1 Introduction

Under the name of PMs (Precious Metals) or noble metals are grouped the six elements of the platinum group of metals, PGMs: ruthenium, rhodium, palladium, platinum, osmium and iridium, together with gold and silver. The property that is common to all these metals is their noble character, owing to their passivity before chemical reagents.

Platinum, palladium and rhodium are the three principal metals of the platinum group (PGMs), in the economic and commercial context. Currently, their main application is catalytic processes, and this characteristic has justified many studies on their recovery.

In recent decades, several processes have been developed to recover and separate platinum group metals from synthetic or industrial effluents, including sorption, (Beauvais and Alexandratos 1998; Cortina et al. 1998), ion exchange (Clifford and Weber 1983), liquid-liquid extraction and related processes, including impregnated resins and liquid membranes. These are powerful techniques (Cortina et al. 1996; Rovira and Sastre 1998), that may involve environmental drawbacks such as release of solvent or extractant traces. Furthermore, their technical and economic efficiencies are limited by the treatment of dilute effluents. For these reasons sorption and ion-exchange processes on sorbents are the focus of this study.

A wide range of sorbents or ion-exchange systems is available for platinum group metals recovery. However, the research has been focused on natural-based products as chitosan due to their ready availability and their environmental friendly behaviour (particularly in the treatment of the exhausted sorbents). Metals can be recovered by elution using different extractants. Alternatively, recovery can be also performed by the combustion and elimination of the organic sorbent, with resulting combustion products which

are less hazardous for environment than those of conventional ion-exchange resins.

Chitosan results from the alkaline deacetylation of chitin, the most abundant biopolymer in nature after cellulose. It is an aminopolysaccharide made up of both glucosamine and acetylglucosamine moities. It is soluble in dilute mineral and organic acid solutions (except sulphuric acid and to a lesser extent phosphoric acid). Most industrial effluents containing platinum group metals are strongly acidic and chitosan can be used for these metals recovery only after a crosslinking step to increase its chemical stability. Several chemical crosslinking agents have been proposed, such as epichlorohydrin or glutaraldehyde (Kawamura et al. 1993; Hsien and Rorrer 1997; Guibal et al. 1998). In the present work, glutaraldehyde has been selected for chemical stabilization.

Precious metals in their most common states tend to form the most stable complexes with ligands which contain (π-linking) donor atoms such as I, S and N. Pearson (1963) observes that soft acids (B-type metals) are bound preferentially to soft bases (such as amine groups). However precious metals can easily form complexes with chloride anions, and owing to the fact that the majority of processes that are used in hydrometallurgy involve the use of HCl, the metals are found in solution as chloro complexes. In such experimental conditions, nitrogen-containing sites may be protoned and bind hydrochloric moities, forming carbocations, with which metallic anions may react with ion-exchange mechanism as suggested in the following reaction in the case of the anion tetrachloropalladate. Similar behaviour may occur with other mineral acids. Depending on the species of metal, the mechanisms of sorption or ion-exchange can compete or co-exist, and both hypotheses will be examined in this study.

$$RNH_2 + HCl \Leftrightarrow RNH_3^+ + Cl^-$$
$$2RNH_3^+ + PdCl_4^{2-} \Leftrightarrow (RNH_3^+)_2PdCl_4^{2-} + 2Cl^-$$

Chitosan and derived products have been studied for the recovery of a wide range of metals such as uranium, lead, cadmium, chromium, molybdenum, vanadium (Eiden et al. 1980; Muzzarelli et al. 1984; Gonzalez-Davila 1990; Rorrer et al. 1993; Guibal et al. 1995; Dambies et al. 2000) and also noble metals as gold, platinum, palladium, rhodium (Baba and Hirakawa 1992; Inoue et al. 1995; Guibal et al. 1999a; Wan Ngah and Liang 1999). However, in the latter works, most of the studies were carried out using medium to high concentrations or using very costly sorbents derived from complex modifications of the chitosan backbone, which show their obtention and their adsorption capacity before metals without carrying out a complete kinetic study so as to check the effect of perturbation parameters. Few studies were dedicated to the recovery of precious metals from low concentration solutions as encountered in wastewater from mining, metallurgical industries and recycling processes.

Before the start of this thesis, one of the last studies for the recovery of precious metals was carried out by Guibal et al. (1999a), in which the efficacy of chitosan for the elimination from platinum of dilute effluents was shown. It was for this reason that, encouraged by Dr. Ana Sastre Requena, specialist in metal separation and recovery at the Department of Chemical Engineering of the Technical University of Catalonia and who maintains a close collaboration with Dr. Eric Guibal, this investigation of chitosan and the recovery and separation of noble metals, was begun making several visits to the "Laboratoire Gènie de l'Environnement Industriel de l'Ecole des Mines d'Alès" under the tutelage of Dr. Eric Guibal, specialist in the separation of metals with chitosan.

To get this investigation under way and to be able to develop it, the first work consisted of the study of the equilibrium conditions and the adsorption kinetics of Pd in chitosan in the form or flakes. This study was carried out using a closed and open reactor system. The results obtained are shown in papers I, II, and III.

