2
	100	0,47	9,4	2,78	55,6
	125	0,29	5,8	3,07	61,4
	150	0,17	3,4	3,24	64,8
	175	0,14	2,6	3,38	67,4
	200	0,10	2,0	3,48	69,4
G.	25	0,41	16,4	0,41	16,4
	50	0,51	20,4	0,92	36,8
	75	0,64	25,6	1,56	62,4
	100	0,41	16,4	1,97	78,8
	125	0,18	7,2	2,15	86,0
	150	0,08	3,2	2,23	89,2
	175	0,02	0,8	2,25	90,0
	200	0,02	0,8	2,27	90,8
	225	0,01	0,4	2,28	91,2
	250	0,01	0,4	2,29	91,6

Appendix 15

The recoveries of platinum by foam stripping. Eluents used, pre-heated to 70 °C: A = ethanol; B = 2,5% v/v HCl/ethanol; C = 5% v/v HCl/ethanol; D = 10% v/v HCl/ethanol

	Volume eluate/ml	Mass found mg	%	Total Mass found mg	%
A.	25	1,73	69,2	1,73	69,2
	50	0,14	5,6	1,87	74,8
B.	25	2,02	81,1	2,02	81,1
	50	0,22	8,8	2,24	89,9
	75	0,02	0,8	2,26	90,7
C.	25	2,19	87,6	2,19	87,7
	50	0,16	6,4	2,35	94,0
	75	0,02	0,8	2,37	95,8
D.	25	2,17	86,8	2,17	86,8
	50	0,20	8,0	2,37	94,8
	75	0,03	1,2	2,40	96,0

Appendix 16

The recoveries of rhodium by foam stripping. Eluents used: A = 5% v/v HCl/ethanol (room temperature); B = ethanol (70 °C); C = 2,5% v/v HCl/ethanol (70 °C); D = 5% v/v HCl/ethanol (70 °C); E = 10% v/v HCl/ethanol (70 °C)

	Volume eluate/ml	Mass found mg	%	Total Mass found mg	%
A.	25	0,84	33,6	0,84	33,6
	50	0,50	20,0	1,34	53,6
	75	0,26	10,4	1,60	64,0
	100	0,18	7,2	1,78	71,2
	125	0,18	7,2	1,96	78,4
	150	0,08	3,2	2,04	81,6
	175	0,06	2,4	2,10	84,0
	200	0,06	2,4	2,16	86,4
B.	25	1,72	68,8	1,72	68,8
	50	0,18	7,2	1,90	76,0
	75	0,05	2,0	1,95	78,0
	100	0,03	1,2	1,98	79,2
	125	0,02	0,8	2,00	80,0
C.	25	2,31	92,5	2,31	92,5
	50	0,16	6,5	2,47	99,0
	75	0,01	0,4	2,48	99,4
	100	<0.01	0,1	2,49	99,5
D.	25	2,14	85,6	2,14	85,6
	50	0,20	8,0	2,34	93,6
	75	0,04	1,6	2,38	95,2
	100	<0,01	0,1	2,39	95,3
E.	25	2,18	87,2	2,18	87,2
	50	0,30	12,0	2,48	99,2
	75	0,02	0,8	2,50	100,0

Appendix 17

Appendix 17a
The recoveries of platinum and rhodium by foam stripping. A = 10% v/v HCl/ethanol; B = 10% v/v HCl/ethanol + $SnCl_2$ (R_a(Pt, Rh) = 50)

	volume eluate/ml	Mass Pt found mg	%	total %	Mass Rh found mg	%	total %
A.	10	1,61	34,0	34,0	0,90	36,0	36,0
	20	1,23	25,9	59,9	0,50	20,0	56,0
	30	0,78	16,5	76,4	0,43	17,2	73,2
	40	0,49	10,3	86,7	0,29	11,6	84,8
	50	0,27	5,7	92,4	0,18	7,2	92,0
	60	0,13	2,7	95,1	0,10	4,0	96,0
	70	0,07	1,5	96,6	0,06	2,4	98,4
	80	0,03	0,6	97,2	0,03	1,2	99,6
	90	0,01	0,2	97,4	0,02	0,8	100,4
	100	0,01	0,2	97,6	0,01	0,4	100,8
	110	0,01	0,2	97,8			
B.	10	1,13	23,9	23,9	0,59	23,7	23,7
	20	0,81	17,1	41,0	0,44	17,5	41,2
	30	0,69	14,5	55,5	0,39	15,5	56,7
	40	0,50	10,6	66,1	0,30	12,0	68,7
	50	0,38	8,0	74,1	0,20	7,9	76,7
	60	0,29	6,1	80,1	0,15	5,9	82,5
	70	0,21	4,4	84,1	0,10	4,2	86,7
	80	0,15	3,1	87,6	0,07	2,8	89,5
	90	0,12	2,6	90,2	0,06	2,3	91,8
	100	0,10	2,1	92,4	0,05	2,0	93,8
	110	0,07	1,5	93,9	0,04	1,4	95,2
	120	0,05	1,1	95,0	0,03	1,0	96,2
	130	0,04	0,9	95,9	0,01	0,5	96,7
	140	0,03	0,6	96,5	0,01	0,4	97,1
	150	0,03	0,5	97,0	0,01	0,2	97,3
	160	0,02	0,4	97,4	<0,01	<0.1	97,3
	170	0,01	0,3	97,7			
	180	0,01	0,2	97,9			
	190	<0,01	0,1	98,0			
	200	<0,01	0,1	98,1			

