TAILORED ION IMPRINTED POLYMER MATERIALS FOR THE PRECONCENTRATIVE SEPARATION OF NOBLE METALS

THESIS SUBMITTED TO
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN CHEMISTRY UNDER THE FACULTY OF SCIENCE

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JANUARY 2006

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CERTIFICATE

This is to certify that the thesis entitled **'Tailored ion imprinted polymer materials for the preconcentrative separation of noble metals'** embodies the results of bonafide research work done by **Miss. Sobhi Daniel** for the degree of **Doctor of Philosophy** in Faculty of Science, Cochin University of Science and Technology under my guidance. The content of this thesis or part thereof has not been submitted to any other university or institute for the award of any degree or diploma.

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PREFACE

The thesis entitled "**TAILORED ION IMPRINTED POLYMER MATRIALS FOR THE PRECONCENTRATIVE SEPARATION OF NOBLE METALS**" embodies the results of the investigations carried out on the preconcentration and / or separation of palladium(II) and platinum(IV) with ion imprinted polymers. The objective of this work is to generate the knowledge base to achieve better selectivity between palladium(II) / platinum(IV) over the other co – existing inorganics as well as the preconcentration from dilute aqueous solutions. The thesis comprised of seven Chapters.

The introductory chapter highlights the importance of noble metals especially palladium(II) and platinum(IV) and various techniques used for their preconcentration and / or separation. A detailed literature survey on ion imprinted polymer (IIP) technology and the need for development of new solid phase extractant based on ion imprinted polymer technology for the preconcentration / separation of palladium(II) / platinum(IV) has also been brought out in this chapter.

The second chapter deals with the synthesis, characterization and analytical applications of palladium(II) IIP particles prepared by using palladium(II) – dimethyl glyoxime – 4 – vinyl pyridine ternary complex. The influence of post γ-irradiation of IIP particles on the percent preconcentration of palladium(II) have also been included in this chapter.

Chapter 3 describes the results of the investigations on the preconcentrative separation of palladium(II) using different quinoline derivatives as one of the non-vinylated ligands during the synthesis of imprinted polymers. The binding parameters were also derived from the rebinding studies after fitting the experimental binding isotherms with theoretical Langmuir, Freundlich and Langmuir – Freundlich isotherms.

The influence of various polymerization techniques on the analytical performance of the palladium(II) IIP materials is described in chapter 4.

Chapter 5 describes the synthesis of palladium(II) IIPs via a new strategy i.e., by the use of ion association complexes of palladium(II) viz. $[PdI_4]^{2-}(VP^+)_2$ / $[Pd(SCN)_4]^{2-}(VP^+)_2$ as the templates. The IIPs synthesized were also used for the analysis of street / fan blade dust samples using FIA – AAS.

The synthesis, characterization and analytical application of platinum(IV) IIP particles by utilizing the ion association complex of platinum as templates is described in Chapter 6.

The contributions of the knowledge arising out of this thesis have been highlighted in the concluding chapter.

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CHAPTER 1

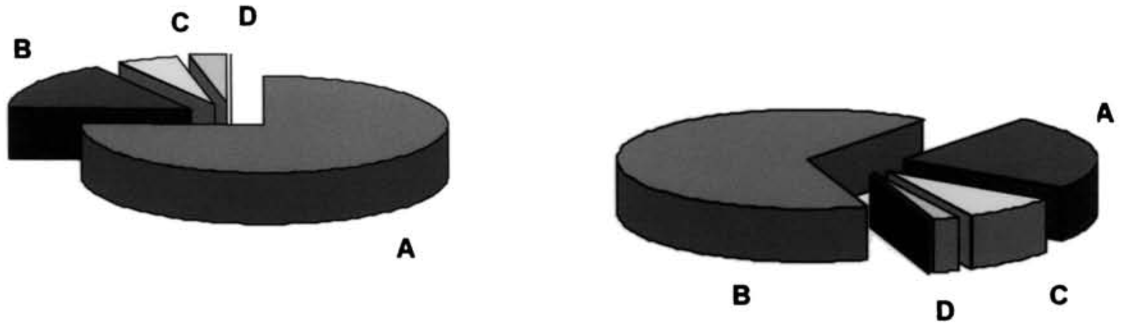
INTRODUCTION

Platinum group metals (PGM) are currently receiving worldwide attention as they offer the dual attraction of rare and high value as well as having major industrial uses. The members of PGM include platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). These metals are classified under one heading due to their similar chemical and physical properties and their common occurrence in nature as mixtures. These metals are also known as noble metals as a result of their superior ability to withstand oxidation, corrosion and possessing very high melting and boiling points and low reactivity.

1.1 OCCURRENCE AND USES

The PGM or noble metals are characterized by low crustal abundance. In ocean sediments the concentration of platinum was found to be 21.9 ng g^{-1}[1]. In sea water it is 0.08 – 0.32 ng g^{-1} and in blood it is < 0.8 – 6.9 ng g^{-1}. The concentration of palladium in water was estimated to be 0.4 – 0.6 ng g^{-1} where as in deep sea it is found to be 3.7 – 11.4 ng g^{-1}. A high palladium concentration of 0.3 μg g^{-1} in dust particles accumulated on plants near busy motor ways has also been reported after the introduction of automobile catalysts [2]. In the earth crust PGM usually occur in native form associated with one or more other noble metals along with gold, iron, copper and chromium. Platinum and palladium are the major elements of the platinum group and are generally chalcophile i.e, sulphur loving and therefore often found in sulphide minerals [3]. South Africa is the leading country with 85 % of the world production of PGM and has 82% of the world's economic resources. The world wide distribution of platinum and palladium are schematically shown in *Fig. 1.1* (a) and (b) respectively.

Platinum group metals are used as catalysts for a wide variety of hydrogenation, oxidation, isomerization, cyclization, dehydrogenation and dehalogenation reactions. The corrosion resistance of platinum group metals enables them to use in electrical, jewellery and glass industries, in extrusion of synthetic fibres and in the manufacture of laboratory utensils, dental and medical devices [4]. Further, alloys of platinum and palladium with rhodium, iridium, ruthenium or osmium increases their strength, hardness and corrosion résistance. Selected platinum(II) complex species are effective cytostatics being used in the therapy of some forms of cancer [5].



(a)

A- South Africa (75.49%)
B- Russia (15.8%)
C – North America (5.45%)
D – Others (3.2%)

(b)

A- South Africa (24.6%)
B- Russia (65.2%)
C – North America (8.1%)
D – Others (2.1%)

Fig 1.1: World wide distribution of platinum (a) and palladium (b)

Platinum complexes based on cis-dichlorodiamineplatinum(II) (cisplatin) have been widely used in cancer therapy for some years. These drugs are highly effective against a variety of solid tumours, however their use is associated with several toxic effects like nausea, neurotoxicity or nephro toxicity [6]. Chronic exposure to soluble platinum compounds may lead to toxic effects known as a syndrome called platinosis. The automobile industry is the other major consumer of PGM. Platinum, palladium and rhodium are used in automobile catalysts for the purpose of reducing levels of carbon monoxide, unburnt hydrocarbons and nitrogen oxides in the exhaust gases. Therefore an increasing amount of these metals has been released in to the environment. Although palladium in its elementary form is rather inert with respect to biological activity, ionic species are regarded as toxic for men. Exposure to metallic palladium and palladium alloys causes dermatitis in human beings. Therefore, preconcentration, separation and determination of noble metals such as palladium have been of great interest [7].

1.2 ANALYTICAL CHEMISTRY OF NOBLE METALS

The determination of noble metals in complex geological and allied materials has always been a fascinating field of analytical chemistry. Thus the trace level occurrence, the economic compulsions and the uncertainties in the world price are the natural causes for the interest in their exploration and analysis [8].The common analytical techniques used for the determination of noble metals are given below.

1.2.1 Spectrophotometry

The application of UV/Visible absorption spectrometry to the determination of noble metals is still popular in many laboratories, especially in developing countries. The complexity of the chemical properties of the PGM or noble metals and the kinetics of their reactions in solutions pose serious problems, especially for separations and determination by spectrophotometric techniques. The use of spectrophotometric methods in PGM analysis is limited due to low sensitivity. However, many new selective and in some cases, even specific reagents are being synthesized and various highly sensitive methods are being developed, increasing the applicability of the procedures. This technique provides easy determination of many metals from low to high concentrations at an affordable cost.

1.2.2 Flame atomic absorption spectrometry (FAAS)

In FAAS the nebulized sample is introduced in to either an air – acetylene or a nitrous oxide – acetylene flame. The absorption of the analyte atoms is recorded against known standards. Due to less sensitivity by the technique and presence of extremely low levels of analyte concentration,.the FAAS technique generally finds use for PGM determinations in concentrates and PGM- rich samples.

1.2.3 Graphite Furnace AAS (GFAAS)

A variant of the AAS technique, graphite furnace AAS, offers the unique advantage of enhanced sensitivity over the flame version. The residence time of individual atoms in the optical path is approximately 1-2 s for GFAAS technique while in the flame atomization it is of the order of milli seconds. The detection limits are thus lowered by at least one or two orders of magnitude depending on the element and sample volume. Thus GFAAS competes favourably in terms of detection limits with other sensitive techniques such as NAA and ICP-MS in noble metal determinations. The major disadvantages however are its inherently lower productivity and severe matrix interferences.

1.2.4 Inductively coupled plasma atomic emission spectrometry (ICP-AES)

Optical emission spectroscopy, with argon plasma as the excitation source (ICP-AES) has gained world wide acceptance as a versatile analytical technique for geological samples. The technique is characterized by low background emission, hence superior detection limits, high temperature (~10000K) leading to few chemical interferences and wide linear response range (5-6 orders of magnitude).The ICP-AES in conjuction with lead fire assay (FA) and AR dissolution of the silver prill has been recognized as a widely applied technique for the determination of gold, platinum and palladium in geological samples. When all the PGM are to be estimated nickel sulphide -FA and tellurium co-precipitation are employed. However, the limited use of ICP-AES in noble metal analysis is mainly due to the large sample to volume ratio required to achieve a detection limit of 1, 2 and10 ppb for gold, palladium and platinum respectively. This leaves no room for repeated analysis and the accuracy in diluting to such low volumes is difficult to achieve.

1.2.5 Inductively coupled plasma mass spectrometry (ICP-MS)

The ICP-MS technique combines the advantages of the high temperature plasma source with the highly sensitive detection capabilities of the mass spectrometer. In this technique the mass spectrometer receives ions from the plasma tail flame after a two-stage vacuum reduction interface. With a very wide linear dynamic range, simultaneous multi-element analytical capability due to rapid scanning facility and a fair degree of tolerance to interference free measurement of analytical signal, the ICP-MS today is a widely used analytical tool for trace metal analysis. A particular benefit of this technique is the possibility of isotope dilution calibration strategies which account for the few interferences and loss of analytes at the preparation stage. The nickel sulphide - FA followed by ICP-MS, after dissolution of the button in concentrated HCl and co-precipitation on tellurium, is the most widely accepted method for noble metal determinations.

1.2.6 Neutron activation analysis (NAA)

Neutron activation analysis is also one of the preferred techniques for noble metal analysis. The two variants of NAA viz. instrumental NAA and radiochemical NAA scores over other techniques due to their sensitivity, accuracy and freedom from contamination.

(a) Instrumental neutron activation analysis (INAA)

For PGM a chemical separation prior to irradiation is necessary to obtain better sensitivities and / or eliminate interferences. Today most INAA results are derived after nickel sulphide fusion, which accomplishes separation of the analytes from the matrix. Due to lower background, better detection limits are obtained. The assay procedure also eliminates the problem of non-homogeneity in analyte distribution.

(b) Radiochemical neutron activation analysis (RNAA)

Neutron activation analysis with radiochemical separation is a precise and accurate method for noble metal determination in certain types of samples. Radiochemical separations coupled NAA have several advantages over other analytical techniques, in particular the avoidance of contamination and the ability to add carrier to monitor and correct for losses. The main limitation of RNAA is the restriction on sample mass so as to limit the activity of irradiated samples that are then subjected to a radiochemical method. The nature of the sample, in particular the mineralogical considerations, strongly influence the precision and accuracy.

Thus in recent years, the development of sensitive and reliable techniques for the determination of noble metals has attracted great interest. The direct determination of platinum and palladium is still difficult because of the insufficient sensitivity, lack of selectivity, presence of complex matrix, poor precision and accuracy. Considering the very low concentration of these metals, analytical strategies are needed for suitable sampling, effective solution preparation, preconcentration and analysis. Since the concentration of these metals, especially in environmental samples, is very low and low detection limits of commonly by available analytical techniques like UV-Visible spectrophotometry and flame AAS, a preconcentration and / or separation step usually preceeds the analytical determination.

1.3 PRECONCENTRATION

Preconcentration is defined as the enrichment process, which involes the isolation of the minor component (analyte) from complex matrix or transfer of a particular analyte from one phase to another. Preconcentration improves the analytical detection limit and selectivity, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results, and facilitates the calibration. The various preconcentration techniques used for platinum and palladium are described below.

1.3.1 Liquid-liquid extraction

Liquid – liquid extraction (LLE) is a technique in which a solution (usally aqueous) is brought in to contact with a second solvent (usually organic), essentially immiscible with the first, inorder to bring about a transfer of one or more solutes in to the second solvent.

a) Palladium

Trace amounts of palladium were preconcentrated by LLE from HCl medium with quaternary ammonium salts in toluene and stripped by alkaline NH_4NO_3 which forms the base electrolyte for subsequent differential pulse polarographic (DPP) determination [9]. A preconcentrative separation of palladium based on the LLE of ion-association complex of $Pd(SCN)_4^{2-}$ ion and cationic potassium complex of dicyclohexyl-18-crown-6 was also reported elsewhere [10].

b) Platinum

Microamounts of platinum were preconcentratively separated from common metals by extraction chromatography with GD X501 resin dipped in tributylphosphate [11]. High molecular weight amines such as trioctylamine or diantipyryl methane in 1,2-dichloroethane [12] were used to preconcentrate platinum after conversion into $SnCl_3^-$ ligands from hydrochloric acid solutions. 25,26,27,28-(2-(2-pyridylthio-N-oxide)ethoxy) calix [4] arene was synthesized by reacting 25,26,27,28-(2-bromo-ethoxy) calix [4] arene with 2-pyridylthiol-N-oxide in the presence of pyridine and used as selective extractant for preconcentration of traces of platinum from aqueous solutions into chloroform [13].

c) Platinum and palladium

Preconcentrative separation of traces of platinum (IV) and palladium(II) has been investigated as a function of iodide concentration with mesityloxide as an extractant [14]. The separation consists of one step of extraction with mesityl oxide from an aqueous phase at pH 4 and potassium iodide (KI) concentration in the range 10^{-7} – 10^{-6} mol l^{-1}. Three scrubbing steps with an aqueous phase maintained at pH 4 and 10^{-6} mol l^{-1} in KI and one step of stripping with 10 ml of water after addition of 40 ml of toluene to mesityl oxide phase. The above procedure is highly selective as seen from the recovery of platinum(IV) and palladium(II) from complex synthetic mixtures consisting of other noble and base metals.

1.3.2 Ion exchange

Ion exchange can be defined as a reversible process in which ions of like sign are exchanged between a liquid and a solid, a highly insoluble solid body in contact with it. The solid ion exchangers must of course, contain ions of its own, and for the exchange to proceed sufficiently, rapidly and extensively to be of practical value. Also the solid must have an open, permeable molecular structure so that ions and solvent molecules can move freely in and out. Ion exchangers are almost insoluble in water and in organic solvents and they contain active or counter ions that will exchange reversibily with other ions in a surrounding solution without any appreciable physical change occurring to the material. The ion exchangers are of complex nature and are in fact polymeric. The polymer carries an electric charge that is exactly neutralized by the charges on the counter ions. These active ions are cations in a cation exchanger and anions in an anion exchanger.

a) Palladium

A neutral polymeric resin, Amberlite XAD-7, packed in small column was used for preconcentrative separation of palladium(II) from manganese and nickel compounds [15]. A column containing Amberlite XAD-16 has been used for preconcentration of trace amounts of palladium (II) with an adsorption capacity of 35.6 mg g^{-1} [16]. The developed preconcentration procedures in conjunction with AAS provide good recoveries (> 98.0%) during the determination of as low as 0.051 μg ml^{-1} of palladium (II) in alloys. The exchange of palladium(II) ion from chloride and nitrite media onto Duolite GT-73 resin was investigated and the adsorption capacities were calculated to be 0.26 and 0.35 mmol g^{-1} of resin [17].

Dithizone immobilized anion exchange resin was used for preconcentration of trace amounts of palladium and the resulting resin-water suspension was used for quantification using GFAAS [18]. A novel spherical epoxy-dicyandiamide chelate resin was synthesized simply and rapidly from epoxy resin and used for preconcentration and separation of trace amounts of palladium(II) [19]. A new macroporous poly (vinyl amino acetone) chelating resin was synthesized and has been successfully employed for preconcentration of trace amounts of palladium (IV) [20].

b) Platinum

Anion exchange resins have been used for preconcentration of nanogram levels of platinum present in two chinese ultra basic SRM's [21] and environmental dust [22] samples. The detection limit for the latter procedure in conjunction with isotope dilution ICP mass spectrometry (ICP-MS) was 1.4 ng g^{-1} of dust sample. An ion exchange extraction chromatographic procedure was developed for preconcentrative separation of platinum(IV) using N-(hydroxymethyl) thioamide resin as stationary phase [23].

c) Palladium and Platinum

Platinum group elements were preconcentrated using strongly acidic cation exchange resin, Amberlite CG 120 and has been used for their separation from large amounts of transition elements [24]. The relative standard deviation was ~8% which is not that impressive. The developed method in conjunction with ICP-MS can be used for reliable determination of platinum group metals in sulphide and magnetite minerals from Sudbury, Canada and copper-nickel sulphide ores. A microcolumn packed with cellex-T resin was used for preconcentration of platinum and palladium from weakly acidic (pH 4) solutions [25]. The preconcentrated metals were eluted with 0.01 mol l^{-1} glycine solution at pH 12.0 for platinum and 4.0 mol l^{-1} of potassium thiocyanate (pH=1) or 1.2 mol l^{-1} of thiourea (pH=0.5) for palladium and determined by Flame AAS or graphite furnace AAS. Anion exchange resins were also used to preconcentrate platinum and palladium and determined by FAAS [26] or neutron activation analysis (NAA) and ICP-MS [27]. Platinum and palladium contents in chromite were established by anion exchange chromatographic preconcentration coupled to ICP-AES determination [28]. The recoveries were found to be 96.1±1.8 and 96.6 ±1.3% respectively.

Traces of platinum and palladium were preconcentrated with p-sulfophenylaxochromotropic acid chelate forming resin from weakly acidic solutions and determined by FAAS [29]. Chelex-100 was used for preconcentration of platinum and palladium present in geological and industrial materials and determined by radiochemical version of NAA [30]. The method was verified by determining platinum and palladium in SARM–7 and PTC-1 reference materials certified for noble metal content and showed good agreement. Metal fix-chelamine Resin was employed for preconcentration of precious metals in geological and related materials and determined with ICP-MS [31]. The detection limits are 2.0 and 1.5 ng g^{-1} for platinum and palladium respectively. Macroporous resins containing imidazoline groups were tested for preconcentration of platinum and palladium [32-33] and determined by ICP-AES. Alizarin Red S chelate resin column [34] was employed for preconcentration of platinum and palladium from 0.1 N HCl solutions and eluted with 3% acidic thiourea. This procedure in conjunction with FAAS was successfully used for analysis of geological samples. The recoveries were found to be in the range 94.5-104.1% which are not that impressive. As low as 0.02 μg ml^{-1} of platinum and palladium were determined by ICP-AES after preconcentration from 5 mol l^{-1} HCl – pH 9 solutions with macroporous poly(vinyl thiopropionamide) chelating resin synthesized from spherical poly(vinyl chloride) resin particles [35].The adsorption capacities were calculated to be 288 and 455 mg g^{-1} for platinum and palladium respectively. The lowest concentrations that could be determined are ~0.04 μg ml^{-1}. Dithizone anchored poly (vinylpyridine) based chelating resin was prepared via the reaction between chloromethylated poly(vinyl pyridine) and dithizone [36]. The resin shows high affinity towards palladium(II) and platinum(IV).

1.3.3 Co-precipitation

The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed co – precipitation. There are two important types of co – precipitation. The first is concerned with adsorption at the surface of the particles exposed to the solution and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles.

a) Platinum and palladium

Platinum group elements which include platinum and palladium were preconcentrated and separated from large amounts of matrix elements by using tellurium co-precipitation [37]. The detection limits of the above preconcentration method in conjunction with ICP-MS are in the range 1-9 pg g^{-1} which is quite good compared to other preconcentration methods. The results obtained on analysis of various reference materials agreed well with the certified values.

1.3.4 Electrodeposition

In electrodeposition, the element to be determined is deposited electrolytically on a suitable electrode. It is mainly carried out in an electrolytic cell, which consist of either two or three electrodes immersed in the electrolytic solution. In this cell, reduction takes place at one electrode called the cathode and oxidation on the other called anode.

a)Palladium

Ohta et al [38] have developed a new preconcentration method using magnesium - tungsten cell electrodeposition which allows the determination of as low as 0.37 ng ml^{-1} of palladium in conjunction with electrothermal AAS (ETAAS). This preconcentration procedure does not need a power supply (electric source) like a potentiostat or battery. The same authors [39] have applied the above procedure for determination of palladium in environmental samples with an average recovery of 102-114%.

Palladium(II) was selectively accumulated using sodium humate modified carbon paste [40] electrode in pH 2.8 (quite critical) Britton-Robinson buffer (B-R) in open circuit mode and determined subsequently by using cyclic voltammetry(CV) and linear sweep anodic stripping voltammetry (LSASV) in 1.0 $moll^{-1}$ HCl as supporting electrolyte. Palladium concentrations in the range 0.009 - 4.7μ mol l^{-1} could be determined. The inner wall of a pyrotically coated graphite tube served as the surface for adsorptive accumulation and/or for electrodeposition of palladium and platinum [41]. After the deposition step, the graphite tube was placed into the graphite furnace and an atomization programme was employed. The developed procedure was successfully applied for the analysis of palladium and platinumin in air borne particulates.

1.3.5 Fire assay

This method involves fusing a sample and flux mixture at ~ 1000^0C. The resultant melt separates in to two immiscible phases. The upper glassy slag, which contains the alumino – silicates and base metals is discarded and the denser phase is composed of collectors.

a) Palladium and platinum

The effects of various factors viz. composition of mixture, relations between the mass of mixture and sample, value of the Ni : S ratio, fusion time and temperature on the fire assay preconcentration of noble metals with nickel sulphide were investigated [42]. The developed method in conjunction with NAA can be used for the determination of as low as 0.001-0.1 ng ml^{-1} of noble metal ores, stones, iron meterorites, chromites, soils and lunar rocks. Mc Donald *et al.* [43] and Biosvert *et al* [44] have developed similar procedures for the analysis of South African Kimberlites and rocks respectively. Juvonen *et al* [45] determined platinum group metals by ICPMS and NAA after nickel sulphide fire assay preconcentration of black shale, magnetite samples and samples containing As, Cu and Fe.

Li *et al* [46] determined platinum group elements in Russian candidate reference materials by ICPMS after nickel sulphide fire assay preconcentration. Sulphide fire assay [47] preconcentration procedures were developed for the estimation of platinum group metals in copper-nickel ores. The detection limits were 0.001-0.06 mg Kg^{-1} for a 5 g sample and an extract volume of 5 ml. The precision is moderate as it varied between 2-17%. The platinum group metals present in some geological samples were preconcentrated in lead buttons through fire assay technique and determined by NAA [48].

1.3.6 Solid Phase Extraction

Solid phase extraction (SPE) is currently being used as a preconcentration and / or separation technique whenever complex matrices or low concentration analytes have to be analyzed. The basic principle of SPE is the transfer of analytes from the aqueous phase to the active sites of the adjacent solid phase. It can also be termed liquid – solid extraction. The solid phase typically consists of small, porous particles of silica with a bonded organic phase or an organic polymer such as cross linked polymer such as cross linked polystyrene. The transfer is stimulated by the selection of appropriate optimal conditions in the system of three major components viz water (liquid phase), analyte and the sorbent [49]. The analyte after sorption on the soild phase is either desorbed with a suitable eluate or the analyte along with the sorbent is dissolved in a suitable solvent and further analyzed. Both on-line and off-line SPE are routinely used in analytical laboratories. In the on-line set up the SPE unit is directly coupled to analytical units such as AAS/ ICP-AES/ ICP-MS etc which greatly simplifies the whole analytical process.

Some of the concepts of liquid – liquid extraction apply to solid phase extraction. Instead of a temporary liquid emulsion, the extractive material in SPE is a suspension of spherical solid particles in the aqueous sample. The extractive particles typically are ~ 10-50 μm in diameter with a very large surface area. A large interfacial area between the particles and the sample solution is needed for rapid mass transfer of the extracted solutes from one phase to the other. The extractive particles must be sufficiently dense and large enough in diameter to settle rapidly when agitation of the solid and liquid phases is terminated.

The SPE process can be divided in to four main steps (1) conditioning (2) adsorption (3) washing and (4) elution. One additional step is of course necessary to complete the analytical process i.e., analysis. The general scheme for the solid phase extraction is given in *Fig.1.2.*

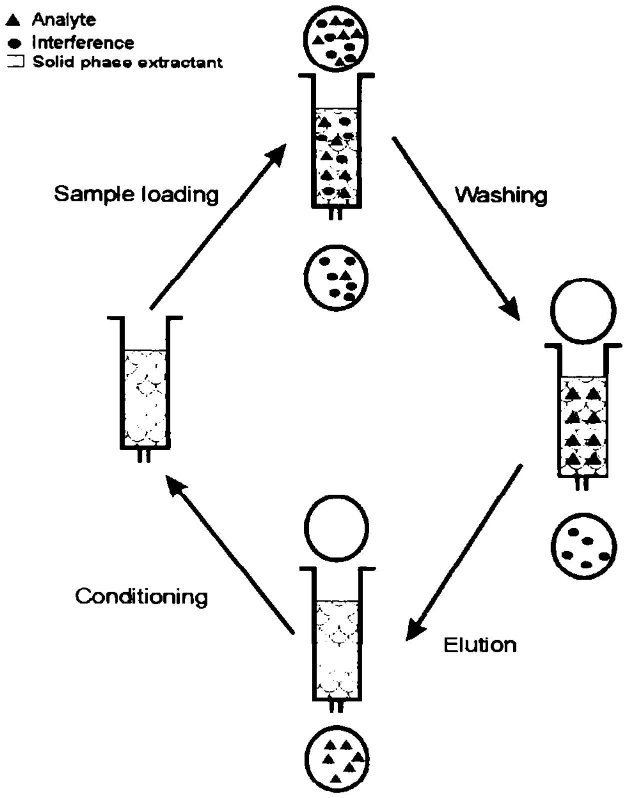


Fig.1.2: Principle of Solid phase extraction

(i) Conditioning

Before adsorption of analytes by the stationary phase can begin, the sorbent bed must be prepared and made compatible with the liquid solution. The necessary pretreatment involves the use of a mediating solvent that will promote better surface contact between the phases. This pretreatment of the adsorbent is known as conditioning.