Once this part of the work had been carried out, the specific interest of this investigation focused on obtaining chitosan derivatives that might improve the sorption capacity for Pd and Pt, by grafting sulphur compounds onto the chitosan, and also including desorption studies for Pd. The results obtained are shown in paper IV.

Owing to the possible transport problems which the high water content of the pearls of chitosan might cause, a drying process was used, comparing the results with those previously obtained (paper V). At the same time the sorption capacity of Pd and Pt was improved, introducing more amino groups in the chitosan chains (paper VI).

Finally, owing to the fact that the main part of the work was dedicated to the sorption of Pd and Pt, it was decided to complete this study by extending it to the metals Rh, Ru, Os, Ir and Re. The results of this study are presented in paper VII.

This work contributes to the study of the sorption of precious metals on chitosan, presenting it as a future alternative at an industrial level to the various existing processes.

1.1 Precious Metals

As it was said before, the name precious metals includes the six elements of the platinum group: ruthenium, rhodium, palladium, platinum, osmium and iridium, together with gold and silver.

The platinum group metals, which are included in group VIII of the periodic table, have different chemical behaviour from the other elements of the group: Fe, Co and Ni. Their metallic properties are such as to suggest classification in pairs: Ru/Os, Rh/Ir, Pd/Pt. At the same time these elements are usually subdivided into two different groups: metals of the primary group, which

comprise platinum and palladium, and the remaining elements of the group, which form the secondary PGMs. This classification comes from the fact that with conventional hydrometallurgical methods, the treatment of concentrates of precious metals is carried out by means of lixiviation with aqua regia, which yields a first separation into a soluble part and an insoluble residue. The soluble metals are gold and the metals of the primary platinum group and the insoluble ones are silver and the secondary PGMs.

The platinum group metals are amongst the 90 elements that comprise less than 2% by weight of the earth's crust - the 10 mile thick outer layer of the earth. They are rare elements, platinum is the most common with an abundance of about 10^{-6} %, whereas the others have abundance of the order of 10^{-7} % (Cotton and Wilkinson 1980).

The major producer of the platinum group metal are South Africa and Russia. Canada is a medium producer, whilst Columbia, China and Western Australia are all minor producers. In the USA, Alaska and Montana is potential producers. South Africa is the only country among the major producers that mines PGM-bearing ores primarily for the recovery of these metals. In Russia and Canada, PGM are derived mainly as a by-product of the processing high grade copper/nickel ores, being the metals recovered from copper anode slimes (Watanabe 1991). Copper anode slimes are obtained when copper anodes are dissolved in an electrolytic solution and the precious metals that these anodes contain as impurities, remain undissolved and form the so-called slimes.

In the past few decades, precious metals have found new applications outside the jewellery and decorative industries due to its excellent physical and chemical properties. Thus, precious metals have become widely used in many technological fields such as: automotive catalytic converters, catalysis in the chemical and petroleum refining industries, electronics, glass industry, medical sciences, etc. Therefore, at present there are available important sources of precious metals based on scrap materials, named secondary sources, in

addition to natural ores which constitute primary sources. In particular, obsolete electronic scraps and spent automotive converters constitute a significant portion of secondary sources of precious metals.

The growing demand for highly pure precious metals to be used in high-tech applications, the need for modern and clean processes and the increasing volume of low grade PGM from secondary sources available for recycling, is having a direct impact today on the industrial practice of recovering and refining precious metals.

Currently, solvent extraction is widely practised in hydrometallurgy. It was during the 60s that effective extractants became commercially available and made possible the industrial expansion of the process. Since that time extensive research has been carried out which has led to the development of several new selective extractants, but parallel to this, new techniques has been proposed for the recovery of the precious metals. Some of these techniques are related to solvent extraction and others to the research of new more selective adsorbents for these metals.

However, many issues remain to be resolved in connection with the final stage of precious metal refining to produce the individual metals of the overall process.

In this work a contribution in the research of these new alternatives through the use of a sorbent of natural origin is presented, chitosan, but before presenting this study it is appropriate to discover a little more about the fundamental chemistry of the precious metal and the techniques that are currently being used for their separation and recovery.

1.2 Chemistry of Platinum Group Metal Separation

Of the many known reactions in PGM chemistry, certain ones have been developed to separate the metals or have been shown to be especially useful for this purpose. This is true both for crude separation and for purification; in many cases the same reaction is equally important in both stages.

Dissolution Properties. Differences in reactivity toward chemical reagents, especially oxidizing acids and molten salts, can often be utilized for coarse separation of platinum group metals. The main strong oxidizing conditions used in the industry for solubilization of PGM feedstocks consist of aqua-regia treatment. Aqua-regia leaching is slowly being phased out in preference for the more efficient wet chlorination technique, in which the leaching agent is hydrochloric acid, with the addition of chlorine to increase the solution's oxidation potential. In addition, the HCl/H_2O_2 lixiviant combination is a common variant (Aprahamian and Demopoulos 1995).