Appendix 17b

The recoveries of platinum and rhodium by foam stripping. A = 10% v/v HCl/ethanol; B = 10% v/v HCl/ethanol + $SnCl_2$ (R_a(Pt, Rh) = 50)

	Volume eluate/ml	Mass Pt found mg	%	total %	Mass Rh found mg	%	total %
A.	10	0,81	17,0	17,0	0,33	13,3	13,3
	20	0,74	15,5	32,6	0,33	13,3	26,6
	30	0,73	15,4	48,0	0,32	12,9	39,5
	40	0,68	14,3	62,2	0,32	12,9	52,4
	50	0,53	11,1	73,3	0,29	11,8	64,2
	60	0,41	8,6	81,9	0,25	10,0	74,2
	70	0,29	6,2	88,1	0,22	8,6	82,8
	80	0,21	4,3	92,4	0,17	6,8	89,6
	90	0,12	2,6	95,0	0,11	4,3	93,9
	100	0,08	1,7	96,7	0,08	3,0	96,9
	110	0,06	1,2	97,9	0,04	1,6	98,5
	120	0,03	0,6	98,5	0,02	0,8	99,3
	130				0,01	0,4	99,7
B.	10	1,03	21,8	21,8	0,44	17,7	17,7
	20	0,85	18,0	39,7	0,39	15,8	33,4
	30	0,67	14,1	53,9	0,35	13,9	47,3
	40	0,53	11,3	65,1	0,30	11,8	59,1
	50	0,43	9,2	74,3	0,25	9,9	69,0
	60	0,38	8,0	82,3	0,20	7,8	76,9
	70	0,30	6,4	88,7	0,17	6,7	83,6
	80	0,24	5,0	93,7	0,14	5,5	89,1
	90	0,16	3,4	97,1	0,10	3,9	93,0
	100	0,10	2,1	99,2	0,07	2,6	95,6
	110	0,07	1,4	100,6	0,05	1,8	97,4
	120	0,04	0,9	101,5	0,03	1,2	98,6
	130				0,02	0,7	99,3
	140				0,01	0,5	99,8
	150				0,01	0,2	100,0

Appendix 18

Calibration of Gilson pipettes (models p1000 and p5000). The masses of 5 ml, 2,5 ml and 1 ml aliquots of water were weighed on a Mettler and Sartorius four decimal place balance. The volumes were calculated as follows:

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

The density for the particular temperature of water was obtained from standard reference tables [224].

Mass water found/g	volume water/ml	Mass water found/g	volume water/ml	Mass water found/g	volume water/ml
5,0169	5,024	2,4961	2,500	0,9916	0,993
4,9949	5.002	2,4955	2,499	0,9894	0,991
4,9908	4,998	2,4934	2,497	0,9921	0,993
4,9751	4,982	2,4980	2,502	1,0112	1,013
4,8482	4,855	2,4827	2,486	1,0088	1,010
4,9385	4,945	2,4914	2,495	0,9945	0,996
4,9597	4,967			0,9938	0,995
4,9871	4,994			1,0028	1,004
4,9742	4,981			0,9875	0,989
4,9590	4,966			0,9867	0,988
4,9412	4,948			0,9926	0,994
4,9320	4,939				
Average: 4,967 ± 0,044 ml[a] (n = 12) for p5000 Gilson pipette set to dispense 5 ml.		Average: 2,497 ± 0,006 ml (n = 6) for p5000 Gilson pipette set to dispense 2,5 ml.		Average: 0,997 ± 0,008 ml[b] (n = 11) for p1000 Gilson pipette set to dispense 1 ml.	

a The manufacturer's specifications are 5,000 ± 0,030 ml (n =30)

b The manufacturer's specifications are 1,000 ± 0,006 ml (n = 30).

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