(ii) Adsorption

This step involves the introduction of liquid sample to be extracted through the packed column with the aid of suction, applied pressure or pump. One important factor encountered during SPE is that the sorbent bed should not be allowed to dry at any point. i.e., the presence of air in the column has to be avoided as it prevents efficient interfacial contact between the liquid and solid phase.

(iii) Washing

A carefully wash liquid affords the opportunity to remove co-adsorbed matrix materials from the SPE column. The right choice of the wash solution during this process is always problematic. So right selection of the washing solvent is very important.

(iv) Elution

In the elution step, the adsorbed analytes are removed from the solid phase extractant and are returned to a liquid phase that is suitable for analytical measurement. The eluting solvent should initially be added slowly and carefully to the resin bed in order to avoid channeling. Also the eluent should be chosen carefully so that it will elute the analytes completely from the solid phase using as small a volume as possible of the eluent. Also the eluent must be compatible with the analytical measurement methods to be used subsequently. Also it should be low cost and non toxic.

The advantages of SPE over other preconcentration techniques include

1. flexibility
2. low cost due to lower consumption of reagents
3. absence of emulsion
4. speed and simplicity
5. sampling in the field
6. safety with respect to hazardous samples
7. ease of automation and environmental friendly.

Pyrzynska [6] and Vlsankova and Sommer [50] have reviewed recent advances in solid phase extraction preconcentration of platinum and palladium and platinum group metals in environmental and biotic materials respectively in 1999.

a) Off-line preconcentration techniques

In off-line SPE the analyte is accumulated from the water sample by a convenient SPE column and subsequently eluted with a suitable solvent. The major advantages of the off-line approach are its operational flexibility and the simplicity of the equipment required. But off-line procedures require a lot of manual work and that can be automated only by means of robotic system, at considerable financial cost.

i) Palladium

Both batch and column preconcentration procedures were employed for the enrichment of palladium using naphthalene/benzophenone as solid phase extractants [51-58].

A novel polyacrylamino imidazole chelating fibre is synthesized simply from nitrilon (an acrylonitrile based synthetic fibre) and used for preconcentration of palladium(II) from pH 3.0 solutions at a significantly high flow rate of 15.0 ml min^{-1} [59].The adsorption capacity is 2.92 mmol g^{-1} which is quite good. The preconcentrated palladium(II) can be desorbed with 15 ml of 4 mol l^{-1} HCl + 3% thiourea from the fibre column. The chelating fibre is reused 10 times with good recoveries of 97-99%. Polyacrylacylisothiourea chelating fibre [60] was synthesized using polyacrylonitrile fibre as starting material and used for preconcentration of as low as 0.008 μg ml^{-1} of palladium(IV) with a precision of 2.5%. New macroporous polymers with an ionogenic group based on triisobutyl phosphine sulphide, with spacer arms containing O or S atoms were evaluated for preconcentration of palladium(II) in presence of other platinum group and base metals [61- 62]. The chelating polymer can be reused for 15 times with good recoveries. Ring opening-metathesis polymerization was used for the preparation of dipyridylcarbamide functionalized polymer suitable for SPE preconcentration of palladium(II) from aqueous solutions [63]. This material showed excellent selectivity for palladium(II) over other divalent metal ions over a broad range of concentrations from complex mixtures.

Silica modified with N-allyl-N'-propyl thiourea [64] and chemically modified nitrogen containing ligands [65] were employed for the preconcentration of palladium(II) and determined by FAAS and X-ray fluorescence (XRF) spectrometry. The detection limits are 0.05 and 0.01 μg ml^{-1} respectively. SPE preconcentration procedures were developed for palladium(II) using activated carbon columns [66-68]. The latter two procedures are applied for the analysis of geological samples [67] and aluminium and manganese salts [68] in conjunction with FAAS. The precision of these procedures is rather poor (~10%) for 5 successive determinations.

ii) Platinum

Modified silica gel was employed for preconcentration of 2-20 μg platinum present in plant ash from 0.1 M HCl in presence of cationic surfactants especially, dimethyl lauryl benzyl ammonium bromide with subsequent elution with 96% ethanol [69]. The recoveries vary from 86-110% for 2 μg of platinum and average RSD was 6.3%.

iii) Platinum and palladium

Sequential SPE preconcentration of platinum(IV) and palladium(II) from thiocyanate solutions was achieved by passing through an organic impregnated filter (OIP) [70]. The extraction of both metals is rapid with quantitative recoveries from flow rates of as high as 600 ml min^{-1}. Once extracted, the metals can be removed from the OIP by conversion to a non-extractable form with a high pH eluting solution. The validitation or application of the developed procedure was not tested by the authors. Polyacrylacylaminothiourea chelating fibre was synthesized simply and rapidly from nitrilon and aminothiourea and successfully used for a 100 fold enrichment of platinum(IV) and palladium(IV) from dilute solutions [71]. The precision and recoveries are 0.7% and 96 - 100% respectively which are quite impressive. The accuracy of the developed procedure was tested by analysing certified reference materials (CRM).

Platinum and palladium were preconcentrated from pH $\leq$ 5.0 solutions onto 2-mercaptobenzothiazole bonded silica gel (MBTSG) prior to their determination by ICP AES [72]. MBTSG was synthesised by the Mannich reaction between 2-mercaptobenzothiazole and 2-aminopropylsilica gel. The adsorbed metals can be readily desorbed with 3% thiourea in 3.0 mol l^{-1} of HCl solutions. Platinum and palladium in fresh waters were analysed by ICP-MS following their preconcentration by adsorption onto activated charcoal [73].

b) On-line preconcentration techniques

The chemical principle of the on-line approach is same as that of the off-line version. The major difference is the direct transfer of sorbed analytes from the SPE column to the analytical column after changing the position of a switching valve. Hence this approach is also called precolumn switching or precolumn technology. The important advantage of the on-line approach is that it minimizes the operator labour required for the sample preparation and the contact with the sample resulting in high precision and minimal contamination.

i) Palladium

Liu *et al* [74] have synthesized new silica gel based chelating sorbent with thourea as functional group and was used for the flow injection (FI) on-line preconcentration and separation of traces of palladium. Its sorption characteristics were evaluated by FI-FAAS. Palladium is preconcentrated on thiourea modified silica gel with a sampling flow rate of 5.0 ml min^{-1} and eluted with 5% thiourea with a flow rate of 2.5 ml min^{-1} and determined by FAAS

Amidinothioureido [75] and Rhodanine [76] bonded silica gel column materials were employed during flow injection online preconcentration and flame AAS determination of palladium over a wide range of acidity 0.1-6.0 mol l^{-1} HNO_3 or HCl. The analytical procedures were optimized for sample acidity, elution, interferences, sampling and eluting flow rates and concentration of sample. Common co-existing cations and anions did not interfere with the preconcentration and determination. A fully automated on-line column separation and preconcentration system was described for the determination of trace and ultratrace levels of palladium by graphite furnace AAS [77]. Palladium was preconcentrated in a microcolumn which has been reversibly loaded with N,N-diethyl-N'-benzoyl thiourea as selective complexing agent. The palladium complex was eluted with 60 μl of ethanol and directly introduced into the graphite furnace.

Palladium was determined in pharmaceuticals by direct GFAAS method with a detection limit of 0.1 μg g^{-1} in 5% solution [78]. The recovery of 0.5 – 7.0

μg g^{-1} palladium spikes was close to 100%. The FI-GFAAS method developed by Schuster and Schwarzer [76] utilize oxime and iminodiacetic acid ethylcellulose microcolumns for palladium in aqueous and 50% methanol solutions. A flow system comprising of a microcolumn packed with activated carbon fibre was used for the preconcentration of palladium [79]. The method was sensitive and operates easily with a sampling rate of 15-20 $h.^{-1}$. The recovery of palladium spiked solutions were 103-107% which was on little higher side. A new on-line column separation and preconcentration system for the selective determination of trace and ultratrace levels of palladium was described using FI-GFAAS [80]. Lesniewska *et al* [81] have preconcentrated palladium(II) from environmental samples by using ammonium pyrrolidine carbodithioate coated fullerene, C_{60} prior to determination by GFAAS.

ii) Platinum

A flow injection on-line preconcentration and separation system with microwave assisted desorption is proposed for the FAAS determination of trace amounts of platinum [82] using thiourea modified silica gel column. Thiourea (2%) was used to elute the adsorbed platinum into the nebulizer of the spectrometer with microwave irradiation. Common co-existing ions did not interfere in the determination of platinum(IV). A flow injection on-line sorption preconcentration method for the ET-AAS determination of platinum has been developed [83]. The pyrrolidine dithiocarbamate complexes of either platinum(IV) or platinum(II), formed in 0.7 M HNO_3 are online adsorbed on the inner walls of PTFE knotted reactor and subsequently eluted with methanol.

On-line preconcentration of platinum was carried out by using alumina microcolumn with subsequent detection by FAAS [84] or ICP-AES [85]. A flow injection system incorporating an alumina microcolumn has been coupled to ICP-MS for on-line preconcentration and determination of platinum(IV) in natural waters [86]. An on-line preconcentration using electrodeposition onto a flow through graphite tube cell coupled to an ET-AAS was developed for preconcentration and determination of platinum [87]. After the deposition step, the graphite tube was placed into the graphite furnace and atomization programme was applied. Platinum present in tobacco, beans, slag and dust samples was electrochemically deposited at - 0.9 to – 1.2 V in a flow system incorporating 3-electrode flow through cell with a graphite counter and Ag/AgCl reference electrodes after mineralization with nitric and hydrochloric acids in high pressure PTFE bomb [88].

iii) Platinum and palladium

A simple and highly selective flow injection on-line preconcentrative separation FAAS method was developed for routine analysis of trace amounts of palladium and platinum in geological and metallurgical samples [89]. The selective preconcentration of noble metals was achieved over wide range of acidities (0.5-3.0 M HNO_3 or HCl) on a microcolumn packed with an isodiphenyl thiourea immobilized silica gel.

A flow injection on-line microcolumn method packed with α-aminopyridine resin has been studied for the preconcentration and separation of noble metals followed by FAAS determination [90]. Non-noble metals could be eliminated by 2M HCl as rinsing solution. Separation of individual noble metals could also be accomplished using selective eluents. The method has been applied to certified samples. Bogacheva *et al* [91] have developed a flow injection FAAS method for palladium and platinum determination in solution. This procedure includes sorption preconcentration of platinum/palladium ion associates with n-octyldiethylenetriamine using reversed phase styrene-divinyl benzene copolymer. A flow system combined with segmentation technique was used to develop an efficient on-line sorbent extraction preconcentration system for palladium and platinum for subsequent determination of GFAAS or ICP-AES [92]. Ultratrace determination of platinum group metals in environmental samples was achieved by depositing on the inner wall of a graphite tube in a flow through cell of 1 ml volume [93].

1.4 MOLECULAR IMPRINTING: THE STATE OF ART

Molecular imprinting is a versatile method of creating macromolecular matrices that display selective molecular recognition behaviour. This has shown considerable promise as a technique for preparing materials with spacial recognition ability toward target molecule or ion by mimicking the "key" and "lock" principle in biosphere [94-95]. Molecularly imprinted polymer (MIP) materials are prepared by the copolymerization of functional and crosslinking monomers in the presence of target analyte (the imprint molecule) which acts as a molecular template. The functional monomers initially form a complex with the imprint molecule and following polymerization, the functional groups are held in position by the highly crosslinked polymeric structure. Subsequent removal of imprint molecule reveals binding sites that are complimentary in size and shape to the analyte (*Fig.1.3.)* Thus, a molecular memory is introduced in to the polymer, which is now capable of binding the analyte with high specificity [96]. This remarkable memory effect has been attributed to interaction between the substrate and functional groups of the polymer during production. Also their unique selectivity is due to the manufacturing procedure. Thus the recognition sites are tailor made in situ by copolymerizing the functional monomers and cross linkers around the template. The peculiar molecular recognition properties of MIPs are due to the presence of nanocavities formed during polymerization and according to the key–lock principle, the shape of the nanocavities are complimentary to that of the template [97].

1.4.1 Factors affecting imprinting process

Many factors influence the imprinting process. The most important among them is the selection of the template. The type and availability of functional groups on the template molecules play important roles. The structure, size and solubility of the template etc also affect the imprinting technique. The nature of the functional monomer also depends on the imprinting strategy. The functional monomers need to be chosen so that a good template – monomer complex can guide the formation of the template - specific recognition sites. The association between the imprint molecule and the monomers can be based on non – covalent interactions such as hydrogen bonds, ionic bonds, Vander walls forces or on reversible covalent bonds. For covalent imprinting, a polymerisable derivative of the imprint molecule has to be synthesized, and after synthesis of the polymer, the imprint molecule has to be removed by chemical cleavage. Protocols have also been suggested that combine the advantages of both covalent and non covalent imprinting known as "sacrificial methodology" [98]. Other components such as the crosslinker, the polymerization initiator, and the porogen (solvent) will also influence the structure and performance of the polymer and therefore should be carefully selected. When free radical polymerization is employed, polymerization can be initiated either thermally or photochemically, thus starting the cleavage of the initiator to generate free radicals. The radical formation then initiates the polymerization of the functional monomers and cross linker, which leads to the formation of cross linked polymer net work. The polymerization is carried out in the presence of the template and therefore, the template molecules are "embedded" inside the polymer net work at the end of the process [99]. If the polymer is made in a solid monolith, a particle fragmentation is normally performed by grinding and sieving, where particles with an average size of 10 - 25μm are collected. Prior to use of MIPs for rebinding studies, one step remains – extraction of the template molecules from the polymer matrix. The general procedure for the synthesis of imprinted polymers is schematically shown in *Fig.1.4*

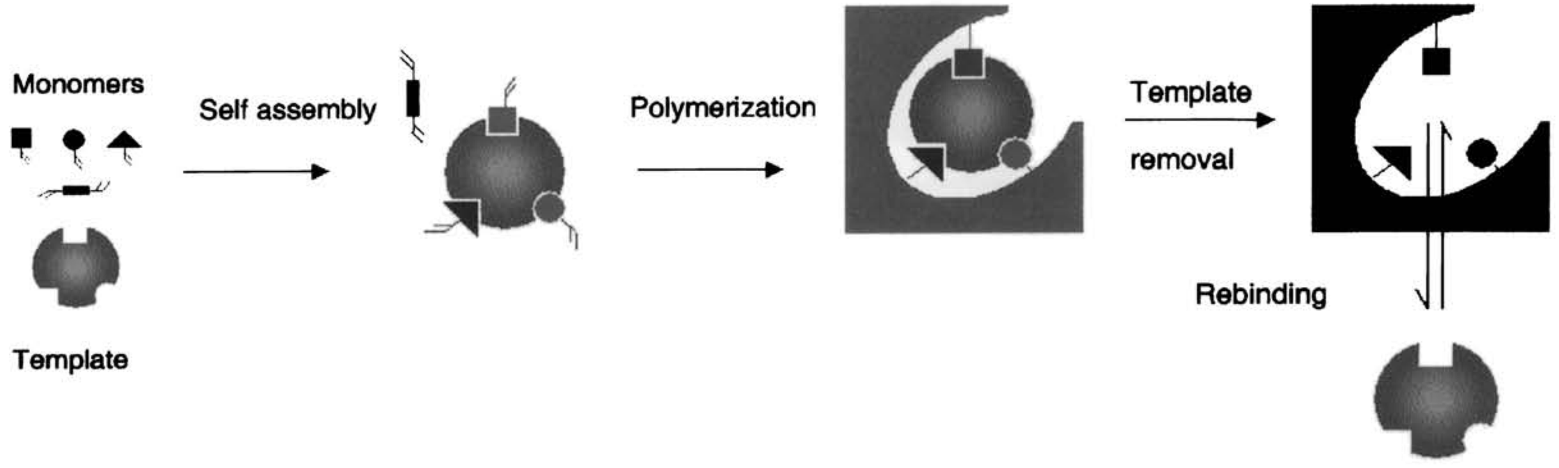


Fig.1.3: Schematic representation of the imprinting process

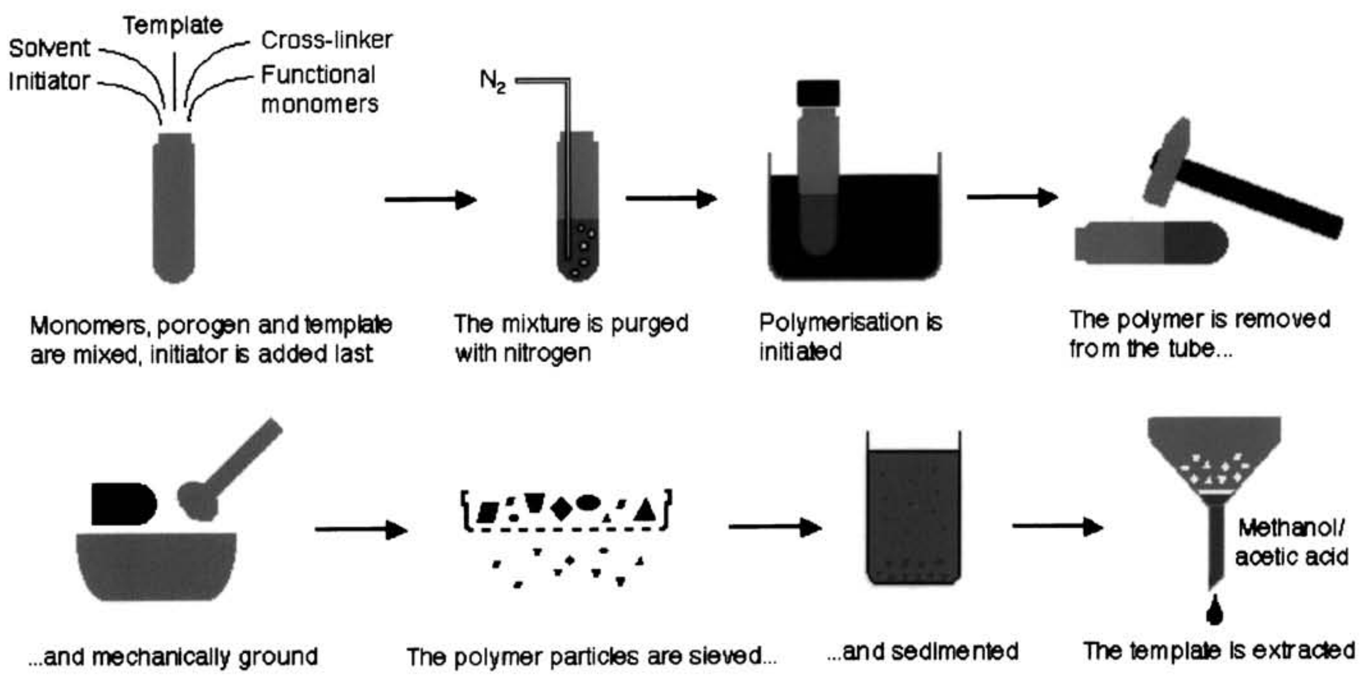


Fig. 1.4: General procedure for preparation of imprinted polymeric materials

1.4.2 Characteristics of MIPs

Apart from the more obvious recognition properties of MIPs, their physical and chemical characteristics are highly appealing [100]. These materials exhibit high physical and chemical resistance towards various external factors. Thus MIPs are remarkably stable against mechanical stress, elevated temperature and high pressure, resistant against treatment with acid, base or metal ions and stable in a wide range of solvents. The storage endurance of the polymers is also very high. Furthermore, the polymers can be used repeatedly in excess of 100 times during periods of years without the loss of the "memory effect".

1.5 ION IMPRINTED POLYMERS (IIPs)

Ion imprinted polymers (IIPs) are exactly similar to MIPs, but they recognize metal ions after the imprinting process and retain all the virtues of MIPs [101-103]. IIPs have outstanding advantages such as predetermined selectivity in addition to being simple and convenient to prepare. IIPs are currently being explored in other areas such as catalytic applications, stationary phases in chromatographic and flow injection columns, membrane separations and developing sensors.

1.5.1 Important applications of IIPs

i) Recognition and binding of proteins

Proteins are highly delicate substrates and contain large and complex arrangements of functional groups [104]. As a result, the design of molecularly imprinted polymers for this class of substrates is practically challenging. The mildness of metal-coordination interaction and its affinity for specific functional groups present on protein surfaces make it an attractive binding mode to prepare protein recognizing polymeric receptors. Arnold and co-workers prepared metal-coordinating polymers for proteins [105]. Mosbach *et al* attempted to use metal-coordination interaction to prepare polymeric adsorbents for selective recognition of proteins [106].

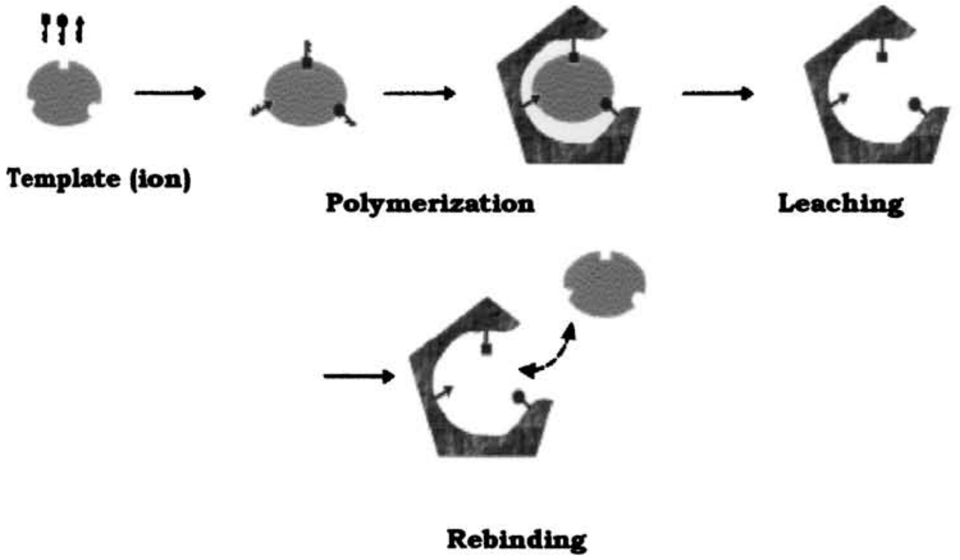


Fig. 1.5: Schematic representation of the ion imprinting process

b) Sensors

The first ion imprinted polymer potentioselectrode was described for calcium and magnesium ions by Mosbach group [107]. Murray's group have described a fluoro optrode for Pb^{2+} for the first time by employing Pb(II) – methyl – 3,5 – divinyl benzoate (DVMB) as template [108]. Same group [109] has subsequently prepared uranyl vinyl benzoate/ vinyl salicilaldoxime complexes as templates for the preparation of IIP materials. The imprinted polymeric materials used for the sensing device is pictorially represented in *Fig. 1.6*. Copper(II) – methyl – β – glucopyranoside complexes was employed for synthesizing copper IIP which senses glucose [110]. Gladis and Rao [111] have described uranyl ion potentioselectrodes by employing uranyl – DCQ – VP ternary mixed ligand complex as template. Novel molecular imprints for aluminium was prepared via non-covalent imprinting technique, using the aluminium(III)-Morin chelate as the template [112]. Based on the fluorimetric properties of the chelate, it was possible to design a selective optical flow through sensor for aluminium(III). The affinity of the polymer binding sites was higher for aluminium(III) than other divalent and trivalent ions viz. beryllium(II), calcium(II), magnesium(II), europium(III), zinc(II) and iron(II), suggesting that the nature of the metal ion, its ionic radius and metal-Morin stoichiometry play important roles in the ionic recognition.