Solution Equilibria. In the crystallization process (by either evaporation or precipitation), the solubilities of chloro complexes of the platinum group metal are very important, as is the possibility of altering these solubilities. The temperature dependence of these solubilities is generally quite large and can be considered at many stages of the processes. An even more useful phenomenon in separation technology is the effect on solubility of the addition of a common ion, which is utilized in precipitation crystallization.

Redox Reactions and Stability of Complexes. The precious metals show a wide variety of oxidation states. Many separations are made possible by valence changes in redox systems. This applies mainly to precipitation crystallization, but also to solvent extraction and distillation. In practice, the kinetic and thermal stabilities of the valences in complexes are important, as is the redox stability (Table 1).

Table 1: Stability of platinum group metal chloro complexes (Renner 1997).

Metal	Oxidation state	Complex	Redox stability	Kinetic stability	Thermal stability
Pt	IV	$[PtCl_6]^{2-}$	stable	very stable	very stable
Pt	II	$[PtCl_4]^{2-}$	unstable	unstable	
Pd	IV	$[PdCl_6]^{2-}$	unstable	stable	unstable
Pd	II	$[PdCl_4]^{2-}$	stable	very stable	
Ir	IV	$[IrCl_6]^{2-}$	stable	stable	
Ir	III	$[IrCl_6]^{3-}$	stable	stable	
Rh	III	$[RhCl_6]^{3-}$	stable	stable	unstable
Ru	IV	$[RuCl_6]^{2-}$	unstable		unstable

The platinum group metal complexes formed vary considerably with the oxidation state. Whereas the majority of PGMs form full chloro complexes, the trivalent metals form mixtures of chloroaquo species in equilibrium with each other that are very dependent on the total chloride concentration (Table 2).

Table 2: Platinum group metals oxidation and chloro complexes (Harris 1993).

Metal	Electron Config.	Co-ord. Number	Ionic Structure	Complexes Formed low ——— $[Cl^-]$ ——— high		
Au(III)	d^8	4	Sq. Pl.	$AuCl_4^-$		$AuCl_4^-$
Ag(I)	d^{10}	2	Linear	$AgCl_2^-$		$AgCl_4^{-3}$
Ru(III)	d^5	6	Oct.	$RuCl_3(H_2O)_3$		$RuCl_6^{-3}$
Ru(IV)	d^4	6	Oct.	$Ru_2OCl_8(H_2O)_2^{-2}$		$RuCl_6^{-2}$
Rh((III)	d^6	6	Oct.	$RhCl_4(H_2O)_2$	$RhCl_5(H_2O)^{-2}$	$RhCl_6^{-3}$
Pd(II)	d^8	4	Sq. Pl.	$PdCl_4^{-2}$		$PdCl_4^{-2}$
Pd(IV)	d^6	6	Oct.	$PdCl_6^{-2}$		$PdCl_6^{-2}$
Os(III)	d^5	6	Oct.	$OsCl_4(H_2O)_2^-$	$OsCl_5(H_2O)^{-2}$	$OsCl_6^{-3}$
Os(IV)	d^4	6	Oct.	$OsCl_6^{-2}$		$OsCl_6^{-2}$
Ir(III)	d^6	6	Oct.	$IrCl_4(H_2O)_2^-$	$IrCl_5(H_2O)^{-2}$	$IrCl_6^{-3}$
Ir(IV)	d^5	6	Oct.	$IrCl_6^{-2}$		$IrCl_6^{-2}$
Pt(II)	d^8	4	Sq. Pl.	$PtCl_4^{-2}$		$PtCl_4^{-2}$
Pt(IV)	d^6	6	Oct.	$PtCl_6^{-2}$		$PtCl_6^{-2}$

Chloro complexes differ in the greater or lesser degree of ease with which they can show substitution reactions. In general terms, these substitutions are slower than for base metals and follow the sequence: Pd(II)>Pt(II)>Ru(III)>Ir(III)>Os(III)>Ir(IV) and Pt(IV). Because of this it is very important to consider kinetic factors, given that the reactions that are thermodynamically possible, afterwards, in practice, do not show the same returns or are not so easy to carry out.

Furthermore, PGMs may exist in the divalent to octavalent state and the change in the oxidation state is complicated. The redox behaviour of the PGMs is shown in Table 3:

Table 3. Redox behaviour of precious metals in acidic chloride media (Grant and Matthey 1990).

(Elements situation as in the Periodic Table. Standard reduction potentials are given in V)

Ru(VIII)/Ru(IV)/Ru(III) E^0 >1.4 E^0=0.83	Rh(IV)/Rh(III) E^0 >1.4	Pd(IV)/Pd(II) E^0 = 1.29
Os(VIII)/Os(IV)/Os(III) E^0=1.0 E^0=0.42	Ir(IV)/Ir(III) E^0=0.96	Pt(IV)/Pt(II) E^0=0.74

Reduction to Metal. Since the PGMs are all electrochemically noble metals, selective reduction and cementation by base metal is not possible. In the past, collective cementation from aqueous solutions by zinc was often an important step, both for separation and for recovery of PGMs from recycled solutions. However, the use of zinc as a cementation agent is not possible for environmental reasons. Where cementation cannot be avoided, iron, aluminium, or Fe-Al alloys can be used instead. In aqueous media, hydrazine, formate, or borate can be used to reductively precipitate elemental PGMs (Harris 1993).

1.3 Metal Separation Techniques for the Platinum Group Metals

The variety of processes used in the recovery and refining of precious metals can be classified into two major process categories. These process categories are based on the differences in the raw material sources: one, on the recovery and refining of precious metals from the concentrates obtained from mined platinum-bearing copper-nickel sulphide ores, etc.; and the other from secondary raw material sources such as recycled industrial products. Examples of the latter include spent catalysts, electronic scrap, spent electrolytes, and jewellery scrap.

After the platinum group metals have been dissolved, the individual metals must be recovered. Depending on the raw material, the solution may contain all or some of the PGMs, together with gold, silver, and base metals.

Numerous separation processes have been developed and used. In general, coarse separation is followed by a purification stage. The process used for coarse separations is determined largely by the composition of starting solution, and the purification process depends on the particular PGM. The purification stage is necessary because, with few exceptions, an individual platinum group metal of commercially acceptable purity cannot be isolated from complex solutions in a single step.

The most important separation processes today make use of various combinations of precipitation, crystallization, distillation and solvent extraction. Some of the techniques mentioned in this section have current industrial applications, as well as those mentioned above and others are considered to be emerging technologies.

1.3.1 Precipitation

This basic process has been used for the separation of the largest quantities of platinum group metals since the beginning of separation technology- precipitation crystallization of ammonium hexachloro complexes $(NH_4)_2[MCl_6]$. This process can be optimized in many ways by influencing solubilities (e.g., by valence changes, addition of a common ion, or changing the temperature and rate of precipitation) (Renner 1997).

Platinum. The first step in separation is usually to precipitate platinum as $(NH_4)_2[PtCl_6]$. If the dissolved platinum is present as Pt(II), it must first be oxidized to Pt(IV) (e.g., by chlorine). Excess dissolved chlorine is driven off by boiling, which also causes the palladium that had been oxidized to Pd(IV) to be reduced to Pd(II). Any iridium(IV) present must be selectively reduced to iridium(III), for example, with iron(II) salts or ascorbic acid. The ammonium hexachloroplatinate(IV) is precipitated preferably by slow addition of concentrated ammonium chloride solution at room temperature with stirring. The hydrochloric acid concentration should be 1M, and the platinum content should be 50-200 g/L.

Iridium. To precipitate iridium as $(NH_4)_2[IrCl_6]$, iridium(III) is converted to iridium(IV) by treatment with an oxidizing agent at ca. 100ºC, while palladium remains in the divalent state at this temperature. Black $(NH_4)_2[IrCl_6]$ is filtered off from the cold solution. For a correct separation, the concentration of NH_4Cl is kept at 0.5-0.1 mol/L.

Palladium. From the previous solution, chlorine is then passed at room temperature and Pd(II) becomes Pd(IV). In these conditions when the concentration of NH_4Cl>1 mol/L, palladium is precipitated in the pure state in the form of the sparingly soluble, brick-red ammonium hexachloropalladate(IV), $(NH_4)_2[PdCl_6]$.

Rhodium. The classical precipitation/dissolution schemes for the recovery of rhodium are no longer considered satisfactory. This technique is also tedious, since the precipitation must be carried out several times in order to ensure that the final product is of acceptable purity, thereby making the overall process labour intensive and costly.

In this process the first step involves the formation of the nitrite complex $[Rh(NO_2)_6]^{3-}$ from $RhCl_6^{3-}$. Since this complex is extremely stable to hydrolysis, the impure rhodium-containing solution can be subjected to neutralization with caustic soda in order to precipitate some of the impurities. After filtration, the rhodium is precipitated with ammonia as $Na(NH_4)_2[Rh(NO_2)_6]$, which is a partially selective precipitation step over the other PGMs which may be present in the rhodium solution. For this precipitation, however, it is important that a high concentration of ammonia be used to suppress the solubility of the rhodium complex, in order to achieve almost complete rhodium precipitation. The precipitate is redissolved in hydrochloric acid and the cycle repeated until the required degree of purity is attained.

As with the other classical precious metal recovery processes, it is this cycle of precipitation-dissolution that renders the process inefficient and time consuming. Once the ammonia nitrite rhodium complex is of acceptable purity, the final dissolution in hydrochloric acid is followed by the precipitation of rhodium with ammonia to give $(NH_4)_3[RhCl_6]$, (Benguerel et al. 1996).

1.3.2 Distillation

Ruthenium. The most important industrial process for the isolation of ruthenium is distillation of the very volatile ruthenium(VIII) oxide, RuO_4, from aqueous solution. This compound is formed in solutions of potassium ruthenate(VI), $K_2[RuO_4]$, and hexachlororuthenate(III), $K_3[RuCl_6]$, by oxidation with chlorine at around neutral pH. The volatile RuO_4 is absorbed by dilute

hydrochloric acid, and is converted into water soluble chlororuthenate complexes (Renner 1997).