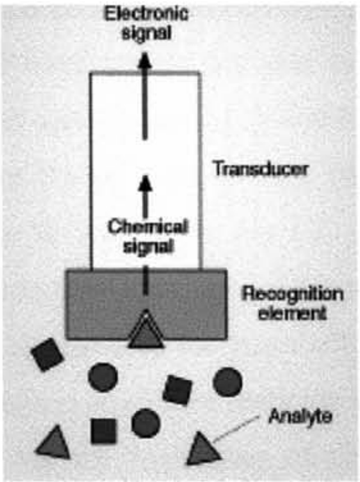


Fig.1.6: Sensing device used for the analyte recognition

c) Membranes

Kimaro *et al* [109] reported the preparation of uranyl ion selective membrane via bulk polymerization of uranyl vinyl benzoate and styrene/DVB after addition of 2-nitrooctylphenylether (plasticizer) and polyester prepared from diglycollic acid and 1,6 – hexane diol. In 2005, Araki *et al* [113] have prepared zinc (II) ion selective membrane by surface molecular imprinting technique utilizing water-in-oil (W/O) emulsion polymerization. Murray [114] has filed a patent describing the MIP based membrane for removal of phosphate, nitrate and ferric ions by copolymerizing a matrix monomer, crosslinking agent, ion imprinted complex, permeability reagent and polymerization initiator.

d) Catalysts

A combination of immobilized transition metal catalysts within molecularly imprinted polymers affords catalytic systems that closely resemble metalloenzymes. The first example in this area was reported by Lemaire *et al* [115], and they investigated the enantioselective hydride transfer reaction on a catalytic rhodium complex. Polborn and Severin [116] developed a MIP catalyst for the reduction of benzophenone employing an immobilized ruthenium catalyst ligated to a transition state analogue as the catalytic precursor. Cammidge *et al* species in cis geometry for catalysis of Suzuki and Stille coupling reactions. These imprinted palladium catalysts were found to be as active and selective than homogeneous systems, which was attributed to their semi-rigid ligand geometry retained by the imprinting process. The potential for induced chirality of transition metal catalysts within MIP binding sites has been elegantly explored by Gagne *et al* [118-119] and employed metals such as rhodium, titanium and platinum. The schematic representation of the polymer binding sites obtained by imprinting of transition metal catalysts is shown in *Fig.1.7.* Crown ether functionalized palladium catalysts by molecular imprinting were also reported by Gagne *et al* [120]. Yamazaki *et al* [121] described the preparation of synthetic enzyme mimic for the hydrolysis of the organo phosphate pesticide paraxon. The active site in the polymer was introduced via the imprinting of cobalt(II)- 4,5-vinyl imidazole complex. Matsui *et al* [122] mimicked a class II aldose for aldol condensation by imprinting a cobalt complex of reaction intermediate. Iwasawa group [123-125] have prepared SiO_2 attached imprinted rhodium catalysts by molecular imprinting. Fache *et al* [126] applied polymer – matrix MIP catalysts with rhodium complexes. Morihara *et al* [127] reported a pioneering work on foot print catalysts prepared by incorporation of aluminum(III) and loading of template molecules in silica matrix. Say *et al* [128] have combined molecular imprinting with the ability of histidine to chelate metal ion to create active centrum of phosphotriesterase on microbead surfaces for selective catalytic degradation of the nerve agent paraxon. An enzyme mimic polymer was prepared by surface imprinting technique using the active site as a complex of cobalt(II) ion and alkyl imidazole which acts as the catalyst for the hydrolysis of aminoacetic ester [129]

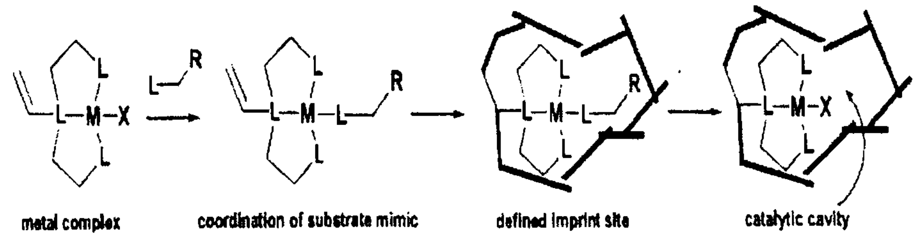


Fig.1.7: Schematic representation of polymer binding sites obtained by imprinting of transition metal catalysts.

e) Ion imprinted polymer particles for the solid phase extraction (IIP-SPE)

A particularly promising application of IIP is the solid phase extractive preconcentration of analytes present in low concentration or separation from other coexisting ions or complex matrix, which may lead to selective environment or clean up of analytes not achievable by hitherto existing methods. Metal ions can also serve as templates for forming crosslinked polymers via imprinting.

One of the first ionic template effects in the synthesis of chelating polymers was reported by Nishide *et al* [130] in the mid 1970's. They crosslinked linear chain polymers (poly(4-vinylpyridine)) with a bifunctional agent (dibromoalkane) in the presence of metal ions. Recently Takagi and coworkers [131-132] introduced the concept of surface-imprinting polymers. The specific solids were prepared by emulsion polymerization involving a functional host monomer (phosphoric acid derivatives), an emulsion stabilizer, a crosslinking agent and a metal cation template, which was selectively complexed by the metal-binding groups at the aqueous-organic interface to form recognition sites. The template cation was removed by acidic stripping to yield microspheres with a metal ion templated surface. A third and alternate approach was based on the copolymerization of isolated/non-isolated monomers/ion complexes with the crosslinking agent [133-135]. In the preparation of IIPs by this approach, suitable ligand groups were brought into contact with metal ions to form a complex which is then covered with a crosslinked polymer. After removal of the template (metal ion), the uptake of metal ions is strongly enhanced in many cases and also more selective. The selectivity arises mainly due to the following factors [136].

i) the specificity of interaction of ligand with the metal ion
ii) the coordination geometry and the coordination number of metal ion
iii) the charge of the metal ion and
iv) to a large extent on the size of the metal ion

Ion Imprinted solid phase extractants developed so far are summarized below.

i) Lanthanides

SPE method based on the use of cation imprinted polymers to separate lanthanum and gadolinium cation copolymers based on diethylene triamine pentaacetic acid (DTPA) derivative have been prepared [137]. Imprinting effect was observed with materials prepared in the presence of gadolinium salts and exhibited higher efficiency and selectivity than the corresponding blank polymers. The selectivity factor was increased up to 13.6 in favour of gadolinium.

The functionalized monomer of DTPA was copolymerized with commercially available divinyl benzene (DVB) containing 45% ethyl styrene in the presence of gadolinium(III) salt. The resulting IIP was found to be more selective to gadolinium compared to lanthanum ($S_{Gd/La} = 20$) than the untemplated one (6.3) [138]. Subsequently, same group [139] have extended the study to determine selectivity coefficient viz. $S_{Gd/Nd}$, $S_{Gd/Eu}$ and $S_{Gd/Lu}$ and evaluated the results obtained with gadolinium imprinted and blank polymeric resins. Biju *et al* [140] have synthesized dysprosium(III) IIP particles by copolymerization of styrene monomers, DVB (crosslinking agent) in the presence of dysprosium(III)-5,7-dichloroquinoline-8-ol - 4-vinyl pyridine ternary complex wherein dysprosium (III) ion is the imprint ion. In addition to providing quantitative enrichment from dilute solutions, the selectivity of dysprosium IIP for dysprosium over ytrrium is much higher, comparable in the case of neodymium and lutetium when compared to conventional extractant such as di-2-ethylhexyl phosphoric acid (D2EHPA) in liquid-liquid extraction (LLE). Subsequently same authors [141] reported the effect of gamma irradiation on dysprosium IIP and control polymer particles. Erbium [142] and Neodymium [143] IIP particles were synthesized on the same lines of dysprosium IIP particles using $Ln(DCQ)_3(VP)_2$ ternary complex. Kala *et al* [144] have patented a process for synthesis of erbium IIP particles polymerized by thermal, photochemical and radio chemical means. A systematic study on the use of different functional and crosslinking monomer combinations during the preparation of erbium IIP particles via γ- irradiation were also investigated [145]. A comparison of selectivity studies with respect to polymers prepared with different functional and crosslinking monomers synthesized by different ways were also reported elsewhere [146].

iii) Actinides

The invention by John *et al* [147] relates to the detection and extraction of UO_2^{2+} ions by polymer imprinting wherein the complexable functionality is of the formula CTCOOH where T is a hydrogen or any halogen (preferably chlorine) methyl and halogen substituted forms thereof or CCOOH or PhCOOH. Saunder's *et al* [148] described the synthesis of UO_2^{2+} ion imprinted copolymer with chloroacrylic acid and ethylene glycoldimethacrylate, which after removal of template selectively extracts uranium from dilute aqueous solutions over a range of +2, +3 and +4 competitor metal ions. Dai *et al* [149] prepared mesoporous sorbent materials by ion imprinting technique for separation of uranium from aqueous solutions using bifunctional ligands such as amines, sulphonic acids and phosphonic acids. The inventions by Dai *et al* [149] and John *et al* [147] do not describe the selectivity of the imprinted polymer particles over other inorganic ions. Bae *et al* [150] have synthesized IIP for UO_2^{2+} ion consisting of 5% uranium-vinylbenzoate binary complex and 4 wt% DVB in styrene using chemical initiation by 1 wt% 2,2'-azobisisobutyronitrile (AIBN) and was used for preconcentration of UO_2^{2+} ion from aqueous and sea water solutions.

Dai and coworkers [151] investigated the properties of sol-gel glasses templated with UO_2^{2+} ions. UO_2^{2+} ion imprinted sol-gel silica glasses were prepared by removing uranyl template ion. A significant increase in affinity and selectivity of the imprinted sol-gel sorbents over control blanks have been observed while the surface areas remain equal.

Recently, Gladis and Rao [152] patented a process consisting of synthesis of solid phase extractant materials by polymer imprinting suitable for uptake of uranyl ions from aqueous and synthetic sea water solutions and also in presence of a host of +2, +3 and +4 inorganic ions. Gladis and Rao [153] described a novel synthesis of IIP particles by employing UO_2^{2+} - 5, 7-dichloroquinoline-8-ol and vinyl pyridine ternary complex in presence of styrene, DVB and AIBN. These polymer particles were found to enrich uranyl ion from dilute aqueous and seawater solutions containing other inorganic ions. Furthermore, in addition to testing the accuracy of the developed enrichment procedure by analyzing standard marine sediment reference material, MESS-3 supplied by National Research Council, Canada, it has been used to analyze soil and sediment samples. Same authors have also studied the influence of porogen i) on the distribution ratios of uranium (D_U) and thorium (D_{Th}), ii) selectivity coefficient of uranium over thorium ($S_{U/Th}$) and iii) retention capacity of CPs and IIPs [154]. An IIP material was prepared with methacryloyl amido glutamic acid (MAGA) and EGDMA and was used for the selective separation of uranyl ions from aqueous solution [155]. Subsequently the same group [156] has prepared thorium IIP particles with MAGA-EGDMA and selectively preconcentrated thorium in the presence of uranyl, cerium and lanthanum ions.

Metilda *et al* [157] have studied percent recovery of uranium from dilute aqueous solutions with uranyl IIP particles synthesized using binary (UO_2^{2+}- DCQ or UO_2^{2+}-VP) and ternary (UO_2^{2+} -DCQ-VP) complex as templates. Uranium – salicylaldoxime- 4- vinyl pyridine complex template was imprinted instead of Uranium- DCQ-VP and the resulting IIP particles were found to extract uranium quantitatively from weakly acidic solutions [158].

iv) Heavy metals and transition elements

Kuchen and Schram [131] prepared macroporous resins (specific surface area ~ 400 m^2g^{-1}) by radical polymerization of copper(II) methacrylate complexes with water, pyridine and 4-vinyl pyridine with ethylene glycoldimethacrylate (EGDMA) as crosslinking agent in presence of benzene/methanol as porogen and AIBN as initiator.

Copper(II) imprinted beads were prepared by dispersion polymerization technique by dissolving 0.2 g of polyvinylalcohol in 60 ml of distilled water. Previously synthesized copper(II)-n-methacrylamidohistidine-dihydrate complex was dissolved in ethanol and mixed with EGDMA in toluene and AIBN and transferred to dispersion mixture. After polymerization, the poly (EGDMA-

MAH/Cu(II) beads were separated, washed with methanol and water and copper(II) imprint ion was leached with EDTA. The effect of imprinting was clearly shown by comparing the adsorption of copper, zinc, nickel and cobalt with copper imprinted and non-imprinted microbeads [159]

Tsukaghoshi *et al* [160] prepared imprinted microspheres by seeded emulsion polymerization of DVB, styrene, butyl acrylate and methacrylic acid. The imprinted structure was introduced on the carboxylated microsphere by surface imprinting, in which the carboxyl groups were reorganized through complexation with metal ions on the surface and then fixed by crosslinking polymerization in their specific orientation. The imprinted effects were verified on copper(II) and nickel(II) imprinted microspheres. Takagi's group [161-166] used surface imprinting for the synthesis of copper(II), nickel(II), and cobalt(III) metal ion imprinted microspheres via seed emulsion polymerization.

Novel zinc ion-imprinted resins were prepared by surface template polymerization with W/O emulsion using dioleylphosphoric acid (DOLPA). A comparison of DOLPA with D2EHPA suggests that interfacial activity is a substantial key for choosing an ion-binding amphiphile [167]. Yoshida *et al* [168] have clearly demonstrated that post gamma-irradiation of IIPs obtained by surface template polymerization resulted in polymer matrices which are more rigid and also allow the functional monomer to attach firmly to the matrices. The irradiated imprinted resin exhibits a tremendously high selectivity for zinc over copper ions. The improved selectivity of zinc over copper using IIPs prepared by surface template polymerization using same bifunctional monomer 1,12-dodecane-diol-O-O'-diphenyl phosphonic acid was clearly shown compared to conventional liquid-liquid extraction [169].

Monomer type functional surfactants, 2-(p-vinyl benzylamino) alkanoic acid and N,N-dialkyl derivatives have been used as both a ligand and an emulsifier for the preparation of surface template resins [170]. Chen *et al* [134] have synthesized 4-vinyl benzyl substituted 1,4,7-triazacyclononane (TACN) ligand by treating 1 or 3 moles of 4-vinyl benzyl chloride with TACN and formed complexes with zinc. The copolymerization of zinc(II) complexes with the crosslinking agent DVB (80%) on the use of AIBN as initiator provided highly crosslinked macroporous polymers. However, attempts to prepare copper IIP or blank polymer were unsuccessful. The overall order of metal ion selectivity for IIP with zinc(II) as imprint ion is manganese(II) $\leq$ nickel(II) $\leq$ zinc(II) $\leq$ cobalt(II) <<< copper(II) which somewhat but not exactly, follows the Irving-Williams order of stability. The authors have postulated that zinc(II) imprinting (the ionic radius of zinc(II) and copper(II) being comparable) accounts for the selectivity for copper(II) over iron(III) ion, because iron(III) ion is usually an ion that can readily compete for any polymer-pendant ligand site due to its favourable charge to radius ratio.

Yoshida *et al* [171] have shown that incorporation of aromatic rings and a suitable straight alkyl chain in the functional monomer (organophosphorus compound) provided high binding affinity to the zinc target metal ion. Uezu *et al* [172] have prepared zinc(II) imprinted microspheres by surface template polymerization with W/O/W emulsions. Dioleylphosphoric acid which has two long alkyl chains in the hydrophobic moiety and DVB were employed as a functional and crosslinking agent respectively. The metal imprinted beads exhibit a high selectivity towards target zinc ions over copper ions. Subsequently, Uezu *et al* [173] have succeeded in enhancing the imprint effect and the selectivity of zinc IIP by systematically studying the optimum polymerization conditions. Novel metal ion imprinted polymer was prepared by the same group [174] via surface molecular imprinting technique. Trimethylolpropane trimethacrylate (TRIM), zinc ions and 1,2-dodecandiol-O,O'-diphenylphosphonic acid (DDDPA) were used as matrix forming monomer, imprint molecule and functional monomer respectively. The template effect of the TRIM based polymer was enhanced by the high rigidity of the polymer matrix compared to the imprinted polymer whose matrix is divinyl benzene. In addition, the adsorption equilibrium constant was evaluated on the basis of the Langmuir analysis for the adsorption data.

The features combining a chemically modified electrode with an artificial receptor system prepared by imprinting and electropolymerized (Ni-(protoporphyrin IX) dimethyl ester in the presence of nitrobenzene were studied [175]. The responses of the modified glassy carbon electrode towards template molecules were analyzed by cycling over the nitrobenzene reduction wave which shows higher selectivity for imprinted polymer. Fang *et al* [176] synthesized a new ion-imprinted thiol functionalized silica gel sorbent by surface imprinting technique in combination with a sol-gel process for selective on-line SPE of cadmium(II). Liu *et al* [177] have prepared mercury(II) IIP particles by using mercury(II)- diazoaminobenzene – VP ternary mixed ligand complex as the template and has been used for offline batch / column SPE studies. A similar ternary mixed ligand complex prepared with cadmium(II) was employed during the preparation of cadmium(II) IIP particles [178]. Copper(II) acetate – picolinamide complex imprinted polymer was prepared by Wu and Li [179] by mixing the above complex with 4-vinyl pyridine in prepolymer mixture. Lu and Yan [180] have prepared organic-inorganic sorbent for selective separation of cadmium through self hydrolysis, self condensation and co – condensation of crosslinking agent and the functional precursor in an alkaline media followed by gelation. The selectivity of the sorbent was investigated by a batch competitive ion binding experiments using copper(II) and zinc(II) mixture. Say et al [181] used nickel(II) methacrylohistidine complex monomers and KCN for the synthesis of cyanide imprinted polymeric beads and this material was packed in a microcolumn and has been used for the determination of cyanide in waste water. Also copper(II) [182] and nickel(II) [183] imprinted beads were prepared with dispersion polymerization technique in presence of a dispersion medium polyvinyl alcohol in water. .

v) Others

Calcium(II) and magnesium(II) ion selective sorbents were prepared by ion imprinting using N,N'-dimethyl-(N,N'-bis-4-vinyl phenyl)-3-oxapentane diamide and used as the ion complexing monomer [107]. The resulting polymers were analysed for their ability to extract calcium ions from methanolic water. The polymers prepared against calcium(II) and magnesium(II) ions were found to bind Ca^{2+} ions with 6 and 1.7 times lower K_{diss} values respectively when compared with reference polymers prepared in the absence of metal ions. In addition, the number of binding sites for calcium(II) ions, determined for the respective polymer preparation fitted well with theoretical values calculated from the stoichiometry of the complexation of the ionophore by calcium(II) and magnesium(II) ions respectively.

vi) Noble metals

Hitherto there are no reports in the literature other than the work described in this thesis describing the use of ion imprinted polymers of noble metals for the solid phase extraction.

1.6 SCOPE OF THE PROPOSED WORK

Development of new preconcentration techniques either with or without separation for PGM or for inorganics in general prior to analysis was found to be fascinating fields in analytical chemistry. The introduction of ion imprinted polymers for solid phase extraction is a fast developing area for the above mentioned applications for inorganics. There are mainly four different approaches for the synthesis of ion imprinted polymers. They are i) linear chain polymers carrying metal binding groups crosslinked with a bifunctional reagent in presence of metal ions. ii) binary complexes of metal ions with ligands having vinyl groups were prepared, isolated and then polymerized with matrix forming monomers iii) surface imprinting and iv) imprinting of binary / ternary mixed ligand complexes of metal ions with vinylated or a mixture of vinylated and non vinylated ligands. In view of this, the scope of the proposed work is

i) To synthesize ion imprinted polymer materials for noble metals.

ii) Characterization of the synthesized polymeric materials.

iii) Application of the above synthesized IIPs for

    a) Selective recovery of palladium(II) from dilute aqueous solutions.

    b) Offline and on-line separation of palladium(II) from co-existing noble and transition metal ions prior to determination .

The studies carried out on the above lines and the results obtained are described in subsequent chapters.

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CHAPTER 2

SYNTHESIS OF PALLADIUM(II) ION IMPRINTED POLYMERIC MATERIALS WITH NANOPORES AND ITS ANALYTICAL APPLICATIONS

2.1 INTRODUCTION

A detailed literature survey as described in chapter 1 indicated that IIP particles for the preconcentration / separation of noble metal ions which include palladium also have not been synthesized so far. However, a few reports exist on the synthesis of heterogeneous palladium catalyst assemblies by molecular imprinting. Cammidge *et al* [1] used polymerizable triphenyl phosphine ligands to fix the labile palladium species in cis geometry for catalysis in Suzuki and Stille coupling reactions. Also crown ether functionalized palladium catalysts by molecular imprinting were reported by Gagne *et al* [2].

Dimethyl glyoxime is a selective gravimetric reagent compared to other such reagents for palladium in weakly acidic solution and can be used for its separation from various transition and p-block elements. However, other noble metals particularly, platinum interferes when it exceeds certain concentration. Hence, it is felt worthwhile to study the separation behavior of palladium from platinum by synthesizing palladium(II) ion imprinted polymer (IIP) particles using dimethyl glyoxime as one of the ligands. This chapter pertains the synthesis, characterization and analytical applications of IIP materials for preconcentrative separation of palladium by copolymerizing palladium(II) - dimethyl glyoxime (after isolation) – 4 - vinyl pyridine (VP) ternary complex, styrene and a cross linker like divinyl benzene in presence of 2,2' - azo bisisobutyronitrile as initiator.

2.2 SYNTHESIS OF ION IMPRINTED POLYMERS

2.2.1 Preparation of ternary complex

The pre- polymerization complex (ternary complex) of palladium ion with dimethyl glyoxime (DMG) and 4- vinyl pyridine (VP) was prepared by stirring a mixture of 0.63g of palladium(II) - DMG complex (prepared as discussed elsewhere [3]) and 0.4ml (4.2mmoles) of VP in cyclohexanol (10 ml) for 2 hrs. The formation of ternary complex was confirmed by UV - Visible absorption spectral studies.

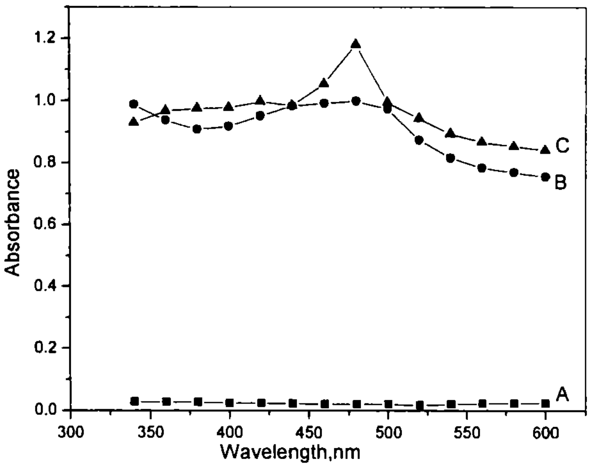
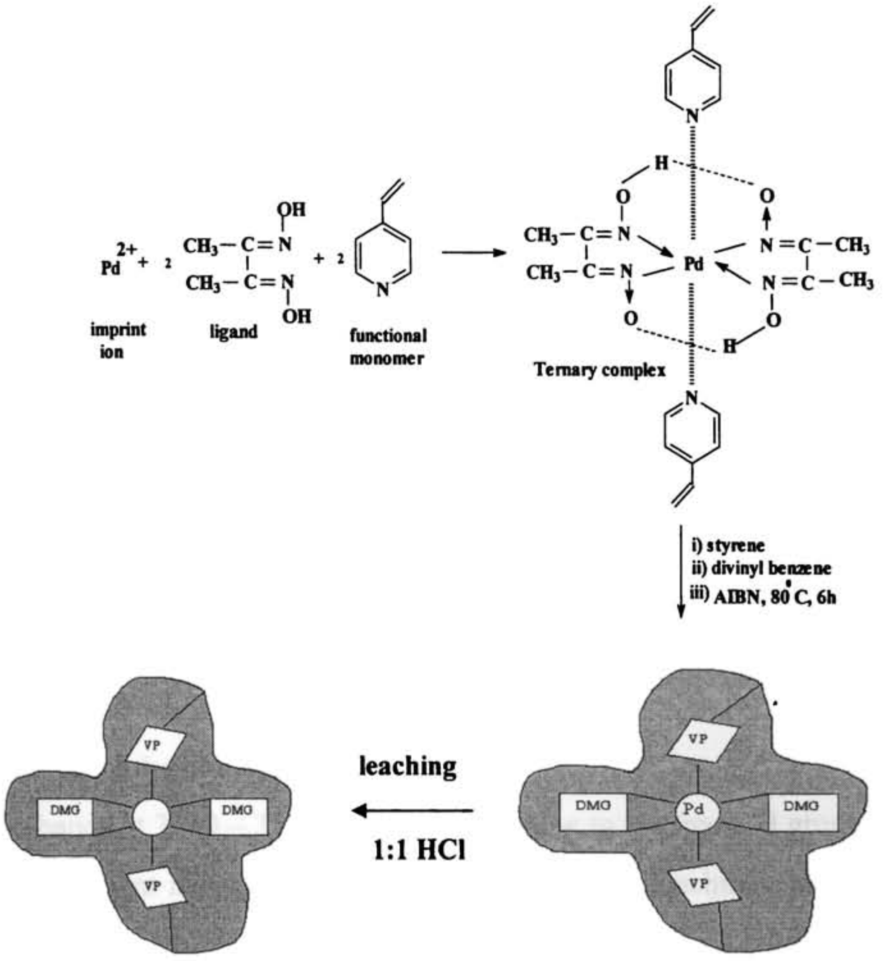


Fig.2.1: UV-Visible absorption spectra of methanolic solutions of dimethyl glyoxime (A) , dimethyl glyoxime + palladium(II) (B) and dimethyl glyoxime + of palladium(II) +vinyl pyridine(C) .

Curve A in *Fig.2.1* shows the absorption spectrum of methanolic solution of DMG (8 mmoles) against methanol. The addition of 4 mmoles of palladium(II) to the above solution resulted in the formation of coloured complex with significant increase in absorbance in the entire wavelength range and a broad peak in the range 425-500 nm. (see curve B). Subsequent addition of 8 mmoles VP resulted in a very clear enhancement in absorbance at 480 nm. This evidence clearly proves the formation of ternary complex - palladium(II) – DMG – VP.

2.2.2 Preparation of Imprinted Polymer (IIP)

The ternary complex was imprinted in styrene-divinyl benzene copolymer as per the scheme proposed in *Fig.2.2.* 4 – VP acts not only as the ligand for the ternary complex but also as functional monomer during polymerization. For polymerization, 20 mmoles styrene (2.08g), 15 mmoles of divinylbenzene (95% pure) (1.95g) and 50 mg of 2, 2'azobisisobutyronitrile were added. The polymerization mixture was cooled to 0°C and purged with N_2 for 10 min, sealed and heated at 80°C in an oil bath with stirring for 6 hrs. The solid formed was ground in a mortar and dried in constant temperature vacuum oven at 80°C for 2 hr and sieved to get particles lower than 45μm, which is schematically represented in *Fig.2.2.* A part of the synthesized material is subjected to γ-irradiation from a Co^{60} source at a total dose of 0.5 Mrad.



F.g.2.2: Scheme for preparation of palladium ion imprinted polymer (IIP) material

2.2.3 Removal of the template ion

The imprint ion i.e., palladium(II) was leached out from the above polymer particles by stirring with 2 x 50 ml of 6 M HCl for 6h. The resultant polymer particles after filtration was dried in a vacuum oven at 80°C to obtain IIP particles for possible preconcentrative separation of palladium (II) ion from dilute solutions.

2.2.4 Preparation of Control Polymer (CP)

Control polymer particles were prepared in a similar fashion as that of IIP except the imprint ion i.e., palladium(II) was not added to the recipe.

except the imprint ion i.e., palladium(II) was not added to the recipe.