Osmium. Solutions obtained from digestion of ores normally contain osmates. Treatment of solutions in dilute sulphuric acid with oxidizing agents such as CrO_3, $K_2S_2O_8$, or HNO_3 causes Os(VIII) oxide to be formed and to distil off. From this distillate, OsO_4 can be isolated directly as a water-insoluble oil. Alternatively, it can be absorbed in potassium hydroxide solution, forming K_2OsO_4, or can be converted to metallic osmium by reaction with formaldehyde solution. Owing to the toxicity of OsO_4, its escape into the atmosphere must be prevented by use of the best possible adsorption equipment (Renner 1997).

1.3.3 Solvent Extraction

Solvent extraction, also known as liquid-liquid extraction, involves the distribution components between two immiscible phases, aqueous and organic, usually with chemical reaction. The organic phase is a solution containing a lipophilic extractant which forms complexes with the metal ions existing in the aqueous solution which are transferred to the organic phase. The reaction is reversible, therefore by changing the chemical conditions the metal transfer from the organic phase to the aqueous phase can be attained, constituting the stripping step.

The variety of chemical species which can be treated by solvent extraction methods is greater than those by other methods such as precipitation or ion exchange, and thus the number of solvent extraction systems which can be employed for a certain purpose is much greater than that of these other methods. This advantage of solvent extraction is especially marked with precious metals, because they easily form species which are extractable into an organic phase with various reagents. Moreover, the relatively high cost of reagents and of the recovery and storage of organic solvents during the solvent extraction process could be outweighed by the value of the precious metals

thus produced. Nevertheless, in spite of the positive aspects, there are still some inherent drawbacks in solvent extraction systems: lower ability for enrichment, generally the volume ratio between an organic phase and an aqueous phase cannot be very large in order to prevent solvent loss, and difficulty in phase separation (Tavlarides et al. 1987).

1.3.3.1 A Short Review on the Solvent Extraction of PGMs

The extractants that have been used for the PGMs fall into three main classes (Mooiman 1993):

- solvating extractants (long-chain alcohols, ethers, and TBP),
- anion-exchange extractants (long-chain alkylamines), and
- coordinating extractants (oximes or dialkylsulphides).

For the first of the classes, selectivity is largely based on the charge-to-size ratio of the chloroanion. Large anions of low charge are most easily extracted, and so this accounts for the selectivity of extraction of PGM chloroanions over the corresponding base metal species. Charge considerations result in differences in the order of extraction within the PGMs themselves: the lower the charge density, the more extractable the species. In general, the order of extraction from strong HCl is:

$$PtCl_6^{2-} \approx IrCl_6^{2-} > PdCl_4^{2-} > RhCl_6^{3-} \approx IrCl_6^{3-}$$

In most processes that employ solvent extraction, gold is removed from the solution first, followed by palladium, and then platinum. The remaining PGMs are recovered in variety of ways, either up-front or at the end of the overall flowsheet (Sole 1999).

Palladium. Only the divalent state is important for the solvent extraction of palladium. Extraction of palladium(II) from nitric and hydrochloric acid solutions

is effective. The extraction with alcohols and tri-n-butylphosphate (TBP) is quantitative (Amer 1983). Dialkil sulphides have been widely used in palladium extraction. Al-Bazi and Chow (1984) investigated the extraction of palladium with dioctylsulphide and the acceleration effect of palladium extraction in a presence of quaternary ammonium salts.

Palladium (II) is effectively extracted with β-diketones and oxine, though the rate is low. The extraction with the former is especially effective when a polar solvent is used as the diluent (Cox 1992). Like nickel(II), palladium(II) is effectively extracted with dimethylglyoxime and its homologues and this extraction can be used for the separation of this metal from other platinum metals (Amer 1983; Sole 1999).

Others reagents widely utilized for the extraction of Pd(II) are: amines and ammonium quaternaries salts (Belova et al. 1997; Sole 1999), 7-substituted-8-hydroxyquinoline derivatives (Côté and Demopoulos 1995), tri-isobutylphosphine sulphide (Hidalgo et al. 1991), (2,2,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) (Kakoi et al. 1994), di-(2-ethylhexyl)thiophosphoric acid (DEHTPA) (Rovira et al. 1999b).

More recently, Sánchez-Loredo and Grote (2000) performed a study of the extraction with dithizone derivatives, which were demonstrated to be effective chelating extractants for palladium(II) recovery.

Platinum. Platinum is recovered subsequent to palladium in most flowsheets. TBP is the most widely used platinum extractant. Amines are also good platinum extractants, and schemes have been proposed in which primary through quaternary amines are employed. The extraction occurs via an anion-exchange mechanism, (Sole 1999).

Platinum in the form of the tetravalent state is suitable and the extraction is, in general, much more effective for platinum than for the other platinum group

metals. Among the existing works, we can cite studies by Fu et al. (1995a) which have reported the extraction of Pt(IV) with trioctylamine, Lokhande et al. (1998), who show the efficiency of N-octylaniline for the extraction of Pt(IV) and Fontàs et al. (1999), who describe the extraction of Pt(IV) by Aliquat 336.

Divalent platinum is, on the other hand, suitable for the extraction with chelating extractants. However, those co-ordinating through oxygen and/or nitrogen atoms are not effective for platinum(II). The extraction of platinum(II) with chelating extractants coordinating through sulphur atoms is widely employed (Hasegawa and Sekine 1991).

Ruthenium. Ruthenium tetroxide in aqueous solutions is effectively extracted into nonpolar organic solvents and this extraction is dependent on pH.

Ruthenium is extracted with solvating-type extractants from nitric solutions as a nitrosyl complex. Ruthenium is also effectively extracted from aqueous chloride, bromide and thiocyanate solutions with solvating-type extractants. Extractions from these solutions with amines and quaternary ammoniums are also effective. Ruthenium(III) is well extracted with chelating extractants coordinating through oxygen and/or nitrogen atoms and if the element is in a higher oxidation state, it is often found to be reduced during the extraction to the trivalent state and then extracted as the chelate. Chelating extractants coordinating through sulphur atoms are more effective for ruthenium. Thiooxine and diethyldithiocarbamate extract ruthenium effectively and reduction of the higher oxidation states into the trivalent state is also found in the extraction with these reagents. It should be noted that the rate of extraction of ruthenium(III) is often very slow (Hasegawa and Sekine 1991).

Extractants reported for ruthenium(III) consist of the use of trioctylamine (Buslaeva et al. 1990), triphnylphosphine (Mojski 1980), di(2-ethylhexyl) phosphoric acid (Gonglai and Aistad 1995), tributyl phosphate (Rozen et al. 1995) and octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide

(Mathur et al. 1992). Recently the extraction of Ru(IV) with N-octylaniline has been reported (Lokhande et al. 2000).

Osmium. Osmium tetraoxide in aqueous solutions is effectively extracted into nonpolar organic solvents but this extraction is dependent on pH, as already mentioned.

Osmium is effectively extracted from chloride, bromide, and thiourea solutions with solvating-type extractants. Chelating extractants coordinating through oxygen and/or nitrogen atoms are not effective for osmium at all. Among chelating extractants coordinating through sulphur atoms, thiooxine is effective but diethyldithiocarbamate is rather ineffective (Hasegawa and Sekine 1991).

Rhodium. Extraction of rhodium from halide and thiocianate solutions with solvating-type extractants is not effective. The Rh(III) chloro-complexe is poorly extracted, which is due to the charge of the complex as well as its labile character toward aquation i.e., formation of $[RhCl_{6-x}(H_2O)_x]^{x-3}$ (x=1-6) (Al-Bazi and Chow 1984; Benguerel et al. 1996). The extraction from halide solutions is very much enhanced by the addition of tin(II). The extraction with amines from halide solutions is also effective when tin(II) is added (Benguerel et al. 1996).

Extraction of rhodium with chelating extractants is often ineffective because the rate of reaction of metal with ligand is low. With chelating extractants coordinating through oxygen and/or nitrogen atoms, rhodium is found to form complexes when the solution is heated to 100ºC. Chelating extractants coordinating through sulphur atoms are also ineffective for rhodium because the rate of chelate formation is very low (Hasegawa and Sekine 1991).

There have been a number of studies on the extraction of rhodium (and the other PGMs) with various organic amine extractants. It has been found that, although rhodium can be extracted under certain conditions, the other PGMs are more readily extracted and therefore amines are useful only when Rh is the only

precious metal in solution. Amines are also capable of extracting a number of base metals and selectivity can, therefore, be problematic (Benguerel et al. 1996).

Studies performed on the extraction of rhodium with primary and tertiary amines (tri-n-octylamine) have shown that it is only significantly extracted at 0.1 M HCl. At HCl concentrations of 1-12 M the extraction drops to zero. The extraction of Rh from chloride solutions with 8-hydroxyquinoline derivatives has also been studied but it was found that only a maximum of 40% Rh could be extracted. Another study focused on the use of pyridine derivatives and encouraging extraction results were obtained, with up to 85% extraction at 3 M HCl. Selectivity over base metals was good, except for Fe, which was highly co-extracted. In addition, other precious metals were found to be quantitatively co-extracted (Benguerel et al. 1996).

Iridium. Extraction of iridium in halide solutions with solvating type extractants is possible but often ineffective. Highly concentrated aqueous halide solutions such as those containing lithium chloride at very high concentrations are necessary for an effective extraction of this metal with these extractants. The effect of addition of tin(II) on the extraction of iridium from halide solutions is sometimes different from that of rhodium. Thus, these two metals can be separated by utilizing this difference. Extractions of iridium from halide solutions with amines and with large cationic extractants are effective when tin(II) is added.

Iridium can react with both types of chelating extractants, those coordinating through oxygen and/or nitrogen atoms and those coordinating through sulphur atoms, but reaction occurs only when the solution is heated. However, extraction with them is ineffective even after the solution has been treated by heating (Hasegawa and Sekine 1991).