2.3 CHARACTERIZATION STUDIES

Control polymer particles, unleached and leached ion imprinted polymer particles were subjected to characterization studies by FTIR, XRD, spectrophotometry and surface area and pore size analysis.

2.3.1 FTIR

The IR spectra of CP (A), unleached (B) and leached (C) palladium(II) IIP particles are given in *Fig.2.3.*The important features obtained are

1) All have similar IR spectra, which indicate that all the polymers have similar backbone.

2) A weak band near 1248cm^{-1} ($\nu_{C\text{-}N}$) present in unleached particles is shifted to higher frequency 1255cm^{-1} while leaching. The same peak is present in the CP also. This shift towards lower frequency in the unleached imprinted polymer and the decrease in strength of vibration can be attributed to the bonding between the palladium and the nitrogen in $>C = N$

3) The bands at 3700 – 3500 cm^{-1} corresponding to the free-OH groups in oximes which is present in both CP and IIP before and after leaching indicates that only the metal ion is removed during leaching and not the DMG ligand.

4) The bands at 3700-2700 cm^{-1} corresponds to the intra molecular hydrogen bonding, which are present in the imprinted polymeric particles confirm that during the ternary complex formation, the intra molecular hydrogen bonding present in the binary complex were not collapsed or broken.

These observations indicate that the polymer backbone is same in both unleached and leached IIP particles thus suggesting DMG is held onto the polymer even after leaching.

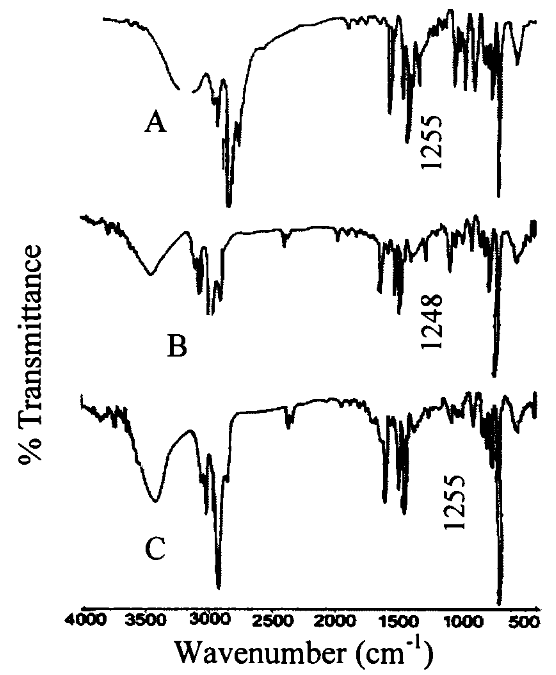


Fig.2.3: IR spectra of CP (A), unleached (B) and leached (C) palladium ion imprinted polymer particles.

2.3.2 X-ray diffraction Studies

The XRD patterns of CP (curve A), unleached (curves B&C) and leached (curves D&E) IIP particles with and without irradiation are given in *Fig.2.4*.

The peaks obtained at 2θ values 12.5, 17.4, 19.9, 21.4, 23.3, 30.2 and 32.3 in the unleached material were absent in the leached one indicating that the palladium(II) is completely removed from the particles during leaching. The same observation was noted in the case of leached and unleached irradiated polymeric particles. It can be noted from the XRD patterns that all of the peaks in the irradiated sample were significantly shifted to higher angle compared with that of samples with out irradiation. This can be attributed to the contraction of the polymeric material and availability of more palladium sites during irradiation, which is further confirmed by the preconcentration studies.

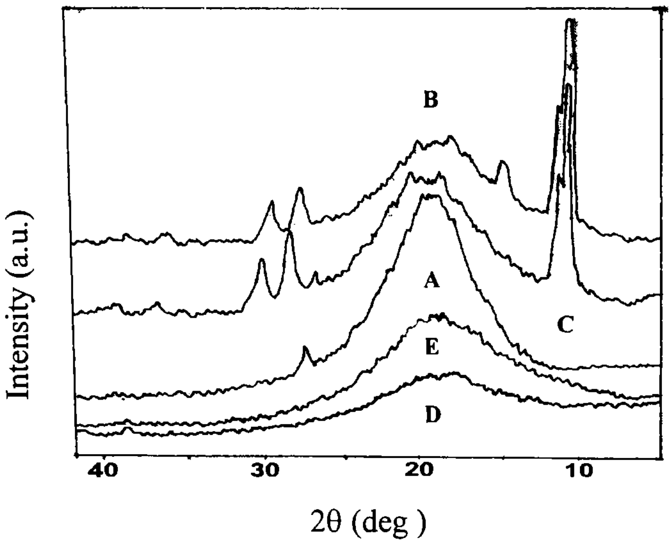


Fig.2.4: X-ray diffraction patterns CP (curve A), unleached (curves B and C) and leached (curves D and E) palladium ion imprinted polymer particles with and without irradiation.

2.3.3 Spectrophotometry

UV- visible spectrophotometric determination of palladium present in leached solution of IIP particles confirms the quantitative removal of palladium during leaching of unleached polymer with 2 x 50 ml of 6 M HCI for 6h. Further, the absence of precipitate on reducing the acidity of leached solution to ~ 0.5 N or by addition of excess palladium ion to the above solution clearly proves the absence of DMG in leachant solution. On the other hand, the leaching of palladium(II) from unleached polymer is confirmed by the occurrence of palladium - DMG precipitate on addition of DMG to leachant solution in addition to UV -visible absorption spectra of leachant solution.

2.3.4 Surface area and Pore size

Surface area and pore size analysis of CP, unleached and leached ion imprinted polymer (IIP) materials before and after irradiation are given in *Table 2.1*, from which following observations can be made. i) The BET, Langmuir and cumulative surface areas for leached palladium(II) IIP particles are higher than that of unleached and CP particles. Further, these surface areas are 10 fold higher than that for the MIP's prepared by Yilmaz [4] ii) BJH adsorption cumulative pore volumes are higher for leached particles compared to unleached IIP and CP particles and iii) BJH average pore diameter during adsorption are in the range 2-3nm in all the synthesized (compared to pore sizes of ~250 for MIP's [4]) polymers indicating polymer particles with nanopores were obtained in the present study.

Table2.1: Surface area and pore size analysis data of control (CP) and ion imprinted (IIP) particles

Parameters	Control polymer	Ion Imprinted polymer			
		unleached	leached	irradiated	
				unleached	leached
BET Surface area (m^2/g)	217.6	261.3	372.5	144.6	180.9
Langmuir surface area (m^2/g)	383.4	876.2	956.7	393.6	479.3
BJH ads. average pore dia (nm)	2.6	2.6	2.8	2.7	2.8
BJH ads. Cumulative surface area (m^2/g)	325.8	381.2	486.1	339.9	423.6
BJH ads. Cumulative Pore volume (cm^3/g)	0.2	0.2	1.3	0.2	0.3

2.4 OPTIMIZATION OF EXPERIMENTAL CONDITIONS

The influence of various parameters such as effect of acidity during preconcentration, weight of IIP particles, preconcentration time, elution time and the aqueous phase volume on the solid phase extractive preconcentration of palladium(II) was studied using IIP particles.

2.4.1 Effect of acidity during preconcentration

The acidity of the solutions were varied from 0.1-0.5 M HCl for a series of solutions containing 25µg of palladium(II) in 1 litre. 0.05g of IIP particles were added to above solution and stirred for 20 minutes. The palladium(II) ion preconcentrated on IIP particles were eluted by stirring for 15 minutes with 2 x 10 ml of 6 M HCl. Suitable aliquots of eluent were taken, pH was adjusted to 4.0 after addition of 0.4 M citrate buffer and the palladium(II) content was established by following iodide- Rhodamine 6G procedure [5] reported elsewhere. It was evidenced from the *Fig. 2.5* that the sorption of palladium(II) is constant and maximum when the overall acidity is in the range of 0.2- 0.4 M in HCl which is expected in view of the maximum stability of ternary Pd- DMG - VP complex in this acidity range. At acidities > 0.5M, the percent extraction of palladium(II) by IIP particles decreases due to the dissociation of palladium - DMG- VP complex at these acidities. In all subsequent work, the overall acidity was adjusted to ~ 0.25M HCl. As seen from the figure, the percent extraction for IIPs is higher than CPs at all acidities indicating the imprinting effect.

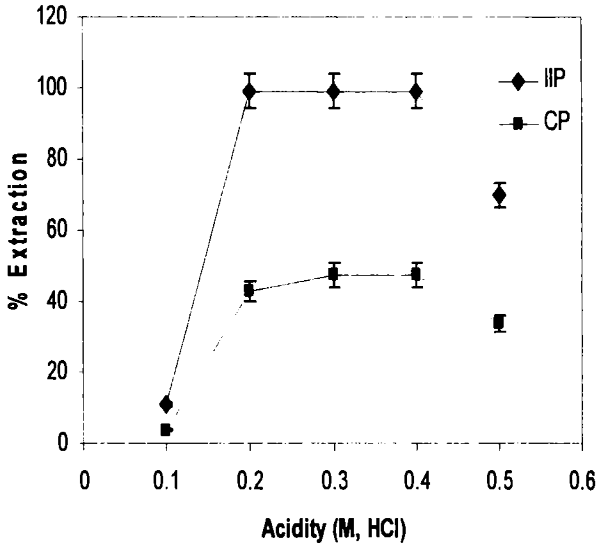


Fig.2.5: Effect of acidity during the preconcentration of palladium(II)

2.4.2 Effect of amount of IIP particles

The amount of IIP particles were varied from 0.01 – 0.1g using a series of solutions containing 25µg l^{-1} of palladium(II).The enriched palladium(II) was determined as described in section 2.4.1.The percent enrichment for various amounts of IIPs and corresponding CPs are given in *Fig. 2.6.* The minimum weight of palladium(II) IIP particles per litre of solution was ascertained to be 0.02g. Hence, 0.05g of Pd IIP particles were used for preconcentration of ultratrace amounts of palladium(II) from aqueous solutions. It is clear from Fig. 2.6 that there is a significant imprinting effect as the % extraction is higher for IIPs compared to CPs at all weights.

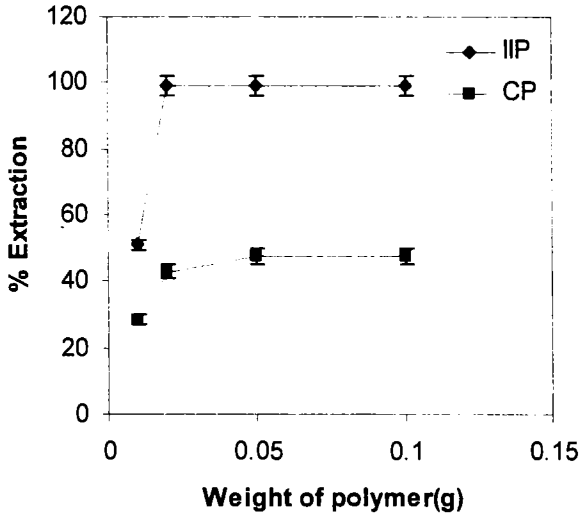


Fig.2.6: Effect of amount of polymer particles on the preconcentration of palladium(II)

2.4.3 Effect of preconcentration time and elution time

In order to study the effect of preconcentraton time and elution time on the percent extraction of palladium(II), the preconcentration and elution times were varied between 10-30 min. The results obtained are given in *Table2.2.* As seen from the *Table 2.2*, 20 minutes of stirring is enough to quantitatively preconcentrate 25 μg of palladium present in 1 litre of solution using 0.05g of palladium(II) IIP particles. Further, it was established that 15 minutes of elution with 50 % (v/v) HCl is required for the recovery of preconcentrated palladium(II) from dilute aqueous solutions.

Table2.2: Effect of preconcentration time and elution time on preconcentration of palladium(II)

Parameter	% Extraction
Preconcentration time (min)	
10	66.7 ± 1.3
15	99.0 ± 1.9
20	>99
30	>99
Elution time (min)	
10	47.6 ±1.2
15	>99
20	>99
30	>99

2.4.4 Effect of aqueous phase volume

The volume of the aqueous phase was varied between 25-1000 ml during preconcentation to estimate the effect of it on the percentage extraction of palladium(II). It can be seen from the *Fig. 2.7* that the change of aqueous phase volume from 25 to1000 ml did not affect the preconcentration efficiency of 25μg of palladium using 0.05 g of Pd IIP. As observed earlier in case of acidity and weight of polymer particles, the imprinting effect is noticed at all aqueous phase volumes.

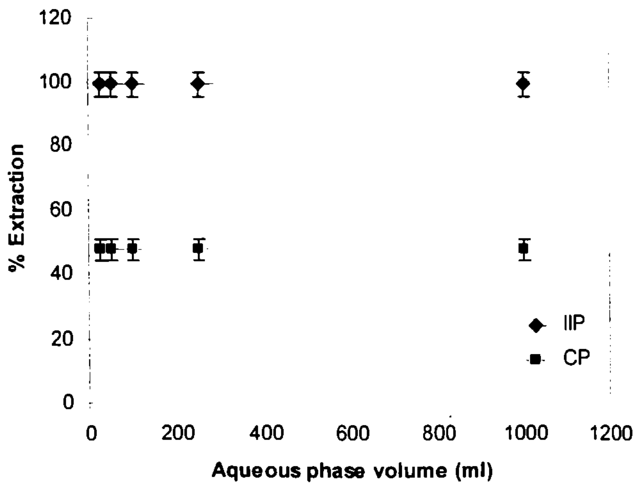


Fig.2.7: Effect of aqueous phase volume

2.5 STATISTICAL AND CALIBRATION PARAMETERS

A set of solutions (Vol.1000 ml) containing palladium(II) in the concentration range 0-100 μg were adjusted to the pH 4.0 ± 1.0 after the addition of 0.4M citrate buffer and palladium(II) content was established by described in section 2.4.1

Under the optimum conditions described above, the calibration curve was linear over the concentration range of 0 -100 μg of palladium(II) present in 1 litre of sample solution as evidenced from *Fig.2.8*. Five replicate determinations of 50 μg of palladium(II) in 1 litre of solution gave a mean absorbance of 0.200 with a relative standard deviation of 2.05 % (Table 2.3). The detection limit corresponding to 3 times the standard deviation blank was found to be 2.5 μg l^{-1}. The linear equation with regression is as follows.

$$A = 0.004\ C - 0.0003$$

Correlation coefficient = 0.99998

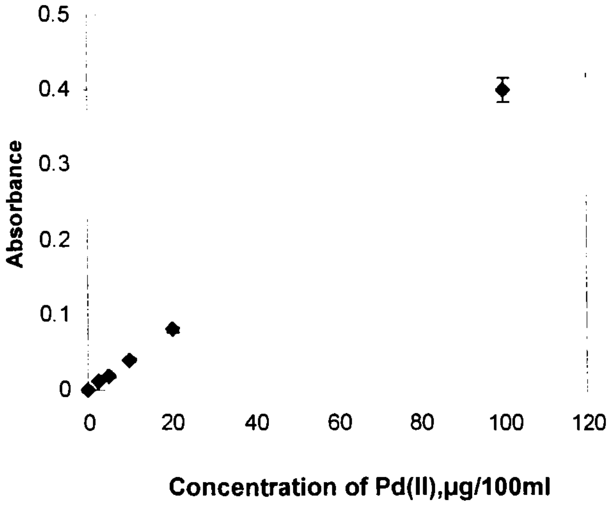


Fig.2.8: Calibration plot

Where A is the absorbance and C is the amount of palladium in μg per 1litre of sample solution. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

Table2.3: Precision studies

S.No	Absorbance	Pd found (µg) X_n	$X_n - \overline{X}$	$(X_n - \overline{X})^2$
1	0.200	50.00	0	0
2	0.195	48.75	1.25	1.562
3	0.193	48.25	1.75	3.062
4	0.203	50.75	0.75	0.5625
5	0.200	50.00	0	0
6	0.205	51.25	1.25	0.1562
7	0.198	49.50	0.50	0.250
8	0.207	51.75	1.75	3.062
9	0.197	49.25	0.75	0.5625
10	0.202	50.50	0.50	0.250

$X = 50.00$

$\Sigma (X_n - \overline{X})^2 = 9.4672$

$$\sigma = \sqrt{\frac{\sum (X_n - \overline{X})^2}{n-1}}$$

$\sigma = 1.025$
Coefficient of variation (C.V) = 2.02 %

2.6 RETENTION CAPACITY OF IIP PARTICLES

The retention/binding capacities of CP and IIP particles were determined by saturating 0.05g of polymer material with 1mg of palladium(II) under optimal conditions described above. The palladium(II) uptaken after saturation was determined spectrophotometrically after eluting with 2 x 10 ml of 6 M HCl. The retention/binding capacities of CP and IIP particles were found to be 20 and 21.5 mg of palladium per g of polymer particles respectively.

2.7 INFLUENCE OF POROGEN AND γ - IRRADIATION

A study was undertaken by using THF instead of cyclohexanol as porogen on the percentage extraction of palladium using IIP particles (*Fig.2.9*). As the hydrogen bonding capacity is lower in THF compared to cyclohexanol we have observed a little increase in percent extraction of palladium(II) using IIP particles which is expected in view of the observation by Sellergren and Shea [6].

Uezu *et al* [7] reported that on post γ -irradiation of IIP particles obtained by surface imprinting resulted in better separation of zinc from copper. Biju *et al* [8] have also reported similar enhancement in separation of dysprosium from co - existing lanthanides on post γ- irradiation of dysprosium IIP particles. It will be interesting to study the effect of γ-irradiation on palladium(II) ion imprinted polymer particles obtained by covalent polymer imprinting. The unleached IIP particles containing 17 mg of Pd per gram of polymer was taken in a test-tube, flushed with N_2 and subjected to γ-irradiation from Co^{60}source to a total dose of 0.5Mrad.The percent extraction of palladium (II) from dilute aqueous solutions is enhanced from 67.0% to >99.0%. (*Fig2.9*).Thus quantitative enrichment of palladium was noticed even with half the amount of palladium loading ie, 17 mg of palladium(II) per gram of unleached IIP particles.

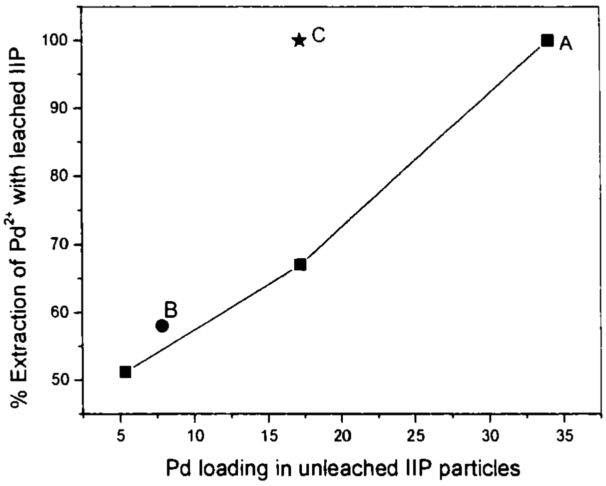


Fig2.9: curve (A) Effect of palladium loading in unleached IIP particles (mg of pd^{2+}/g) on percent extraction of Pd^{2+} with leached IIP particles. Porogen = cyclohexanol, (B) Porogen = THF (C) On γ- irradiation of leached IIP particles.

2.8 SELECTIVITY STUDIES

The percent extraction, distribution ratio and selectivity coefficients of palladium(II) over the other selected inorganics that coexists with palladium in its mineral deposits for CP and IIP particles were summarized in *Table 2.4*. From

Table, the following observations can be made.

1. The CP material shows minimal selectivity for palladium over platinum.
2. On imprinting, the selectivity coefficient ($S_{Pd}^{2+}/_{Pt}^{4+}$) increases from 3.03 to 521 which indicates reasonable preconcentrative separation of palladium from platinum when present together.
3. The IIP material showed good selectivity for palladium compared to base metals such as copper, zinc and nickel which coexist with palladium in noble metal mineral deposits.
4. On imprinting, the % E and D values increases for palladium(II) alone while retaining these parameters at the same level for base metals resulting in quantitative separation of palladium(II) from copper, zinc and nickel.

Table 2.4*: Percent extraction, distribution ratios and selectivity coefficients ((**$S_{Pd}^{2+}/_{M}^{n+}$) of leached CP and IIP particles***

Element	CP			IIP		
	%E	D	$S_{Pd}^{2+}/_{M}^{n+}$	%E	D	$S_{Pd}^{2+}/_{M}^{n+}$
Pd	47.5	0.91	-	>99	99	
Pt	23.33	0.30	3.03	16.05	0.19	521
Cu	1.76	0.018	50.56	1.78	0.018	5500
Zn	1.10	0.011	82.72	1.01	0.010	9900
Ni	1.72	0.018	50.56	1.72	0.018	5500

2.9 EXPERIMENTAL

2.9.1 Reagents

A stock solution (1 mg ml^{-1}) of palladium(II) was prepared by dissolving 0.1666g of palladium chloride (Loba chemie, India) in 6 M HCl and diluted to

100 ml with deionized water. Rhodamine 6G (0.005% Aldrich,USA) was prepared by dissolving 0.0125g of reagent in 250 ml of deionized water. Potassium iodide (5%, E Merck,India) was prepared by dissolving 5g in 100ml of deionized water. A citrate buffer 0.4 M (pH 4) was prepared by dissolving 8.4g of citric acid and 11.8g of trisodium citrate in deionized water. Dimethyl glyoxime, 4- vinyl pyridine, styrene, divinyl benzene (95 %), 2,2'- azobisisobutryonitrile were obtained from Aldrich (Milwauke, USA). All other chemicals were of Anal R grade.

2.9.2 Apparatus

A HITACHI-220 Microprocessor controlled double beam spectrophotometer (Hitachi, Japan) was used during enrichment and separation studies. A Perkin Elmer A Analyst 100 atomic absorption spectrometer (Perkin Elmer,USA) was used for measuring distribution ratios of copper, zinc and nickel. A LI -120 pH meter (ELICO, India) was used for pH measurements. IR spectra (4000-400 cm^{-1}) were recorded by KBr pellet method using MAGNA IR -560 spectrometer (Nicolet, USA). The X- ray diffraction (XRD) patterns were obtained using Cu K_α X-ray source and Philips PW 1710 diffractometer (Holland). The surface area analysis was carried out by using GEMINI-2735 (Micromeritics, USA)

2.9.3 General procedure for preconcentration / separation of palladium

A portion of solution containing 2.5-100 μg of palladium was diluted to 1litre and the final acidity was adjusted to 0.25 M with HCl and transferred to 2 litre beaker. 0.05g of IIP particles were added to above solution and stirred for 20 minutes. The palladium(II) ion preconcentrated on IIP particles was eluted for 15 minutes with 2 x 10 ml of 6M HCl . Suitable aliquots of eluent were taken, pH was adjusted to 4.0 after addition of 0.4 M citrate buffer and palladium content was established by following iodide- Rhodamine 6G procedures [13] reported elsewhere.

Constants

The percent preconcentration of palladium and other selected inorganic ions is given by

$$\text{Percent preconcentration (\%E)} = \frac{(C_A - C_B)}{C_A} \times 100$$

where C_A and C_B are the concentrations of palladium(II) before and after extraction.

The distribution ratio (D) was given by

$$D = \frac{(C_A - C_B)}{C_A} \times \frac{v}{m}$$

Where v is the volume of the solution and m is the mass of the polymer

Selectivity coefficient is defined as

$$S_{Pd^{2+}/M^{n+}} = \frac{D_{Pd^{2+}}}{D_{M^{n+}}}$$

2.10 CONCLUSIONS

Quantitative enrichment of palladium from dilute aqueous solutions was achieved with palladium(II) IIP particles prepared by using Palladium - dimethyl glyoxime - 4-vinyl pyridine ternary complex as template and by thermally copolymerizing with styrene and divinyl benzene in presence of 2,2'-azobisisobutyronitrile as initiator. Only palladium(II) IIP particles showed much higher selectivity towards palladium over platinum and quantitative separation from other base metals which normally coexist with palladium in noble metal deposits. It was also demonstrated that the γ-irradiated palladium IIP particles can enrich with half the amount of palladium per g of unleached polymer compared to unirradiated particles.

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CHAPTER 3

SYNTHESIS OF PALLADIUM(II) ION IMPRINTED POLYMER PARTICLES WITH DIFFERENT QUINOLINE DERIVATIVES AND EVALUATION OF BINDING PARAMETERS

3.1 INTRODUCTION

Palladium(II) IIP particles has been synthesized as described in chapter 2, wherein Pd – dimethylglyoxime -VP complex is polymerized in the presence of styrene and divinyl benzene using AIBN as initiator, which enabled better separation factors compared to platinum, copper, zinc and nickel [1]. 8-Aminoquinoline is a selective spectrophotometric reagent for palladium wherein it forms yellow insoluble complex in weakly acidic solutions [2]. A number of transition and p-block elements were found not to interfere in the above determination. However, other noble metals particularly platinum and gold interfere when they exceed certain concentrations. In our quest to improve the separation factors of palladium with respect to other noble and transition elements, it is felt worthwhile to investigate various selective chelates of palladium viz. 8-amino or 8-hydroxy or 8-mercaptoquinoline instead of DMG of the ternary complex and subsequent imprinting with a more efficient functional monomer such as HEMA and crosslinking monomer viz. EGDMA.

The main aim of the present chapter is to compare the percent enrichment of palladium(II) and separation of palladium(II) from selected inorganics using different quinoline derivatives viz 8-aminoquinoline (AQ), 8-hydroxyquinoline (HQ) and 8-mercaptoquinoline (MQ) as one of the ligands during the synthesis of IIPs employing ternary mixed ligand complex with palladium(II) in presence of 4-vinyl pyridine. The polymerization was carried out by solubilizing ternary complexes in 2-methoxy ethanol (porogen) and using HEMA and EGDMA as functional and crosslinking monomers in the presence of AIBN as initiator. Also, the rebinding studies were carried out and different mathematical models viz Langmuir, Freundlich and Langmuir - Freundlich were used (i) for the evaluation of binding parameters and (ii) for elucidation of the nature and type of bonding exist in IIPs. Thus, this chapter highlights the synthesis, characterization, analytical applications (preconcentration and selective separation) and rebinding studies of palladium(II) IIP particles using derivatives of quinoline as one of the ligand.

3.2 SYNTHESIS OF ION IMPRINTED POLYMERS

3.2.1 Preparation of ternary complexes

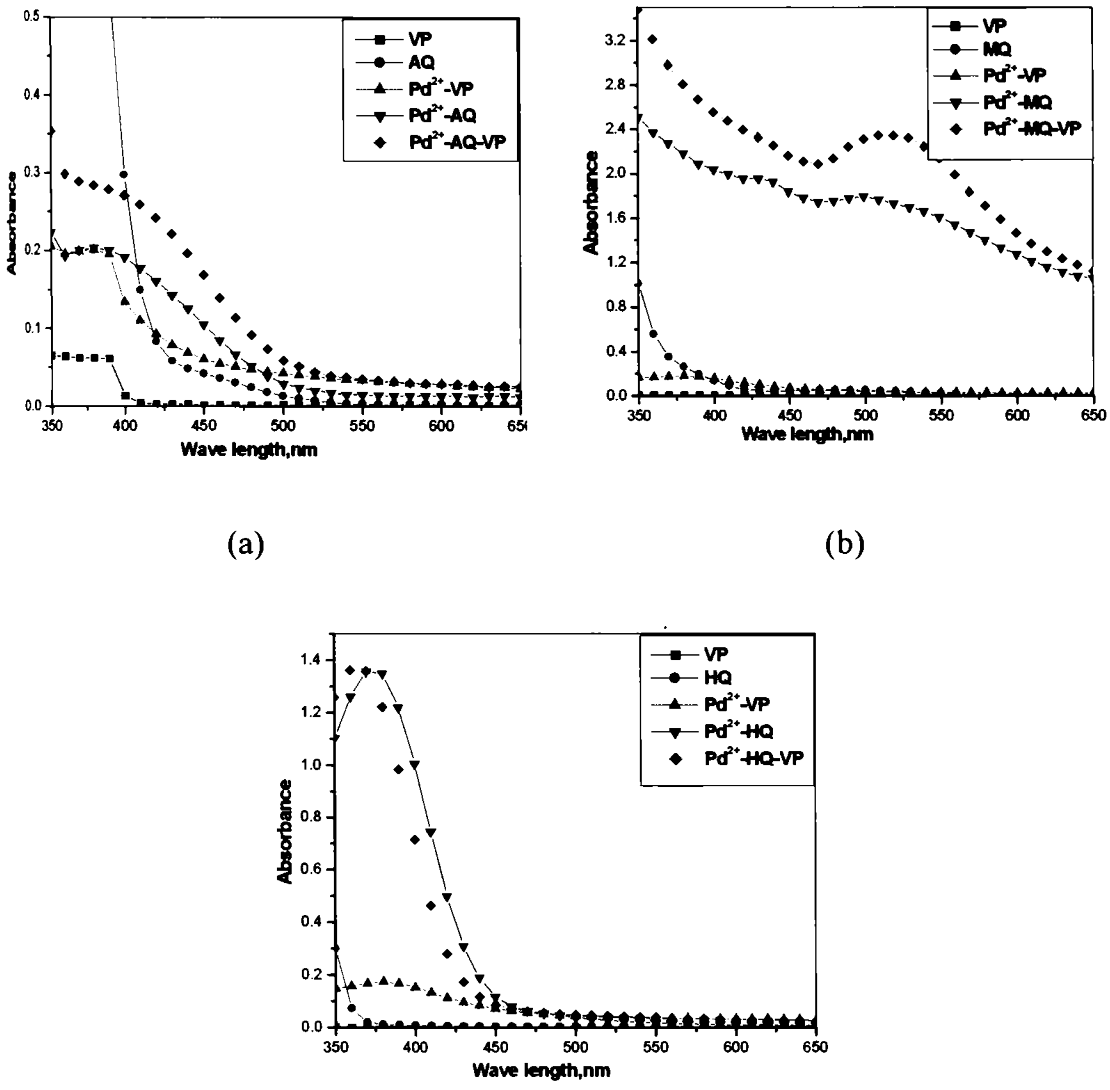
There are three main steps in the synthesis of tailored palladium(II) IIP particles: (i) formation of ternary complex of imprint ion (palladium) with AQ or Q or MQ and 4- vinyl pyridine and (ii) polymerization of ternary mixed ligand complex with HEMA and EGDMA. The formation of ternary complex was carried out by mixing binary palladium(II)-AQ or palladium(II)-Q or palladium(II)-MQ precipitates with 4-vinyl pyridine in 2-methoxyethanol (porogen). Evidence for formation of binary and ternary complexes with palladium was monitored by recording UV-visible absorption spectra. *Figs.3.1(a),(b)& (c)* show the absorption spectra of AQ or MQ or HQ, VP, Pd(II) - AQ or Pd(II) - MQ or HQ, Pd(II) -VP and Pd(II) –AQ -VP or Pd(II) - MQ -VP or Pd(II) – HQ -VP. These spectra clearly show the formation of binary and ternary complexes in 2-methoxyethanol solution.

3.2.2 Stoichiometry of the ternary complex

The stoichiometry of the ternary complex in polymerization mixture was established by using continuous variation method. This method is based on the principle that the analytical signal due to the complex ML_n, formed by the interaction of metal ion M with a ligand L according to the equilibrium

$$M + nL \rightleftharpoons ML_n$$

will attain a maximum at { [M] / ([M] + [L])} = 1/n+1, provided the variation of metal and ligand concentration is done by keeping their combined concentrations, i.e. [M] + [L], a constant. The ratio of Pd (II) to AQ and Pd(II) to VP were established by converting the ternary complex into a pseudo-binary complex by keeping the concentrations of VP or AQ in large excess over palladium (II) respectively. The results obtained are shown in *Fig.3.2*, from which it is clear that a maximum occurs at the mole fractions of [Pd] / {[Pd] + [AQ]} and [Pd] / {[Pd] + [VP]} at 0.36, 0.37 respectively.



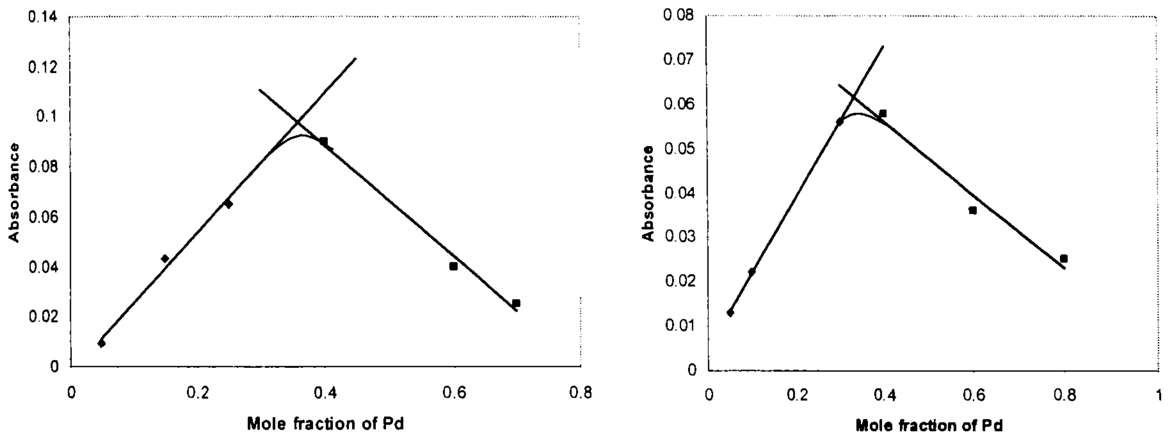
(a)

(b)

(c)

Fig.3.1: The UV-Visible absorption spectra of quinoline derivatives (a) AQ (b) MQ and (c) (HQ) systems

Hence the stoichiometry of the ternary complex in the polymerizing mixture is 1:2:2.



(a) *(b)*

Fig.3.2: Job's plots for (a) 8 - aminoquinoline, (b) 4 - vinylpyridine

3.2.3 Preparation of Ion imprinted polymers (IIPs)

The ternary complexes viz. Pd(II) – AQ -VP or Pd(II) – HQ - VP or Pd(II) - MQ - VP were imprinted on addition of HEMA, functional monomer (91.72 mmol) and EGDMA, crosslinking monomer (6.88mmol) in presence of AIBN. The molar proportion of ternary complex, functional monomer and crosslinking monomer were kept as 1:8:32. The resulting IIP materials were dried in an oven at 60°C. *Fig.3.3* shows the schematic representation of polymer imprinting process. These materials were ground and sieved to obtain palladium(II) IIP particles. The solids thus formed after polymerization were dried in an oven at 80°C for 2 hrs and sieved. The particles with sizes between 45 - 212 μm were collected.

3.2.4 Pretreatment of IIPs to leach the imprint ion

The imprint ion, i.e. palladium(II) was leached from the above polymer particles by stirring with 100 ml of 6 M HCl for 18 h. The resultant polymer particles after filtration were dried in an oven at 80°C to obtain IIP particles for possible preconcentrative separation of palladium(II) from dilute aqueous solutions

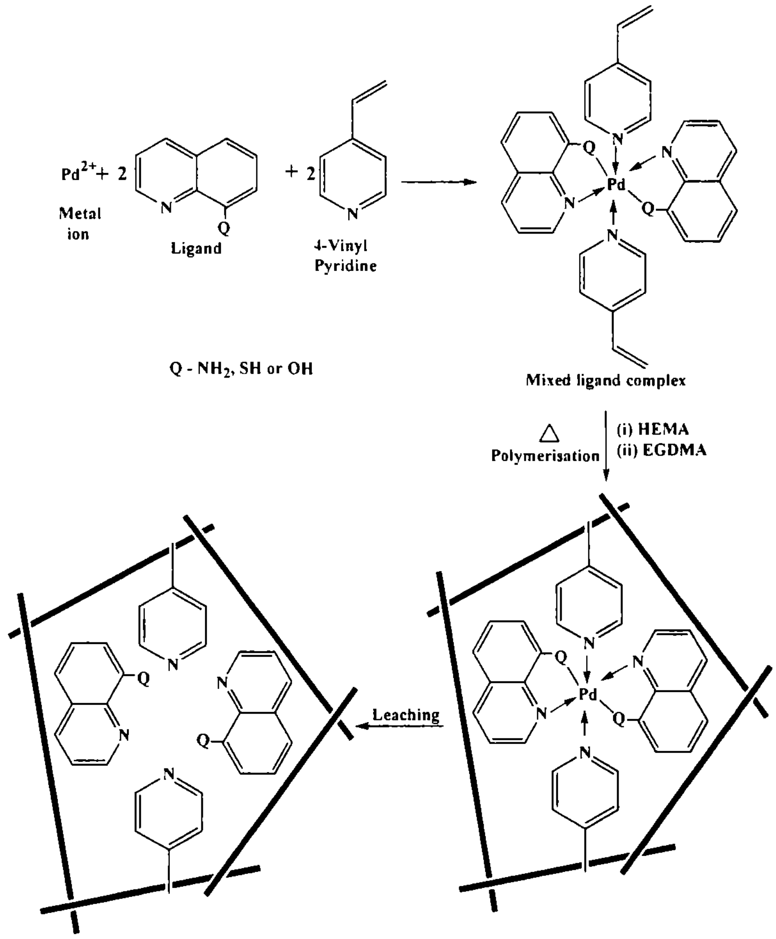


Fig.3.3: Scheme for the preparation of palladium(II) IIP materials

3.2.5 Synthesis of control polymer particles (CPs)

CPs were prepared in a similar fashion as that of IIPs except that imprint ion i.e. palladium was not added to the AQ, HQ or MQ based recipes. The resulting CP materials were subjected to same pretreatment as in the case of IIPs to compare their performance (i) for enrichment of palladium(II) from dilute aqueous solutions and (ii) for separation of palladium (II) from selected inorganics.

3.3 PERCENT ENRICHMENT AND RETENTION CAPACITIES

The comparative account of percentage enrichment and retention capacities of palladium(II) using CPs and IIPs prepared based on AQ, HQ, MQ ligands are given in *Table.3.1.* As seen from the table, AQ based IIP particles alone gave quantitative enrichment of palladium (II) from dilute aqueous solutions. On the other hand the retention capacities are in the same order for all polymer particles.

Table 3.1: Percent enrichment and retention capacities of IIPs

Polymer	Percent Enrichment		Retention capacity ($\mu g\ g^{-1}$ of polymer)	
	CP	IIP	CP	IIP
AQ	47.5 ± 1.2	> 99.0	26.1 ± 0.47	28.82 ± 0.52
HQ	49.0 ± 1.2	66.2 ± 1.7	26.9 ± 0.43	27.51 ± 0.55
MQ	40.4 ± 1.0	68.1 ± 1.4	25.4 ± 0.50	27.70 ± 0.55

3.4 CHARACTERIZATION STUDIES

Since the percent extraction and selectivity coefficients of AQ based IIPs were superior over other two IIPs, the characterization studies were limited to AQ based IIP only.

3.4.1 FTIR spectra

The IR spectra of control polymer (CP), unleached and leached IIPs were found to be almost similar which indicates that all the polymer particles have similar backbone.

The N-H stretching vibration at 3441 cm^{-1} in the unleached material was shifted to 3467 cm^{-1} in the leached IIP, indicating that the nitrogen of the $-NH_2$ group is involved in the metal bonding.

Also the C = N stretching vibration of the aromatic ring at 1258 cm^{-1} in the unleached IIP was shifted to 1268 cm^{-1} in the leached one due to the involvement of -N of the quinoline ring in the metal bonding. The vibration band of Pd - N usually occurs at 340cm^{-1}. We didn't notice this band in IR spectra as we have scanning facility in the range 4000-400cm^{-1}only.

The similarity in the standard IR spectra of 8-amino quinoline and that of leached IIP shows that the ligand is tightly intact in the polymer matrix even after leaching.

3.4.2 X-ray diffraction

The XRD patterns of ternary complex, CP, unleached and leached amino quinoline based IIP particles are given in *Fig. 3.4*. The peaks obtained at 2θ values 12.37, 18.92, 21.22, 28.20 and 32.85 in the Pd-AQ-VP ternary complex and unleached IIP particles were absent in the leached IIP particles. This indicates that all the palladium ions were completely removed during leaching and the XRD patterns of leached IIP were found to be exactly similar to that of the control polymer particles.

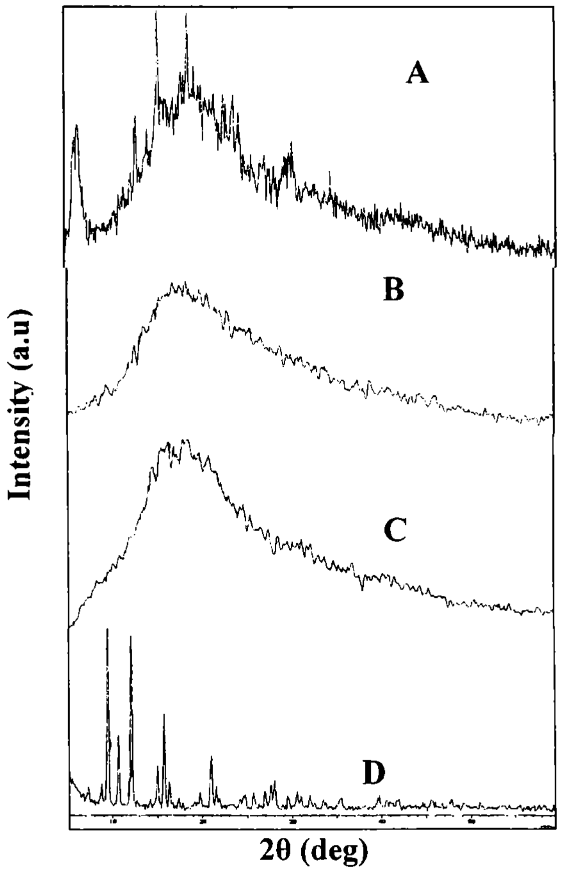


Fig3.4: XRD patterns of CP (Curve B), unleached (CurveA) and leached (Curve C) palladium (II) IIP particles and Pd-AQ-VP ternary complex (Curve D)

3.5 OPTIMIZATION OF EXPERIMENTAL CONDITIONS

Various parameters such as effect of acidity during preconcentration, weight of polymer particles, preconcentration time, elution time, eluent volume and aqueous phase volume were systematically carried out for both IIP and CP.

3.5.1 Effect of acidity during preconcentration

A set of solutions (volume = 500 ml) containing 25 μg of palladium(II) ions were taken and acidity was varied between 0.004 – 1.0 M in HCl. Palladium(II) IIP particles (0.05g) prepared using AQ-VP ternary complex were added to above solution and stirred for 30 min with 2 x 10 ml of 6 M HCl. Suitable aliquots of the eluent were taken, pH was adjusted to 4.0 ± 1.0 after addition of 0.4 M citrate buffer and the palladium (II) content was established by employing Rhodamine 6G procedure [3] reported elsewhere. The results obtained were shown in *Fig.3.5*. From the graph it can be seen that the enrichment of palladium is constant and maximum in the acidity range 0.004- 0.5 M HCl which is expected in view of the maximum stability of Pd-AQ-VP complex [2]. In all subsequent work, the acidity was maintained at ~ 0.5 M by adding 20 ml of Con. HCl. The percentage enrichment of palladium(II) ions by using CP particles is also shown in *Fig. 3.5* for comparison, which indicates the imprinting effect in all instances.As seen from the figure, the percent extraction for IIPs at all acidities are higher than CPs indicating the imprinting effect.

3.5.2 Effect of amount of polymer particles

The influence of weight of polymer particles (IIP and CP) on the percent enrichment of 25μg of palladium(II) present in 500 ml of solution was systematically investigated. The results obtained are shown in *Fig.3.6*, from which it is seen that (i) for quantitative preconcentration, a minimum of 0.025 g of palladium (II) IIP particles are required and (ii) imprinting effect is noticed in all instances once again. Hence, 0.05 g of palladium(II) IIP (AQ) was used for subsequent preconcentration studies.

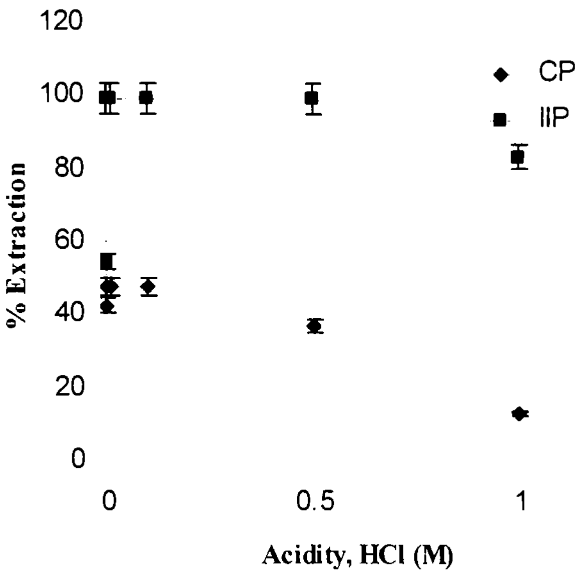


Fig.3.5: Effect of acidity during preconcentration

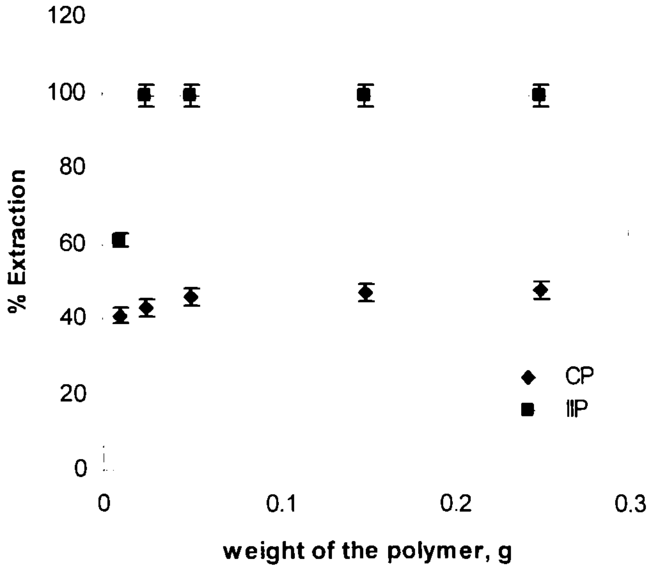


Fig.3.6: Effect of amount of polymer particles

3.5.3 Effect of preconcentration and elution time

The influence of preconcentration time and elution time on the percentage enrichment of palladium(II) using CP and IIP were investigated and the results obtained are compiled in *Table3.2*. As seen from the Table, a minimum of 25 min of stirring is necessary to quantitatively preconcentrate 25μg of palladium(II) present in 500 ml of solution using 0.05 g of palladium (II) IIP particles. Further, it was established that stirring for 30 min with 2 x 10 ml of 6 M HCl is necessary for the quantitative elution of palladium (II) sorbed on palladium(II) IIP particles.

Table3.2: Effect of preconcentration time and elution time on the percentage extraction of palladium(II)

Parameter	% Extraction	
	IIP	CP
Preconcentration time (min)		
10	50.7 ± 1.3	30.5 ± 0.77
20	62.5 ± 1.6	40.0 ± 1.0
25	98.0 ± 1.9	45.5 ± 1.1
30	>99	45.5 ± 1.1
Elution time (min)		
10	64.25 ± 1.6	40.0 ± 0.8
20	95.3 ± 1.9	43.0 ± 1.0
30	>99	45.5 ± 0.9

3.5.4 Effect of volume of eluent and aqueous phase volume

The variation of eluent volume and aqueous phase volume on the percentage extraction of palladium(II) using CP and IIP particles are given in *Table 3.3* From the table it is established that stirring for 30 min with 2 x 10 ml of 6 M HCl is necessary for the quantitative elution of palladium(II) sorbed on IIP particles. Also the variation of aqueous phase volume from 25 to 1000 ml indicates that the preconcentration efficiency was unaffected upto 500 ml.

3.5.5 Reusability studies

The palladium(II) IIP particles were subjected to repeated preconcentration and elution steps to check the reusability. The retention / binding capacities of palladium(II) IIP particles were fairly constant even after 10 cycles. These studies clearly indicate the availability of reversible nature of binding sites for picking palladium(II) ions using palladium(II) IIP particles

Table3.3: Effect of volume of eluent and aqueous phase on the percentage extraction of Pd(II)

Parameter	% Extraction	
	IIP	CP
Eluent volume (ml)		
2 x10	>99	45.5 ± 1.0
2 x 15	>99	45.8 ± 0.9
2 x 20	>99	45.6 ± 0.8
Aqueous phase volume (ml)		
25	>99	45.2 ± 1.0
50	>99	45.8 ± 1.0
100	>99	45.5 ± 1.0
500	>99	45.0 ± 1.0
1000	63.5 ± 1.3	40.0 ± 1.0

3.6 STATISTICAL AND CALIBRATION PARAMETERS

A set of solutions (volume 500ml) containing palladium(II) in the concentration range 2.5 – 100 μg (Fig.3.7) were adjusted to the pH 4.0 ±1.0 after the addition of 0.4 M citrate buffer and the palladium content was established as described in section 3.5.1.

Under the optimum conditions described above, the calibration curve was linear over the concentration range of 0-100 μg of palladium(II) present in 500 ml of solution. Five replicate determinations of 50 μg of palladium(II) in 100 ml of solution gave a mean absorbance of 0.200 with a relative standard deviation of 2.03%. (Table 3.4). The detection limit corresponding to three times the standard deviation of the blank was found to be 2.5 μg l^{-1}. The linear equation with regression is as follows

$$A = (0.00401 \times C) + 0.0009$$

Correlation coefficient = 0.99997

where A is the absorbance and C is the amount of palladium in micrograms per 500ml of sample solution. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

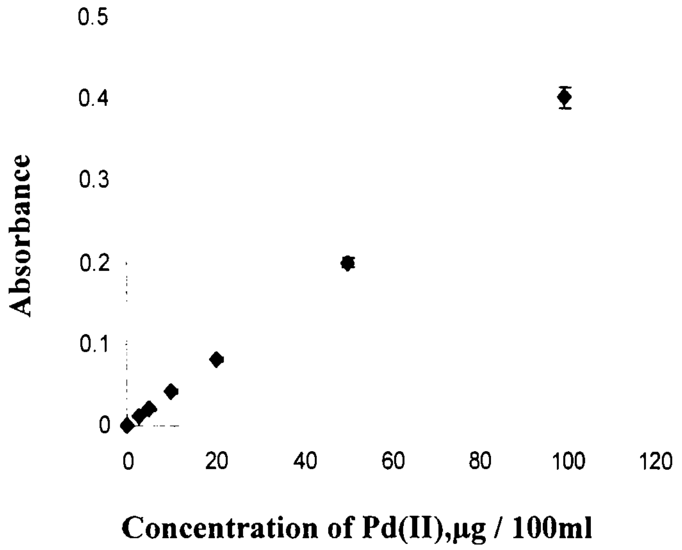


Fig.3.7: Calibration plot

Table3.4: Precision studies

S.No	Absorbance	Pd found (µg) X_n	$X_n - \overline{X}$	$(X_n - \overline{X})^2$
1	0.195	48.75	1.25	1.562
2	0.200	50.00	0	0
3	0.207	51.75	1.75	3.062
4	0.193	48.25	1.75	3.062
5	0.198	49.50	0.50	0.250
6	0.203	50.75	0.75	0.563
7	0.205	51.25	1.25	1.562
8	0.197	49.25	0.75	0.563
9	0.200	50.00	0	0
10	0.202	50.50	0.50	0.250

$X = 50.00$

$\Sigma (X_n - \overline{X})^2 = 9.47$

$$\sigma = \sqrt{\frac{\sum\left(X_n - \overline{X}\right)^2}{n-1}}$$

σ = 1.03
Coefficient of variation (C.V) = 2.03 %

3.7 SELECTIVITY STUDIES

The selectivity coefficients of palladium(II) with respect to platinum, gold, copper, zinc and nickel were determined by using AQ, HQ or MQ based CP and IIP particles and the results obtained are compiled in *Table 3.5*

The following observations can be made from the table

i) CP particles show minimal selectivity for palladium over gold and platinum.

ii) On imprinting, the selectivity coefficients increases with AQ, HQ and MQ based polymers.

iii) The increase in selectivity is in the order: AQ > HQ > MQ

iv) Eventhough the selectivity coefficients of palladium over platinum are 4.40 and 3.03 in case CP particles of AQ-VP and DMG-VP complexes, AQ based IIP particles gives $S_{Pd^{2+}/Pt^{4+}}$ of 5500 compared to 521 with DMG based IIP particles [1].

v) The CP particles based on AQ, HQ or MQ showed good selectivity for palladium(II) compared to base metals such as copper(II), zinc(II) and nickel(II), which usually coexist with palladium in its mineral deposits.

vi) On imprinting, the selectivity coefficients of palladium over base metals improve further by about 100-400 fold.