1.3.4 Liquid Membranes

In liquid membrane extraction, the extraction and stripping operations are combined in a single process and the usage of solvent is greatly reduced. Furthermore, very high enrichment factors can be obtained in a single stage. The use of liquid membranes significantly reduces the relative amount of the organic phase necessary for the extraction. Hence, highly selective and expensive extractants can also be used, which would not be economical in solvent extraction (Danesi 1985).

Two kinds of liquid membranes are commonly used. One is a thin layer highly microporous polymer film impregnated with carrier material (supported liquid membrane, SLM). The other is the liquid surfactant membrane, LSM (Tavlarides et al. 1987).

1.3.4.1 Supported Liquid Membranes (SLM)

The configuration of SLM consists in a thin layer microporous polymer film in which the organic phase is adsorbed. This membrane separates the feed from the strip solution. As the carrier is immobilized, solutions can be continuously fed and withdraw. SLM are generally thinker than LSM resulting in lower metal fluxes, and with flat sheets the size of the feed and strip interfaces are the same. The SLM configuration allows easy scale-up as performance is directly related to the membrane area. Similarly to LSM, the mechanism of the mass transfer consists in the formation of a solute carrier complex in the aqueous-membrane interface which diffuses across the membrane to the other side where it decomposes to form the solute and regenerate the carrier (Tavlarides et al. 1987).

In the laboratory, SLM experiments are usually carried out in a two-compartment membrane cell provided of agitation where a flat-sheet membrane is sandwiched between the two compartments. For industrial

purposes, a planar geometry is not very effective since the ratio of surface area to volume is too low. Hollow fiber modules may be used to supply high surface area. A set of few hundred hollow fibers are used in a standard module and the organic carrier solution is held within the pores of the membrane cell. The source and receiving phases are in and outside the follow fibers, respectively or viceversa (Alonso and Pentelides 1996; Daiminger et al. 1996).

The advantages of SLM over other separation techniques are listed as follows: 1) combination of the processes of extraction, stripping and regeneration into a single stage with the possibility of achieve high enrichment and separation factors, 2) small amount of organic phase is necessary, hence the usage of solvent and extractant is considerably reduced, it is outstanding from the environmental point of view since many chemicals used in metal recovery are toxic, moreover very expensive reagents can be employed and 3) low capital and operating cost as well as energy consumption (Danesi 1985).

Concerning the handicaps in the use of SLM we can enumerate: 1) absence of a scrubbing section and difficulties in multistaging processes, 2) loss of extractant by solubility in the adjacent aqueous solutions which may be magnified because of the small inventory of organic phase in the system, 3) progressive wettability of the support pores and 4) the production of deposits of reaction products could reduce flux by blinding the membrane (Danesi 1985).

SLMs represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of metal ions from solutions, and interesting papers have been published describing their possible application to the recovery of metals such as Cr (Ortiz et al. 1996), Cs (Dozol et al. 1995), Sr (Dozol et al. 1993) and the precious metals, Au (Sastre et al. 1998; Alguacil et al. 2000; Kumar and Sastre 2000), Pt (Fu et al. 1995a ; Fontàs et al. 1999), Pd (Antico et al. 1994; Fu et al. 1995b; Rovira and Sastre 1998; Fontàs et al.

2001), Rh (Ashrafizadeh et al. 1998; Fontàs et al. 1997) and Ir (Fu et al. 1995c).

1.3.4.2 Liquid Surfactant Membranes (LSM)

The LSM process consists in the creation of an organic membrane film by making a stabilized water-in-oil emulsion with the strip liquor and organic phase and then suspending this stabilized emulsion in the feed solution. Metal complexes are formed at the organic-feed interface and due to the thinness of the membrane, they permeate very rapidly to the interface organic-strip where decompose causing metal enrichment in the stripping phase. LSM can offer greater areas for the transport and, thus, have an advantage over the SLM (Borwankar et al. 1987), but they are some inconveniences in the application of this technology, for example the need for intermittent breakdown and reforming of the membrane to recover the stripping phase once is fully loaded, and the differences in ionic strength between the feed and strip solutions on either side of the membrane can lead to swelling due to osmotic diffusion of water.

Thus, while liquid membrane (either surfactant or supported) separation processes posses definitive advantages over solvent extraction , they suffer from the lack of a "scrub" section. In solvent extraction the scrub section is utilized to purify the loaded organic phase from small amounts of unwanted co-extracted species. The absence of a scrubbing stage in liquid membrane processes is a serious drawback and leads to a much higher requirement for carrier selectivity. The actual and future practical applications of liquid membranes for very clean separations depend strongly (among others factors) on research efforts aimed at the synthesis of new very selective organic extractants (Chiarizia 1987).

The LSM has been studied as an effective method for metal separation by many investigators. However, there are only a few studies on the extraction of

platinum group metals by LSMs, some of this studies has been realized by Izatt et al. (1987) and Kakoi et al. (1996a; 1996b; 1997).

1.3.5 Solid-Liquid Extraction

Solid-liquid and liquid-liquid extraction involve similar chemical principles but differ in technological aspects. In solid-liquid extraction the solid or resin phase plays the role of the organic phase in solvent extraction process.