Table 3.6 shows the percent extraction, distribution ratios and selectivity coefficients of palladium(II) with respect to various base metals, when present in admixtures, in case of AQ, HQ or MQ based IIP particles

Table3.5: Selectivity coefficients of CP and palladium(II) imprinted polymer particles

Metal ion	AQ		HQ		MQ	
	Selectivity coefficient S		S		S	
	CP	IIP	CP	IIP	CP	IIP
Pd(II)	-	-	-	-	-	-
Pt(IV)	4.40	5500	3.02	14.25	1.44	8.19
Au(III)	0.26	670	0.35	34.70	0.485	4.710
Cu(II)	$0.45\text{x}10^4$	$1.0\text{x}10^6$	$0.90\text{x}10^4$	$1\text{x}10^6$	$0.90\text{x}10^4$	$1\text{x}10^6$
Ni(II)	$0.1\text{x}10^4$	$1.0\text{x}10^6$	$0.1\text{x}10^4$	$1\text{x}10^6$	$0.2\text{x}10^4$	$1\text{x}10^6$
Zn(II)	$0.45\text{x}10^{-4}$	$1.0\text{x}10^6$	$0.90\text{x}10^4$	$1.0\text{x}10^6$	$0.30\text{x}10^4$	$1.0\text{x}10^6$

Table 3.6:Percent extraction, distribution ratio and selectivity coefficients of palladium ($S_{Pd^{2+}/M^{n+}}$) from admixtures of copper, zinc and nickel using IIP particles

	Percent extraction			Distribution ratio x 10^4			Selectivity coefficient x 10^6 ($S_{Pd^{2+}/M^{n+}}$)		
	Cu	Zn	Ni	Cu	Zn	Ni	Cu	Zn	Ni
AQ IIP	0.01	0.01	0.01	1.0	1.0	1.0	1	1	1
HQ IIP	0.02	0.01	0.02	2.0	1.0	2.0	0.5	1	0.5
MQ IIP	0.01	0.09	0.01	1.0	9.0	1.0	1	0.9	1

It is clear from Table 3.5 and 3.6 that the selectivity coefficients of palladium(II) over base metals are same, when they present individually or in admixtures.

3.8 REBINDING / ADSORPTION STUDIES

A binding isotherm measures the binding efficiency of a polymer over a range of analyte concentrations. The binding parameters such as total number of binding sites (N_t), median binding affinity constant (K_0), heterogeneity index (m) and binding capacity (N_t x a) etc can be calculated from the binding isotherms by fitting the experimental adsorption isotherm to specific binding models. Experimental binding isotherm were obtained for AQ, HQ and MQ based IIP particles by equilibrating with known concentration of palladium over the range 94 µmoles l^{-1} to 3762 µmoles l^{-1}. The Scatchard plots as well as Langmuir, Freundlich and Langmuir- Freundlich plots were employed to compare AQ, HQ and MQ based palladium IIPs.

3.8.1 Scatchard plots

The conventional form of utilizing scatchard plot to generate the binding parameters requires a plot of B/F vs B. For homogeneous systems that contain only one type of binding sites , the scatchard plot yields a straight line with a slope equal to the negative of the binding affinity (K_0) and the X-intercept equal to the number of binding sites (N_t). For AQ polymer the scatchard plot gives a straight line with N_t and K_0 values of 963.8 and 24.8 respectively. In contrast, the scatchard plots for the HQ and MQ based IIPs were curved as observed for most MIPs. This curvature has been cited as evidence for binding site heterogeneity. Heterogeneity can be incorporated into the scatchard plot analysis by modeling the curved isotherm as two or more straight lines, normally done by using bi, tri or tetra Langmuir models. However, the number of tangents to be drawn and finding the positions for the tangents is a cumbersome task. Moreover, this analysis is based on a series of approximations and the estimates of the binding parameters will be accurate only under certain conditions and thus the results often lead to ambiguous conclusions. From the limiting slope analysis of straight lines, the curved lines yield more than one set of binding parameters corresponding to the high and low affinity sites. Thus complications quickly arise while using this analysis to compare different polymers [4].

3.8.2 Binding isotherm models

Batch rebinding studies represent a key method for characterizing and comparing imprinted polymers. The binding parameters can be estimated from the binding isotherms using various mathematical models. However, in the choice of the proper model, many important features should be taken into account, apart from the numerical complexities involved in the fitting procedure. The important among them are that the model should be thermodynamically sound and have a clear physical meaning, limiting the introduction of supplemental parameters to the bare necessities. Many isotherms have been reported in the literature to calculate the binding properties of MIPs. However the most commonly used models were Langmuir (L), Freundlich (F) and Langmuir - Freundlich (LF).

The LF isotherm can be given as

$$B = \frac{N_t a F^m}{1 + a F^m} \qquad (1)$$

where N_t is the number of binding sites, a is related to the median binding constant K_0 ($K_0 = a^{1/m}$) and m is the heterogeneity index. For a homogeneous material, m is equal to 1, whereas when m is between 0 and 1, the material is heterogeneous. For homogeneous material (m = 1), the LF isotherm reduces to the Langmuir isotherm

$$B = \frac{N_t a F}{1 + a F} \qquad (2)$$

and on the other hand as either F or a approaches 0, the LF isotherm reduce to the Freundlich isotherm

$$B = a\,F^m \qquad (3)$$

In the present study, the isotherm data were fitted to the above three isotherm models, (i.e.) the Langmuir, Freundlich and Langmuir - Freundlich models. The B vs F and log B vs log F plots obtained are shown in *Figures 3.8 and 3.9* respectively. The isotherm model parameters were obtained by a non-linear least square fitting of the experimental data using Marquardt-Levenberg algorithm in Microcal Origin 6.0®

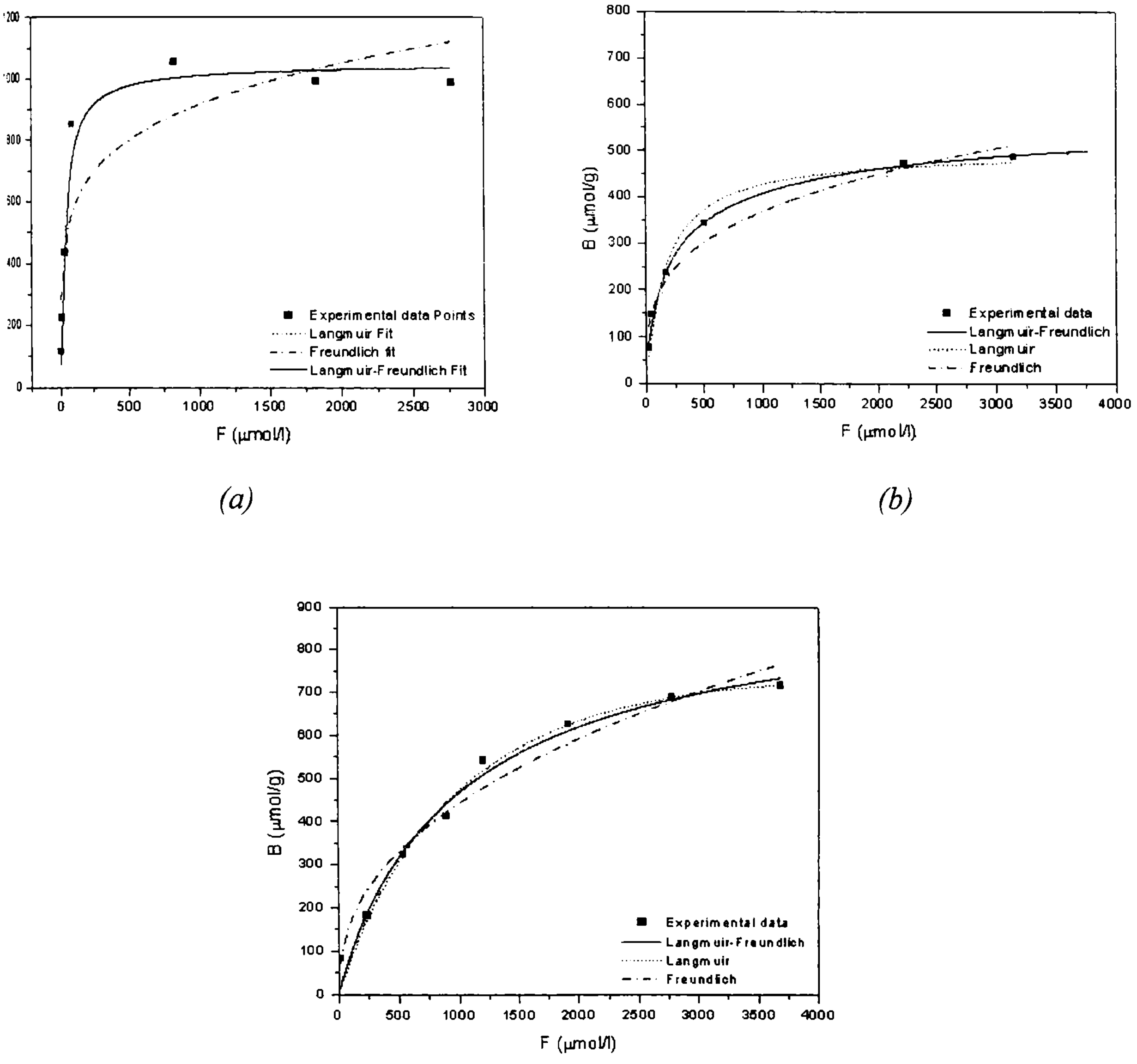
(Microcal Software, Inc., 2000) data analysis package. The following function is minimised in order to obtain the best coefficients for the isotherm parameters

$$F^2 = \frac{\sum_{i=1}^{N}\left(X_i^{\exp} - X_i^{th}\right)^2}{X_i^{th}} \qquad (4)$$

where, N is the number of data points, X_i^{exp} and X_i^{th} are the experimental data points and the points corresponding to the model. To avoid being trapped in local minima, which give incorrect results, the fitting was carried out several times using different initial guess values for the isotherm parameters. The coefficient of determination (R^2) values for the adsorption isotherms was also found out. The isotherm that correlates better with the experimental data is the one that exhibits the R^2 value closer to 1. The fitting coefficients or binding parameters obtained by fitting L, F and LF curves to the experimental adsorption isotherms of palladium(II) IIP particles are shown in *Table 3.7.*

Comparing the suitability of isotherms in fitting the adsorption data, the LF isotherm seems to provide better fits for the three IIPs [5-7]. It does explain the degree of heterogeneity of the IIP in an explicit manner.

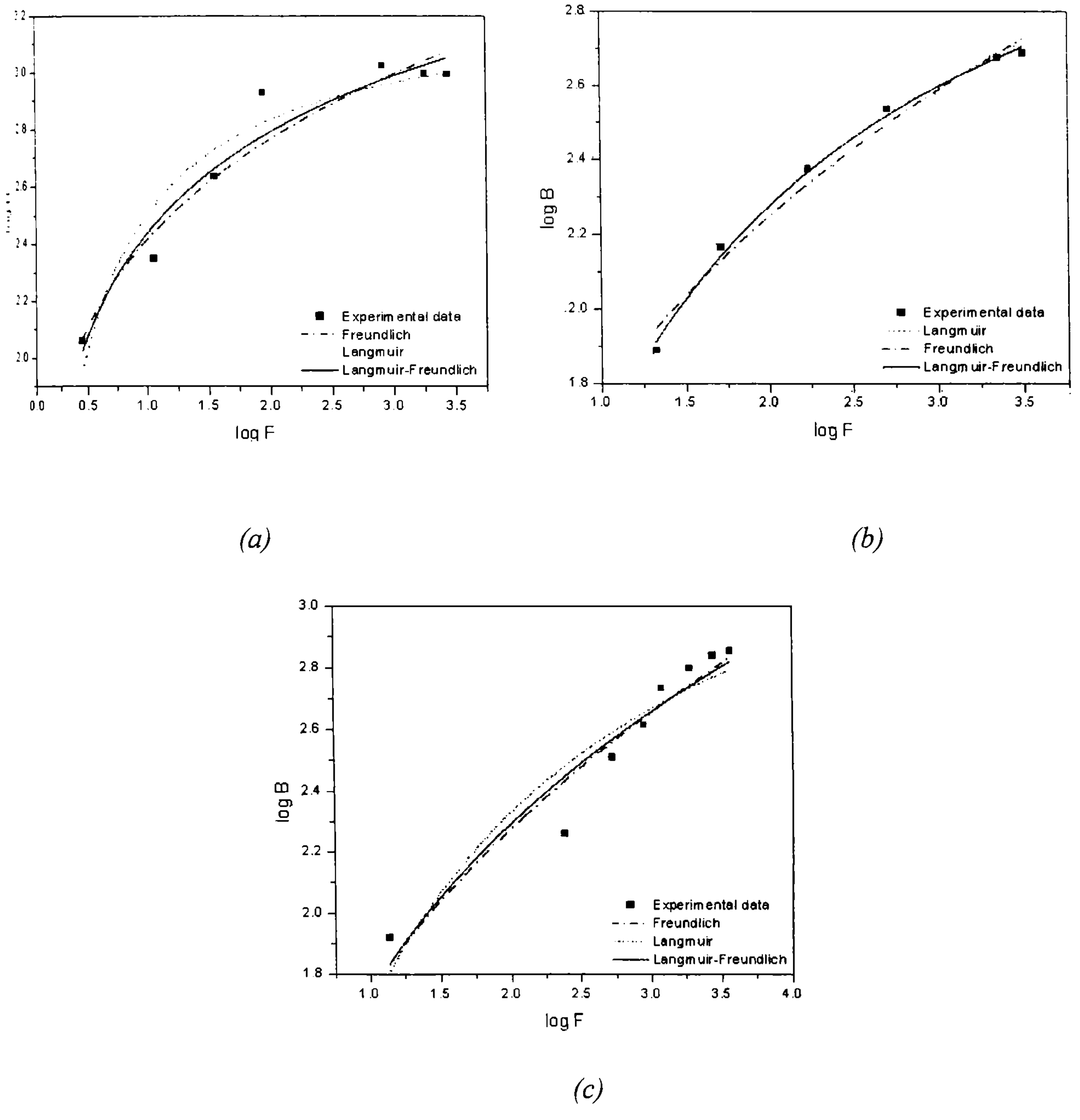
Considering the values of (R^2) calculated for the IIPs, it is quite clear that the AQ based IIP shows good agreement with the homogeneous distribution of binding sites and so it gives high selectivity and percent extraction compared to other two IIPs. Eventhough the MQ based IIP had a higher number of binding sites (N_t) than the AQ based IIP, it is the heterogeneity of the polymer that causes a reduction in selectivity and percent extraction due to the lack of accessibility of the sites. The decrease in selectivity and percent extraction for HQ based IIP can be attributed to the less number of binding sites and lower m value. It should be pointed out that heterogeneity is normally detrimental to the binding properties, temper and limits the capacity and selectivity of IIPs.



(a) *(b)*

(c)

Fig.3.8: B vs F plots for AQ (a), HQ (b) and MQ (c) based polymers. The experimental data (*) were fit to the Langmuir (L) (dotted line), Freundlich (F) (dashed line) and LF (solid line) isotherms.



(a)

(b)

(c)

Fig.3.9: logB vs logF plots for AQ (a), HQ (b) and MQ (c) based polymers. The experimental data (*) were fit to the Langmuir (L) (dotted line), Freundlich (F) (dashed line) and LF (solid line) isotherms.

Table 3.7: Fitting parameters for the F, L and LF fit to the experimental adsorption isotherms of studied IIPs [a]

Fitting parameters	Isotherm models								
	F			L			LF		
	AQ	MQ	HQ	AQ	MQ	HQ	AQ	MQ	HQ
N_t (μmol g^{-1})	-	-	-	1048.14	922.0	500.22	1048.2	1161.29	593.61
a (mmol^{-1})	231.50	23.92	50.36	0.027	0.0028	0.0057	0.0274	0.0032	0.0215
Binding capacity (N_t x a)	-	-	-	28.708	2.6277	2.886	28.720	3.727	12.786
m	0.199	0.422	0.287	-	-	-	0.9998	0.69522	0.66843
K_o (mmol^{-1})	-	-	-	-	-	-	0.02738	2.590×10^{-4}	3.2102×10^{-3}
K limits (mmol^{-1})^b	-	-	-	-	-	-	3.607×10^{-4} to 0.3534	2.5716×10^{-4} to 0.0733	3.1717×10^{-3} to 0.0472
R^2	0.80537	0.93676	0.96790	0.97123	0.88799	0.98060	0.97123	0.93667	0.99888

[a] *The fitting coefficients are mean values calculated from three independent experimental binding isotherms. The relative standard deviation obtained for each coefficient was lower than 10%*

[b] *Calculated from experimental maximum and minimum free analyte concentration (F_{max} and F_{min}) by the relationships*

$K_{min} = 1/F_{max}$ *and* $K_{max} = 1/F_{min}$

Also from the *Table 3.7*, it is clear that the variable 'a' that is relating to the median binding affinity is higher for the AQ based IIP compared to the other two IIPs, which is in agreement with the stability of the complexes of palladium(II) ion with different donor atoms of the ligands.

The accuracy of the calculated fitting parameters must be evaluated regarding the concentration range studied, i.e. the binding curves have to be measured over a wide concentration range (covering both saturation and subsaturation regions) which is assessed whether K_0 falls between the limits $1/F_{max}$ and $1/F_{min}$, as reported elsewhere [8]. From the table, it is clear that the K_0 falls within the required limits.

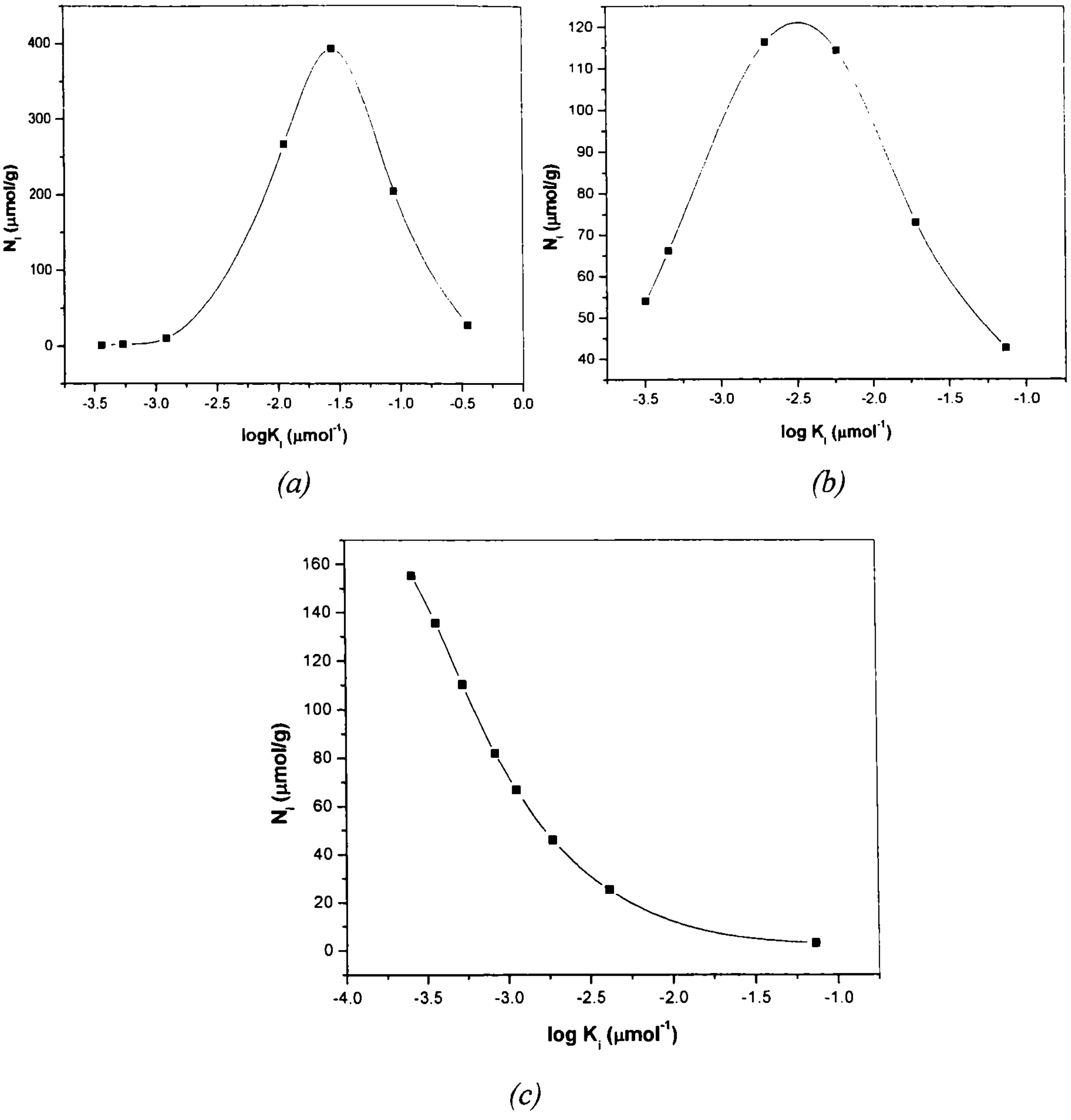
3.8.3 Affinity distribution studies

An affinity distribution is a plot of the number of binding sites (N_i) against the association constant (K_i). The affinity distribution is commonly presented in two formats viz. N versus log K and log N versus log K. The first one is also known as the site energy distribution as log K is proportional to the binding energy. In this case, the area under the distribution is the number of sites. To address the heterogeneity in IIPs and for the accurate comparison of the binding properties, we have calculated the affinity distribution of the AQ, HQ and MQ based IIPs. In the present study LF isotherm seems to be the most applicable isotherm among the three isotherm models as seen from above comparisons as it can model both the saturation and sub saturation behaviour. Hence, we have limited to generation of the affinity distribution curves corresponding to LF isotherm alone (see *Fig.3.10*).

The affinity distribution expression for the LF isotherm as derived by Umpleby II et al [5] is used for plotting the affinity distribution curve. The expression is given by

$$N_i = \left[N_t am(1/Ki)^m\right]\left\{\frac{\left[\left(1+2a(1/K_i)^m + a^2(1/K_i)^{2m} + 4a(1/K_i)^m m^2 - a^2(1/Ki)^{2m} m^2 - m^2\right)\right]}{\left[1+a(1/K_i)^m\right]^4}\right\} \quad (5)$$

Two distinct ADs were measured for most of the MIPs. One is the unimodal peak and the other is the exponentially tailing distribution [9]. These distinct regions of the AD of MIPs were arising from measuring different portions of the experimental binding isotherm. The experimentally tailing portion corresponds to the lower concentration portion of the binding isotherm and the unimodal distribution corresponds to the saturation region. For most of the MIPs it is very difficult to reach the saturation region due to the generation of heterogeneity in the matrix. The less common region of the AD is the unimodal peak with a maximum at K_0. From the affinity distribution curves for AQ and HQ (*Fig 3.10 (a) and (b)*) it can be seen that the peak of the distribution is centered at $K_0 = a^{1/m}$. Also the shape of the distribution gets broadened as the heterogeneity index reduces to lower values from 1. In this case the AQ based polymers showed a homogeneous distribution and so it can find extensive applications in the chromatographic analysis. In the case of MQ *Fig.3.10 (c)* based polymer the tailing portion corresponds to the lower concentration and in this case it is very difficult to reach the saturation due to the heterogeneity. Generally, the stability of the metal complexes (PK_{HB}) having N, O and S as donor atoms decreases in the order $N < 0 < S$. But elements which have a particular tendency to form donor π bonds (Hg, Pt, Pd, Ag etc) show the reverse order $N > O > S$ for the change in stability [10]. The results obtained in the present investigation is in tune with this observation as the AQ based polymer showed higher selectivity and percent extraction compared to HQ and MQ based IIPs.



(a) *(b)*

(c)

Fig.3.10: Affinity distribution curves for AQ (a), HQ (b) and MQ (c) based polymers

3.9 EXPERIMENTAL

3.9.1 Reagents

A stock solution of 1 mg ml^{-1} of palladium(II) was prepared by dissolving 0.1666 g of palladium chloride (Loba Chemie, India, 99.9%) in 10 ml of 50% (v/v) HCl and diluted to 100 ml with deionized water. Rhodamine 6G (0.005% (w/v)) (Aldrich, USA) was prepared by dissolving 0.0125 g of reagent in 250 ml of deionized water. A citrate buffer, 0.4 M (pH 4) was prepared by adjusting to 4.0 ± 1.0 after dissolving 8.4 g of citric acid (E-Merck, India) and 11.8 g of trisodium citrate (E-Merck, India) in 100 ml of deionized water and thus adjusting the pH to 4.0 ± 1.0. Potassium iodide (E-Merck, India) (5%, w/v) was prepared by dissolving 5 g of KI in 100 ml of deionized water. 8-aminoquinoline (AQ), 8-hydroxyquinoline (HQ), 8-mercaptoquinoline (MQ), 4-vinylpyridine (VP), 2-hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) and 2,2′-azobisisobutyronitrile (AIBN) were obtained from Aldrich (Milwauke, USA). All other chemicals used were of analytical reagent grade.

3.9.2 Apparatus

A Shimadzu-UV-2401 PC controlled double beam spectrophotometer (Shimadzu, Japan) was used for preconcentration and separation studies. A Perkin-Elmer A Analyst 100 atomic absorption spectrometer (Perkin Elmer, USA) was used for measuring distribution ratios of copper, zinc and nickel during selectivity studies. A LI-120 digital pH meter (ELICO, India) was used for pH measurements. IR spectra were recorded in the range 4000-400 cm^{-1} using MAGNA FTIR-560 spectrometer (Nicolet, USA). The X-ray diffraction (XRD) patterns were obtained using Cu K_α X-ray source and Philips PW1710 diffractometer (Holland).

3.9.3 General procedure for the preconcentration / separation of palladium

A portion of solution containing 2.5-100 μg of palladium was taken in one litre beaker and diluted to 500 ml and the acidity of this solution was maintained at ~0.5 M after addition of 20 ml of Conc. HCl. Palladium(II) IIP particles (0.05 g) prepared using AQ-VP ternary complex were added to above solution and stirred for 30 min. The palladium(II) ions preconcentrated onto above IIP particles were eluted for 30 min with 2x10 ml of 6 M HCl. Suitable aliquots of the eluent were taken, pH was adjusted to 4.0±1.0 after addition of 0.4 M citrate buffer and the palladium(II) content was established by employing iodide-Rhodamine 6G procedure [3] reported elsewhere.

3.9.4 General procedure for rebinding studies

About 200 mg of the leached IIP particles were equilibriated with 94 μmoles/l - 3762 μmoles/l of palladium(II) as described in preconcentration procedure. The free concentration of palladium(II) was calculated using the equation

$$F = (A_f . T) / A_t$$

where T is the total concentration of palladium(II) ions. A_f and A_t are the blank corrected absorbance values of palladium(II) ion before and after the addition of palladium(II) IIP particles. The amount of analyte bound to the polymer particles was calculated using the equation

$$B = T - F$$

3.10 CONCLUSIONS

Palladium(II) IIP particles were synthesized using the ternary complex of palladium(II) with AQ, HQ or MQ as one of the ligand and 4-vinyl pyridine as the other ligand. Eventhough, imprinting effect was noticed with AQ, HQ and MQ based palladium(II) IIP particles, the AQ based IIP particles showed better preconcentration efficiency and higher selectivity coefficients compared to selected noble and base metals. Furthermore, the rebinding experiments enabled the (i) evaluation of binding parameters and (ii) elucidation of nature and type of bonding present in IIPs. These results show that LF isotherm model fits well with experimental adsorption isotherm compared to L or F model. This model also explains the difference in percent extraction and selectivity coefficients on the basis of number of binding sites, heterogeneity index etc.

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CHAPTER 4

INVESTIGATION OF DIFFERENT POLYMERIZATION METHODS ON THE ANALYTICAL PERFORMANCE OF PALLADIUM(II) ION IMPRINTED POLYMER MATERIALS

4.1 INTRODUCTION

The synthesis of ion imprinted polymers developed so far was mainly based on bulk polymerization technique. This preparation was beset with problems such as tedious grinding, sieving and partial destruction of imprinted structures and also due to the possible presence of residual guest molecule [1-4]. Mayes *et al* [5] have discussed relative merits and demerits of bulk, suspension in water or fluorocarbon, precipitation, two-stage swelling, surface rearrangement of latex and aerosol polymerization approaches during the preparation of MIPs with several imprinting molecules. Recently, Perez-Moral and Mayes [6] have undertaken comparative study during rebinding of propranolol imprinted polymer particles prepared by different polymerization methods using photochemical means and found to lie in the order two step swelling $\cong$ suspension $\cong$ bulk > core shell > precipitation approaches from aqueous solutions.

Ion imprinted polymers made by different methods have so far not been directly compared and tested under the identical conditions to assess their potential rebinding characteristics and also the effect of the production method on the analytical performance of the final ion imprinted material. In this study, we have selected bulk, precipitation and suspension polymerizations prepared via thermal means to compare the percent enrichment, retention capacity, distribution ratio, binding capacity and selectivity coefficients of metal ion-imprinted polymer particles prepared with same prepolymer complex. As discussed in chapter 3, AQ based polymers alone gave quantitative enrichment of palladium(II) from dilute aqueous solutions. So we have selected Pd – AQ -VP mixed metal – ligand complex for the comparison of percent enrichment of palladium(II) using different polymerization techniques. In this chapter, a comparison of palladium(II) ion imprinted polymer materials prepared using different polymerization methods mentioned above has been used for preconcentration and separation of palladium(II) from associated platinum group metals and selected transition elements.

4.2 SYNTHESIS OF ION IMPRINTED POLYMERS

The synthesis of IIP materials was carried out in two steps: (i) Ternary complex formation and (ii) Copolymerisation of ternary complex with 2-hydroxy ethyl methacrylate (functional monomer) and ethylene glycol dimethacrylate (crosslinking monomer).

4.2.1 Preparation of the ternary complex

The ternary complex of palladium(II) ion with 8-amino quinoline and 4-vinyl pyridine was prepared by stirring a mixture of 1 mmol of palladium(II) chloride (0.177 g), 2 mmol of 8-amino quinoline (AQ) (0.288 g) and 2 mmol of 4-vinyl pyridine (VP) (0.215 ml) in 10 ml of 2-methoxy ethanol for 2 hrs. The formation of ternary complex was conformed by UV-Vis spectral studies. *Fig.4.1* shows the absorption spectra of 2-methoxy ethanol solutions of palladium(II) + AQ, palladium(II) +VP, palladium(II) + AQ + VP and palladium(II) + AQ + VP + HEMA + EGDMA + AIBN against 2-methoxy ethanol. As seen from the figure the formation of ternary complex (Pd + AQ + VP) is evidenced by a hyperchromic shift at 430 nm. Also the absorption spectrum of the polymerizing solution matches exactly with the spectrum of the ternary complex. This confirms the existence of the ternary complex in the polymerizing solution also.

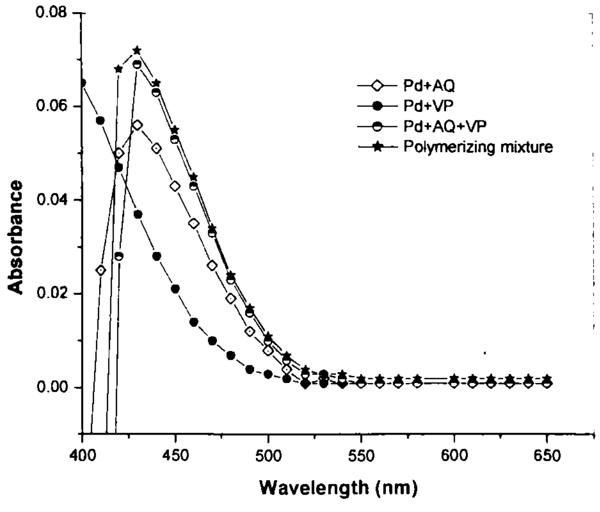


Fig.4.1: UV-visible absorption spectra of (Pd + AQ), (Pd + VP), (Pd + AQ + VP) and polymerizing mixture.

4.2.2 Preparation of IIPs

a) Bulk polymerization

Bulk imprinted polymers were synthesized using a molar ratio of 1:8:32 (template: HEMA: EGDMA). The ternary complex of palladium(II) ion with 8-aminoquinoline and 4-vinyl pyridine was solublized in 10 ml of 2-methoxy ethanol (Porogen) and polymerized with the functional monomer (HEMA) and crosslinking monomer (EGDMA) using AIBN as initiator with constant stirring at 80°C for 2 hrs. The polymers obtained were crushed, ground and sieved to get polymer particles in the size range 45-212 μm.

b) Precipitation polymerization

The synthesis of beads by precipitation polymerization is as follows. The composition used for the preparation was same as that of the bulk polymerization except that the volume of porogen used was 40 ml instead of 10 ml in case of bulk polymerization.

c) Suspension polymerization

The synthesis of microspheres by suspension polymerization is described as below.

Step 1: Polyvinyl alcohol (PVA molecular weight ~ 400, 0.1 g) was dissolved in hot water (about 90°C, 30 ml) and then cooled to room temperature. The solution was purged with N_2, placed in a water bath (60°C) and then stirred at 400 rpm for ½ h.

Step 2: Same compositions to that of the above bulk polymerization viz. porogen, palladium(II) – AQ – VP ternary complex HEMA, EGDMA and AIBN were taken and subjected to N_2 purging. Then the above solution was added dropwise to the above PVA solution with stirring. After 2 h, the polymerizing solution was put in an oil bath at 80°C. After 24 h, the microspheres obtained were collected, washed with hot water and dried.

4.2.3 Removal of the imprint ion from the synthesized polymers

The imprint ion, i.e. palladium(II) was leached from the above synthesized polymeric materials by stirring 2 g of the material with 100ml of 6 M HCl for 18 h. The resultant polymer particles, beads or microspheres obtained after filtration were dried in an oven at 80°C to get IIP particles for possible preconcentrative separation of palladium (II) from dilute aqueous solutions.

4.2.4 Synthesis of control polymers

The synthesis of the corresponding control polymer particles were done under the same conditions as that of the IIPs except the imprint ion (i.e. palladium(II)). The control polymers were also subjected to same pretreatments as that of the IIP particles.

4.3 CHARACTERIZATION STUDIES

4.3.1 FTIR spectra

The IR spectra of control polymer (CP), unleached and leached IIPs synthesized by the three polymerization methods showed similar characteristic peaks, indicating the similarity in the backbone structure of the different polymers. As a result of the metal binding with - NH_2 group of the aminoquinoline, the N-H stretching vibration at 3441cm^{-1} in the unleached IIPs synthesized by three methods were shifted to 3467 cm^{-1} in the corresponding leached IIP materials. The C=N stretching vibration of the aromatic ring at 1258 cm^{-1} in the unleached IIPs were also shifted to ~ 1268 cm^{-1} in the leached IIPs indicating the involvement of nitrogen of the quinoline ring in the metal binding.

4.3.2 X-ray diffraction anaysis

The XRD patterns of the control, unleached and leached IIP particles synthesized by bulk (already given in chapter 3), precipitation (*Fig.4.2*) and suspension (*Fig.4.3*) polymerization showed similar patterns. Also in the corresponding unleached IIPs, the peaks occur at 2θ values of 12.37°, 18.92°, 21.22°, 28.20° and 32.85° (similar to the Pd–AQ–VP complex) confirming the presence of palladium(II) in these materials. After leaching, these peaks get disappeared, thus indicating the complete removal of the metal ions during the leaching process.

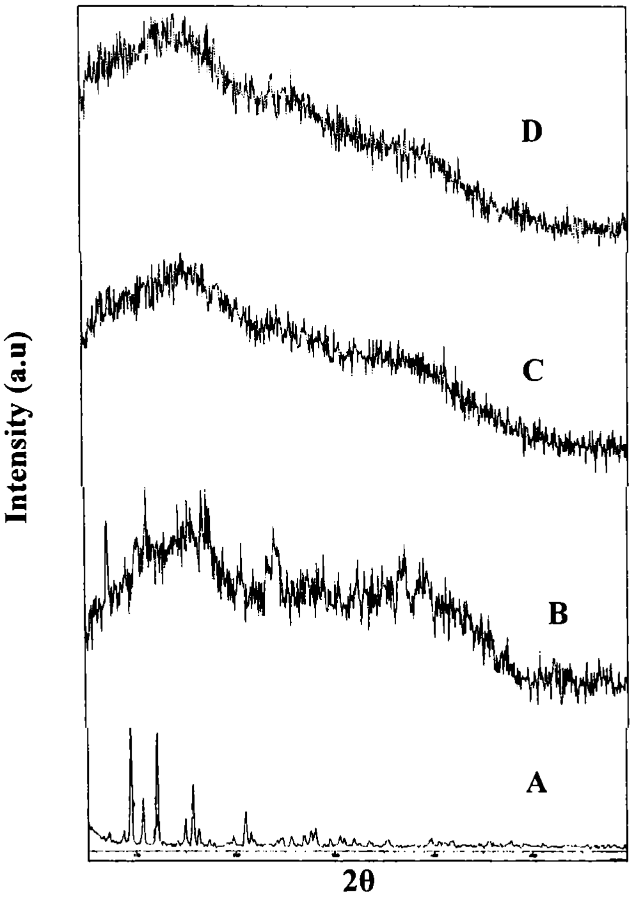


Fig.4.2: XRD patterns of Pd(II) – AQ – VP prepolymer complex (A), unleached (B) and leached (C) palladium(II) IIP and microspheres control polymer (D) obtained by precipitation polymerization.

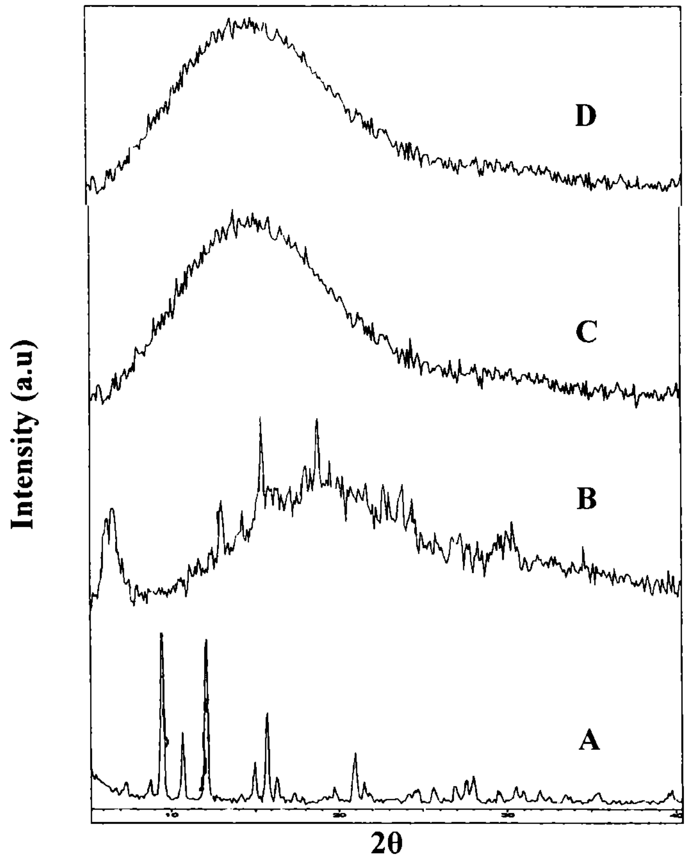


Fig.4.3: XRD patterns of Pd(II) – AQ – VP prepolymer complex (A), unleached (B) and leached (C) palladium(II) IIP beads and control polymer (D) obtained by suspension polymerization.

4.3.3 UV-visible spectral studies

UV-visible spectrophotometric determination of palladium(II) present in leached solutions of IIPs prepared by three different polymerization approaches using iodide-rhodamine 6G procedure confirms the quantitative removal of palladium(II) during leaching of unleached polymer materials with 2 x 50 ml of 6 M HCl for 18 h. These observations confirm the XRD observation that the palladium(II) ions were absent in leached IIP polymer particles, beads or microspheres.

4.3.4 Scanning electron microscopy

The morphology of the polymers produced by bulk, precipitation and suspension polymerization methods were assessed by SEM (micrographs are shown in *Fig.4.4*). In all cases the morphology was as predicted. For bulk polymerization, the morphology of crushed polymer is shown. In other two methods, polymers in the form of beaded particles were produced. As seen from the micrographs, there is a systematic morphological change in the particles shape and size of the polymers synthesized by bulk, precipitation and suspension polymerization methods.

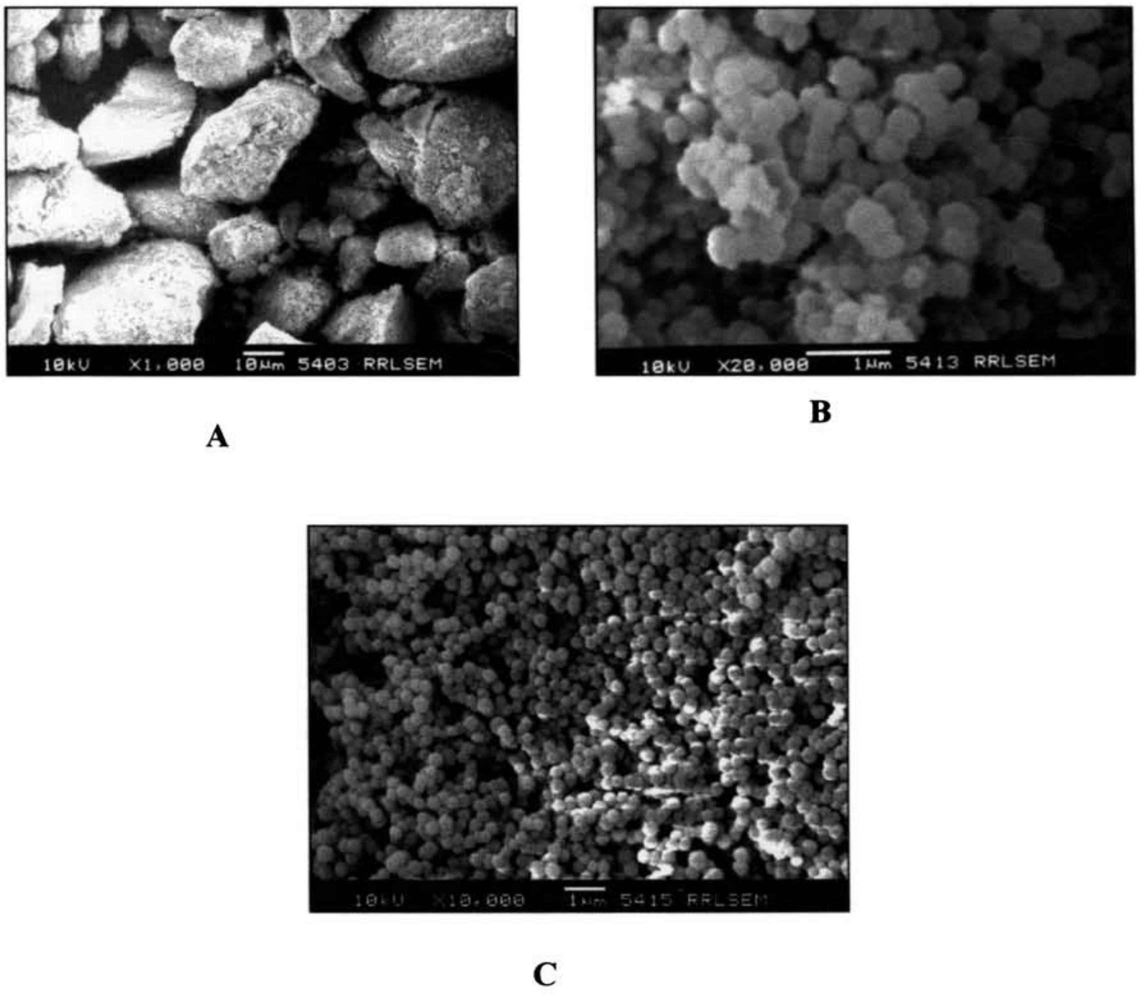


Fig.4.4: SEM photographs of IIPs synthesized via bulk (A), precipitation (B) and suspension (C) polymerization.

Bulk polymerization shows agglomerated polymeric material in irregular shapes in the size range of 1–20 μm. In the case of precipitation method, the polymeric material shapes into regular spherical particles of uniform sizes (300–400 nm). The roundness of the particles is not very perfect. In the suspension method, the material crystallizes into nanosized perfect uniform spherical beads (~200 nm). Also the materials organize into very regular shapes in case of precipitation and suspension polymerization methods only.

4.3.5 Thermogravimetric analysis

The TGA plots of leached IIPs synthesized via bulk (A), precipitation (B) and suspension (C) polymerizations are given in *Fig.4.5.* All the three leached IIPs show similar TGA pattern indicating the analogous thermal stability of these polymers. The initial 10% weight loss in the TGA curves (29–99 °C) is due to the decomposition of the 8-aminoquinoline bound within the polymeric matrix, which is having a melting point of 68 °C. All the three leached IIPs were almost stable up to 290°C. Also after 300 °C, the complete decomposition of the polymeric matrix occurs.

4.3.6 Surface area and pore size analysis

The BET surface area and average pore diameter for leached IIP particles prepared by three different polymerization methods were in the range 130–140 m^2 g^{-1} and 18.15–20.5 Å, respectively. Thus, surface area and pore size analysis studies do not explain the difference in percent enrichment and selectivity parameters of palladium(II) IIP particles obtained by bulk, precipitation and suspension polymerization methods

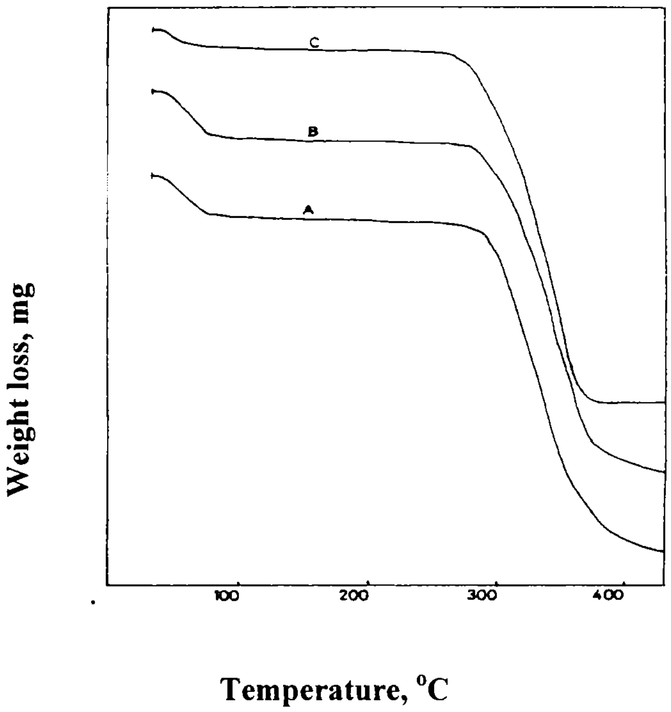


Fig.4.5: TGA plots of leached IIPs synthesized by bulk (A) , precipitation (B) and suspension (C) polymerization.

4.4 ENRICHMENT / PRECONCENTRATION STUDIES

The preconcentration studies of the palladium(II) ion with the various synthesized polymers were investigated and the results obtained on percentage enrichment of palladium(II) with both CP and IIP polymers synthesized by bulk, precipitation and suspension polymerization methods are given in *Table 4.1.* The preconcentration studies were carried out at optimal conditions as described in chapter-3. From the table, it can be clearly seen that the beads obtained by precipitation polymerization gives the highest percent extraction (99.18%) for palladium(II) under identical conditions. Also, it can be seen that the polymer particles synthesized by bulk polymerization were equally good (99.0%) as that of the precipitation beads. However, the percent extraction of palladium(II) with CP and IIP microspheres obtained by suspension polymerization are lowest compared to precipitation and bulk polymerization approaches. The imprinting effect was noticed in all the three cases on comparing the percentage enrichment of all the three IIPs with the corresponding CPs. Thus, the order of specific rebinding of palladium(II) from aqueous solution with different IIPs are precipitation (99.18%) ≅ bulk (99.0%) > suspension (72%).

Table 4.1: Percent enrichment and retention capacities of various polymer materials

Mode of polymerization		% enrichment of palladium(II)	Retention capacity mg of palladium(II) per g of polymer material
Bulk	- CP	47.50 ± 0.86	26.10 ± 0.44
	IIP	99.05 ± 1.9	28.82 ± 0.54
Precipitation	- CP	58.97 ± 1.2	20.17 ± 0.37
	IIP	99.18 ± 1.5	20.16 ± 0.36
Suspension	- CP	29.06 ± 0.52	8.97 ± 0.18
	IIP	72.00 ± 1.3	18.76 ± 0.36

4.5 RETENTION CAPACITY STUDIES

The retention capacities of CP and IIP materials prepared by bulk (particles), precipitation (microspheres) and suspension (beads) polymerization methods were determined by equilibrating 0.05 g of polymer material with 1 mg of palladium(II) at optimal preconcentration conditions. The results obtained are shown in *Table 4.1* from which it is clear that the retention capacities are in the order of bulk > precipitation > suspension. This order of sequence is possibly due to the lower accessibility of the binding sites during rebinding in case of precipitation and suspension polymerizations compared to bulk polymerization even though uniformly sized particles are obtained by latter two approaches. Furthermore, the bulk IIP particles have higher affinity for target analyte, i.e. palladium(II).

4.6 SEPARATION STUDIES

The selectivity of palladium(II) IIP particles synthesized via bulk, precipitation and suspension polymerization approaches were studied for palladium(II) over platinum(IV), ruthenium(III), rhodium(III), and gold(III) ions and selected transition elements copper(II), nickel(II) and zinc(II).The platinum(IV) concentration was established by employing iodide-Rhodamine 6G procedure [7]. The ruthenium(III) [8] and rhodium(III) [9] concentrations were established by thiocyanate-rhodamine 6G procedures reported elsewhere. The concentration of gold (after elution with 2x10 ml of 50% (v/v) HCl) was monitored using the procedure reported in literature [10]. The concentrations of transition elements were determined by flame atomic absorption spectrometry.

The distribution ratios (*D*) of selected inorganics and selectivity coefficients (S) of palladium(II) with respect to other noble and transition metal ions using CP and IIP materials prepared by bulk, precipitation and suspension polymerization methods are summarized in *Table 4.2*. The comparison of percent enrichment (%*E*) and distribution ratio (*D*) values of IIPs and CPs show a significant imprinting effect in case of all the three polymerization methods .

The increase in selectivity of IIPs in comparison to the CPs is due to the multiple interaction or contact between the analyte and the polymer. Again, the selectivity coefficients for palladium(II) with IIPs over platinum(IV) is higher for bulk polymerization compared to precipitation polymerization and are of the same order with respect to gold(III) and ruthenium(III). On the other hand, the selectivity coefficient of palladium(II) over rhodium(III) is higher with precipitation polymerization compared to bulk polymerization. The separation of palladium(II) from other transition elements (which are likely to coexist in its minerals) lies in the order of bulk > precipitation > suspension. Quantitative separation of palladium(II) over copper, nickel and zinc is possible with bulk polymerized palladium(II) IIP particles. However, the palladium(II) IIP materials prepared by suspension polymerization gave inferior distribution ratios compared to bulk and precipitation polymerization methods. Thus, the separation ability of palladium(II) IIP particles during preconcentration of palladium(II) and other selected inorganics from dilute aqueous solutions lies in the order: bulk > precipitation > suspension.