The solid supports most utilized for the recovery of metals have largely been synthetic polymers of organic origin and, less frequently, inorganic natural supports. Attention must also be draw to the use of sorbents of biological origin (biosorption), which have been widely used for the recovery of metals and which are the principal basis of our study. In all these cases, the application of these materials is due to their physical-chemical properties, which allow the retention of the metals whether it be by means of processes of physical adsorption on their surfaces, ionic interchange or by means of the formation of complexes.

1.3.5.1 Ion-Exchange

Processes based on ion-exchange resins consist of the exchange of metal ions present in an aqueous solution with the counter-ions of insoluble polymers containing fixed anionic or cationic groups. Resin ion exchange shows lower mass transfer rates, needs large size equipment, and longer process time compared with solvent extraction. However the equipment is simple, easy to operate, and there are basically no problems of phase disengagement and reagent losses (Tavlarides et al. 1987). Conventional cation exchange resins containing sulphonic acid or carboxilic acid functional groups have limited potential for use in the recovery of transition metal ions from process solutions because of their low selectivity, particularly against alkali and alkaline earth metal cations. A number of chelating ion exchange resins have been produced

by resin manufacturers to overcome this problem and encourage the application of ion exchange to a broader range of process solutions.

1.3.5.2 Chelating Resins

Chelating ion resins are polymers with covalently bound chains containing groups that are able to form complexes with specific metal ions. Condensation or additional polymerization processes are usually employed for the introduction of the chelating function into high polymer matrix. Despite the high selectivity of these resins, their very complicated methods of synthesis and their high cost have limited their application in separation processes on a technological scale (Warshawsky et al. 1997).

Among the work carried out to study the platinum group metals in synthetic polymers, we could mention that done by Kumar et al. (1995) in which the sorption of platinum, palladium, iridium, and gold complexes on polyaniline is demonstrated and that done by Myasoedova et al. (1997) in which a study was carried out with amine polymeric sorbents.

1.3.5.3 Biosorption

Biosorption can be defined as the removal of metal or metalloid species, compounds and particles from solution by biological material (Gadd, 1990). Large quantities of metals can be accumulated by a variety of processes dependent and independent on metabolism. Both living and dead biomass as well as cellular products such as polysaccharides can be used for metal removal.

The term "biosorption" has come to be accepted as referring to "passive" or physico-chemical attachment of a sorbate to a biomass, essentially the binding of chemical species to biopolymers. The definition, thus, specifically excludes metabolic or "active" uptake by living, metabolising, cells (Wase and Forster 1997).

Metal ion sorption on biopolymers is assumed to occur through several single or mixed mechanisms including: ion exchange, complexation, coordination, chelation, adsorption.

The demonstration that the external membranes of the cells contain metal-binding functional groups such as carboxylate, hydroxyl, sulphate, phosphate and amino groups, rendering them capable of metal sorption, encouraged the tendency the separation and use of these cellular walls and afterwards for their main components. Thus, the isolation of the biopolymers of the cell wall and their use for the metal sorption offer other way for the recovery of precious metals. For this reason, the treatment followed in this work is presented under the title of biosorption, doing reference at the use of sorbents of biological origin, biopolymers, based on the same principals as solid-liquid extraction, and which is presented in more detail in Section 2.

1.3.6 Impregnated Resins

Impregnated resins are based on the idea of adsorbing an organic solvent extraction reagent onto a solid polymeric matrix. Two kinds of impregnated ion exchange resins are made, with different methods of preparation. The first approach is based on physical adsorption of an extractant into a high-surface macro-porous polymer bead. These ion-exchange resins are called solved-impregnated resins (SIR). The second approach is more specific, and employs in-situ incorporation of the extractant during the resin copolymerization process. This type of resin is usually made from styrene-divinylbenzene based copolymers and is called Levextrel resin (Tavlarides et al. 1987).

Metal ions which have been extracted through impregnated ion exchange resins include nuclear metals, strategic metals, precious metals, and base metals. Existing extractants for solvent extraction may be employed in these impregnated resin extraction systems.

High molecular weight amines impregnated in resin beads have been used in the extraction of base metals as well as precious metals. By loading tri-n-octylamine (TOA) onto a macromolecular resin, the adsorption of Pd(II) from hydrochloric acid media have been reported (Akita et al. 1993). Selective extraction of Au (III) in the presence of the base metals Zn(II) and Cu(II) has been achieved by using tri-n-dodecylammonium chloride (TOMACl) impregnated in Amberlite XAD2 resin (Villaescusa et al. 1997). The kinetics and equilibrium extraction of Pd(II), Pt(IV) and Rh(III) from hydrochloric acid media using impregnated resins containing Alamine 336 impregnated onto Amberlite XAD2 were studied and compared by Rovira et al. (1998).

The extraction of Pd(II) from HCl solutions by impregnated resins containing di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) on the Amberlite XAD2 polymeric support has been studied by Rovira et al. (1999a) in the presence of other metals: Pt(IV), Rh(III), Cu(II), Fe(III) and Zn(II).

For the other hand, the impregnation of biopolymers offer other alternative to recovery precious metals (Mimura et al. 2001).