The ground and sieved IIP materials obtained by bulk polymerization is proved to be adequate in the development of new imprinting strategies and for mechanistic studies of the imprinting processes, but it is inappropriate for large scale production in view of the crushing, grinding and sieving operations performed either manually or mechanically. Grinding and sieving is slow and produces irregular particles with rather limited control over particle size and shape. This depends on the nature of polymer material and the method used for grinding/crushing. Direct production of imprinted polymer microspheres or beads in contrast, is rapid and gives an almost quantitative yield of useable particles. Hence, the synthesis of palladium(II) IIP beads prepared by precipitation polymerization are preferred over IIP particles obtained by bulk or suspension polymerization.

Table 4.2: Distribution ratio (D) and Selectivity coefficients ($S_{Pd^{2+}/M^{n+}}$) of leached CP and IIP particles

Metal ion	Bulk polymerization				Precipitation polymerization				Suspension polymerization			
	Distribution ratio D x 10^3		Selectivity coefficient ($S_{Pd^{2+}/M^{n+}}$)		D x 10^3		($S_{Pd^{2+}/M^{n+}}$)		D x 10^3		($S_{Pd^{2+}/M^{n+}}$)	
	CP	IIP	CP	IIP	CP	IIP	CP	IIP	CP	IIP	CP	IIP
Pd(II)	4.5	495	-	-	7.18	604	-	-	2.04	12.85	-	-
Pt(IV)	1.02	0.09	4.40	5500	3.69	0.55	1.94	1100	0.88	0.115	2.32	$1.1x10^2$
Au(III)	17.2	0.73	0.26	670	6.38	1.21	1.12	500	1.23	0.095	1.65	$1.3x10^2$
Rh(III)	0.2	0.46	15.37	1080	0.82	0.17	8.69	3560	1.99	0.080	1.02	$1.6x10^2$
Ru(III)	0.54	0.11	8.29	4200	0.78	0.14	9.21	4170	0.41	0.090	4.98	$1.4x10^2$
Cu(II)	0.001	0.0005	$4.5x10^3$	$1.0x10^6$	1.82	0.089	39.58	$6.76x10^3$	0.059	0.048	34.71	$2.7x10^2$
Ni(II)	0.004	0.0005	$1.0x10^3$	$1.0x10^6$	0.107	0.107	67.14	$5.65x10^3$	0.053	0.081	38.64	$1.6x10^2$
Zn(II)	0.001	0.0005	$4.5x10^3$	$1.0x10^6$	0.026	0.012	$2.77x10^2$	$4.84x10^5$	0.078	0.102	26.08	$1.3x10^2$

4.7 ADSORPTION STUDIES

4.7.1 Effect of adsorption time

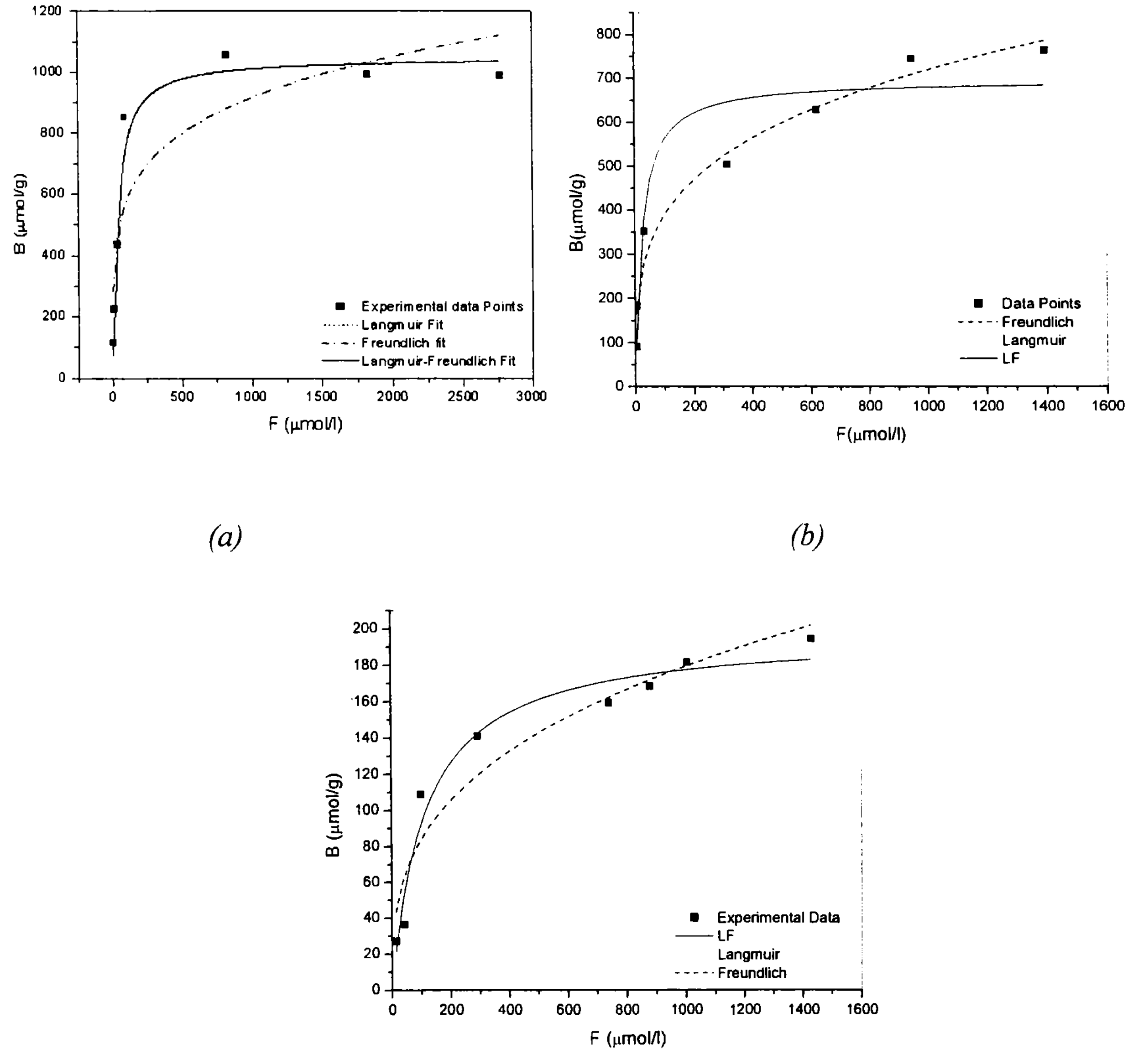
The percent adsorption of palladium(II) during rebinding was studied as a function of time using 0.050 g of CP and IIP particles obtained by bulk, precipitation and suspension polymerization methods. During this study 25 μg of palladium(II) was taken in 250 ml of solution. The results obtained are shown in *Table 4.3*, from which it is clear that in all the three methods a minimum of 25 min is required for maximum sorption.

Table 4.3: Effect of adsorption time on the percent enrichment/extraction by AQ based CP and IIP particles obtained by different polymerization methods

Ads time (min)	Bulk		Precipitation		Suspension	
	CP	IIP	CP	IIP	CP	IIP
10	30.5 ± 0.76	50.7 ± 1.0	37.9 ± 0.75	50.5 ± 1.0	18.4 ± 0.46	37.1 ± 0.74
20	40.0 ± 0.80	62.5 ± 1.3	49.7 ± 1.1	62.0 ± 1.4	24.4 ± 0.56	45.0 ± 1.0
25	47.0 ± 1.1	98.0 ± 1.2	58.5 ± 1.4	>99.0	28.5 ± 0.59	71.5 ± 1.7
30	47.5 ± 0.9	>99.0	59.0 ± 1.1	>99.0	29.0 ± 0.58	72.0 ± 1.4

4.7.2 Binding isotherm studies

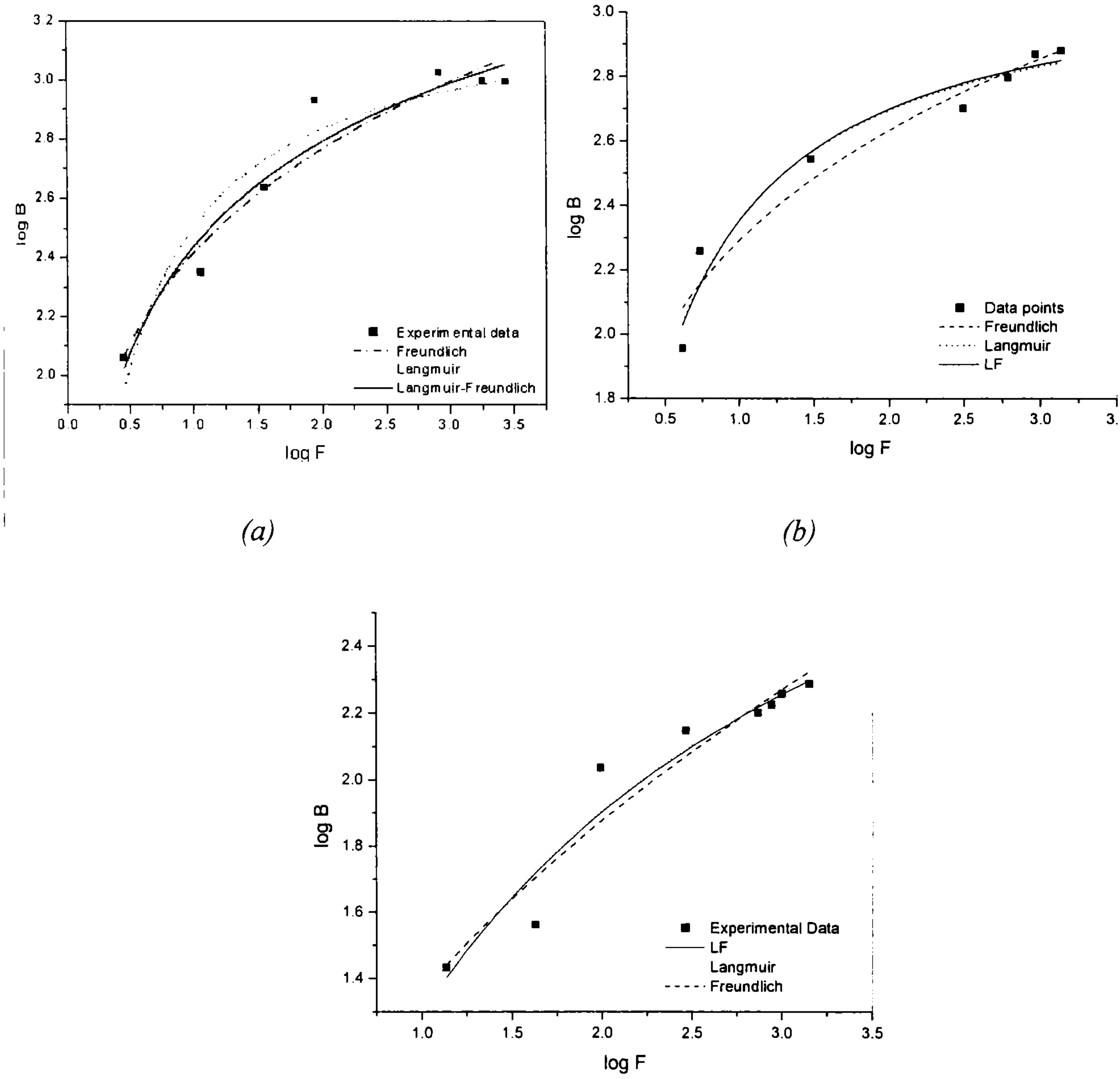
The rebinding studies carried out using amino (AQ), hydroxyl (HQ) or mercapto (MQ) derivatives of quinoline based polymer particles obtained by bulk polymerization and fitted with Langmuir (L), Freundlich (F) and Langmuir–Freundlich (LF) models in chapter 3 revealed that LF model fits well with experimental adsorption isotherm compared to L or F model. We have extended this study to compare IIPs obtained by different polymerization methods. The B vs F and logB vs logF plots obtained for three types of polymers are shown in Fig.4.6 and 4.7 respectively. *Table 4.4* shows the association constants (K_{assoc}), maximum binding sites (N_t), (a) related to median binding constant K_0, binding capacity ($N_t \times a$) and heterogeneity index (m) obtained for IIP prepared via bulk, precipitation and suspension polymerization methods using LF model since it agrees well with the experimental data.



(a) (b)

(c)

Fig.4.6: B vs F plots for the bulk (a), precipitation (b) and suspension (c) polymers



(a)

(b)

(c)

Fig.4.7: logB vs logF plots for the bulk (a), precipitation (b) and suspension (c) polymers

As seen from *Table 4.4*, the association constant for the IIP materials obtained by three polymerization methods are in the order precipitation > bulk > suspension.

On the other hand, the binding capacities of the IIP materials obtained by bulk and precipitation methods are almost same which explains the similarities in percent enrichment and selectivity studies. However, the IIP beads obtained by suspension polymerization method have very low binding capacity compared to bulk or precipitation methods which is in tune with the low percent enrichment of palladium(II) in this case during rebinding. More significantly, all the three IIP materials obtained by different polymerization methods are homogenous in nature as the heterogeneity index is closer to 1.

Table4.4: Fitting parameters for the LF fit to the experimental adsorption isotherms of studied IIPs obtained by different polymerization methods

Fitting parameters	Bulk	Precipitation	Suspension
K_a (mmol^{-1})	0.027	0.041	0.01
N_t (μ mol g^{-1})	1048.2	697.9	197.6
a	0.027	0.041	0.01
Binding capacity (N_t x a)	28.72	28.25	1.98
m	0.9998	0.9980	0.990

4.7.3 Affinity distribution studies

Affinity distribution curves obtained for the three different polymers are given in *Fig. 4.8*. The area under the curves represents the total number of binding sites and it can be seen from the figure that for the bulk and the precipitation polymers it is almost same and for the suspension polymers it is low compared to the other two. But for all the three cases it can be seen that the peak of the distribution is centered at $K_0 = a^{1/m}$. Also the shape of the distribution gets broadened and a unimodal curve was obtained. The polymers synthesized by all the three methods showed a homogeneous distribution and so it can find extensive applications in the chromatographic analysis

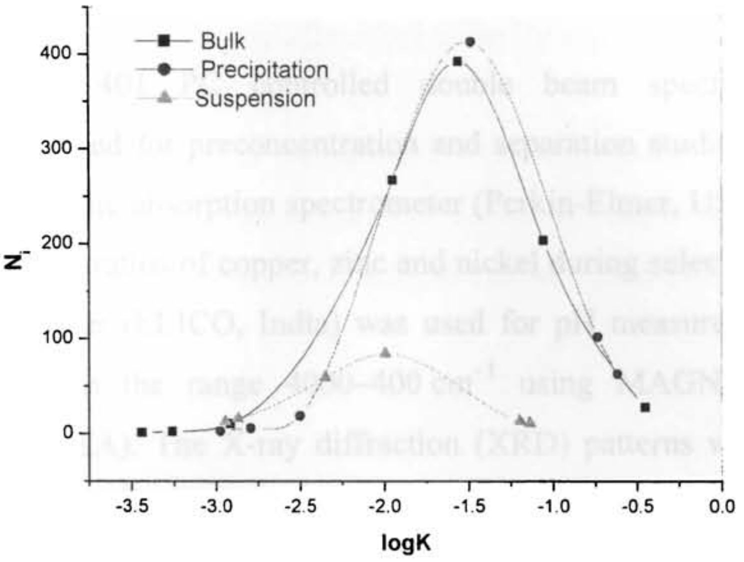


Fig.4.8: Affinity distribution curves of the polymers

4.8 EXPERIMENTAL

4.8.1 Reagents

A stock solution (1 mg ml^{-1}) of palladium(II) was prepared by dissolving 0.1666 g of palladium chloride (Loba Chemie, India) in10 ml of 6 M HCl and diluted to 100 ml with deionized water. Stock solutions (1 mg ml^{-1}) of platinum, ruthenium, rhodium and gold were prepared by dissolving 0.1000 g of platinum foil, 0.2053 g of $RuCl_3$, 0.2035 g of $RhCl_3$ and 0.1541 g of $AuCl_3$ in 100 ml of distilled water. KI (5%, E-Merck, India) was prepared by dissolving 5 g in 100 ml of deionized water. A 0.4 M citrate buffer (pH 4) was prepared by dissolving 8.4 g of citric acid and 11.8 g of trisodium citrate in deionized water. 8-Aminoquinoline (AQ), 4-vinyl pyridine (VP), 2-hydroxy ethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA), 2-methoxy ethanol, 2,2′-azobisisobutyronitrile (AIBN), polyvinyl alcohol (PVA) were obtained from Aldrich (Milwauke, USA). All other chemicals used were of analytical reagent grade.

4.8.2 Apparatus

A Shimadzu-UV-2401 PC controlled double beam spectrophotometer (Shimadzu, Japan) was used for preconcentration and separation studies. A Perkin-Elmer A Analyst 100 atomic absorption spectrometer (Perkin-Elmer, USA) was used for measuring distribution ratios of copper, zinc and nickel during selectivity studies. A LI-120 digital pH meter (ELICO, India) was used for pH measurements. FTIR spectra were recorded in the range 4000–400 cm^{-1} using MAGNA FTIR-560 spectrometer (Nicolet, USA). The X-ray diffraction (XRD) patterns were obtained using Cu K_α X-ray source and Philips X'pert diffractometer (Holland). The surface morphology of the ion imprinted polymer particles were studied using scanning electron microscope (SEM) (JEOL, Model JSM 5600 LV). Thermogravimetric analysis was carried out using TGA-50H (Shimadzu, Japan).

4.8.3 General procedure for the preconcentration / separation of palladium

A portion of solution containing 2.5-100 μg of palladium was taken in one litre beaker and diluted to 500 ml and the acidity of this solution was maintained at ~0.5 N after addition of 20 ml of conc. HCl. Palladium(II) IIP particles (0.05 g) prepared using AQ - VP ternary complex via bulk, precipitation and suspension polymerization methods were added to above solution and stirred for 30 min. The palladium(II) ions preconcentrated onto above IIP particles were eluted by stirring for 30 min with 2 x 10 ml of 6 M HCl. Suitable aliquots of the eluent were taken, pH was adjusted to 4.0 ± 1.0 after addition of 0.4 M citrate buffer and palladium(II) content was established by employing iodide-Rhodamine 6G procedure [11] reported elsewhere.

4.8.4 General procedure for rebinding studies

About 200 mg of the leached IIP particles were equilibriated with 94μmoles l^{-1} to 3762 μmoles l^{-1} of palladium (II) as described in preconcentration procedure. The free concentration of palladium (II) was calculated using the equation

$$F = (A_f \cdot T) / A_t$$

where T is the total concentration of palladium(II) ions. A_f and A_t are the blank corrected absorbance values of palladium(II) ion before and after the addition of palladium(II) IIP particles. The amount of analyte bound to the polymer particles was calculated using the equation

$$B = T - F$$

4.9 CONCLUSIONS

Studies on three different polymerization methods during the synthesis of palladium(II) ion imprinted polymer particles show significant imprinting effects in all the three cases on comparison of IIP and CP materials. Three different methods investigated here have advantages and disadvantages in terms of (i) specificity and effective rebinding, (ii) morphology of the polymer material produced and (iii) ease and scale up potential. The precipitation polymerization method was found to be good for large scale synthesis since it is easy to carry out and time consuming grinding and fractionation operations are not required. Also the small imprinted microspheres can be easily separated by simple centrifugation. Thus, the comparative results obtained in the study for palladium(II) regarding distribution coefficients, percent enrichment, retention/binding capacity and selectivity (for palladium(II) over other selected inorganics) are in the order precipitation $\cong$ bulk > suspension.

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CHAPTER 5

ION IMPRINTED POLYMERS - A NEW STRATEGY BASED ON THE UTILIZATION OF ION ASSOCIATION COMPLEX OF PALLADIUM AS A TEMPLATE

5.1 INTRODUCTION

Metal ion imprinted polymers have been investigated as highly selective sorbents for SPE in order to concentrate and clean up samples prior to analysis. The association between the imprint ion and the monomers can be based on non-covalent interactions such as hydrogen bonds, ionic bonds, hydrophobic interactions, Van der Waals forces etc or reversible covalent bonds [1]. A survey of the synthesis of metal ion imprinted polymers reveal essentially four different approaches viz. (i) linear chain polymers carrying metal binding groups were crosslinked with a bifunctional reagent in presence of metal ions [2-3], (ii) binary complexes of metal ions with ligands having vinyl groups were prepared, isolated and then polymerized with matrix forming monomers [4-7], (iii) surface imprinting conducted on aqueous-organic interface [8-9] and (iv) imprinting of binary/ternary mixed ligand complexes of metal ions with non-vinyl chelate and vinyl ligand [10-16].

This chapter describes the ion imprinting by utilizing the ternary ion-association complex templates of palladium imprint ion viz $[PdI_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$ with $(VP^+)_2$ in presence of 2-hydroxyethyl methacrylate, HEMA (functional monomer) and ethylene glycol dimethacrylate, EGDMA (crosslinking monomer) and methanol or dimethyl sulfoxide (DMSO) as porogen and 2,2'-azobisisobutyronitrile as initiator. The influence of various parameters was optimized and the analytical performance using the two systems by both offline and on-line methods were systematically evaluated. Also, the palladium content present in environmental samples viz street / fan blade dust samples collected from busy cities were determined by using the on-line flow injection-flame atomic absorption spectrometric (FI-FAAS) technique.

5.2 SYNTHESIS OF ION IMPRINTED POLYMERS

5.2.1 Preparation of imprinted polymer

The ion imprinted polymers were synthesized from their corresponding ion association complexes followed by copolymerization with functional and crosslinking monomers.

The ion association complexes of palladium were prepared by adding excess KI or KSCN (5%) to palladium(II) followed by the addition of an aqueous solution of the vinyl pyridinium ion (prepared by adding equivalent amounts of 4-vinyl pyridine and acetyl chloride in dichloromethane). The ternary complex thus formed was floated with cyclohexane in a 60 ml separating funnel and then both the aqueous and organic layers were discarded. The ternary ion-association complex precipitate deposited on the walls of the separating funnel was dissolved in minimum amount of methanol or DMSO and then embedded in polymer matrix formed by thermal means using 6 mmoles of HEMA and 30 mmoles of EGDMA and 50 mg of AIBN as initiator at 60°C. The unleached polymer materials thus formed were dried in constant temperature vacuum oven at 80°C, for 2hrs, powdered and sieved to get particles of lower than 45µm, which is schematically represented in *Fig.5.1.*

5.2.2 Pretreatment of IIPs

The ion imprinted polymer particles synthesized using iodide or thiocyanate system was leached with 6 M HCl for 18 hrs in order to selectively remove the templates viz $[PdI_4]^{2-}$ or $[Pd(SCN_4]^{2-}$. The resulting polymer particles after filtration were dried at 80°C to obtain leached polymer particles for the possible recovery of palladium (II) from aqueous solutions.

5.2.3 Synthesis of the control polymer (CPs)

The control polymers were also prepared in a similar fashion as that of the leached IIP particles but without the palladium ion. The resulting CP materials was also subjected to the same pretreatments as in the case of IIPs to compare their performance for the recovery of palladium from dilute aqueous solution and also for the separation of palladium from selected inorganics.

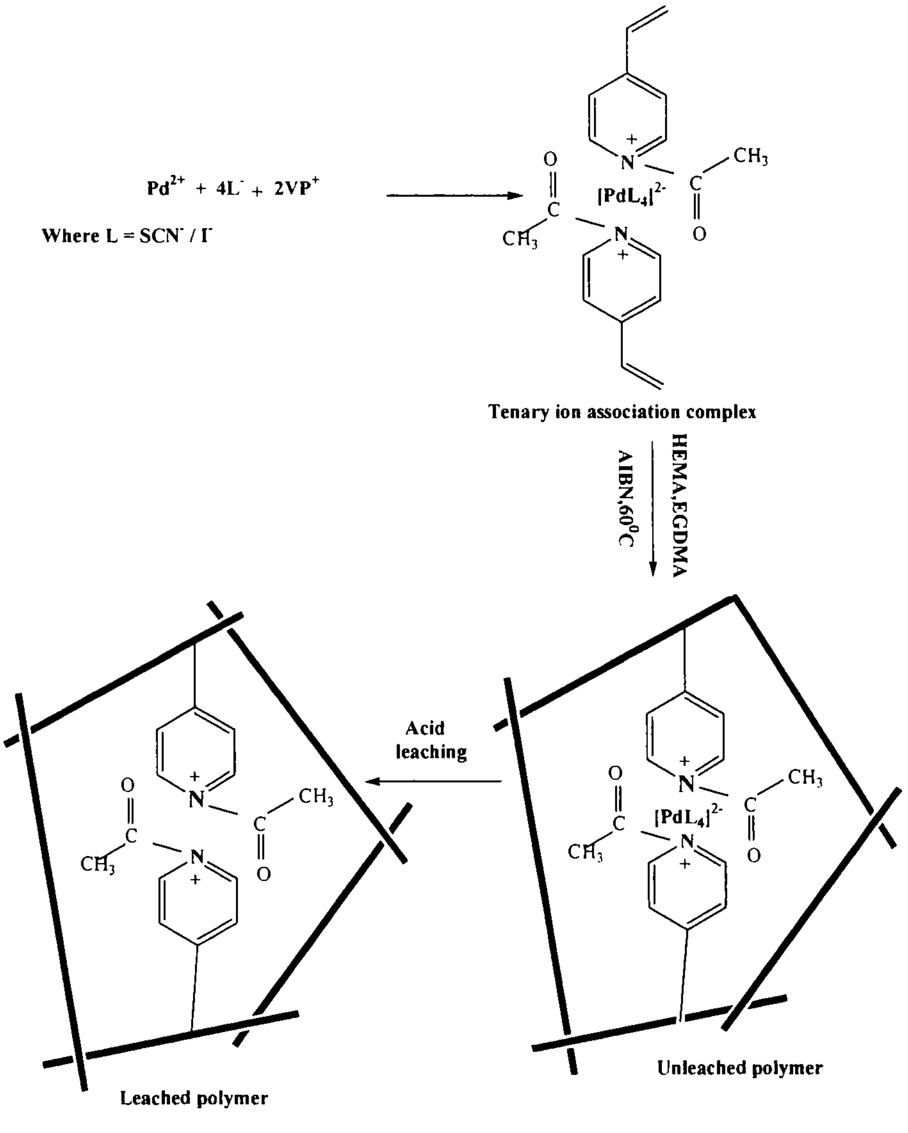


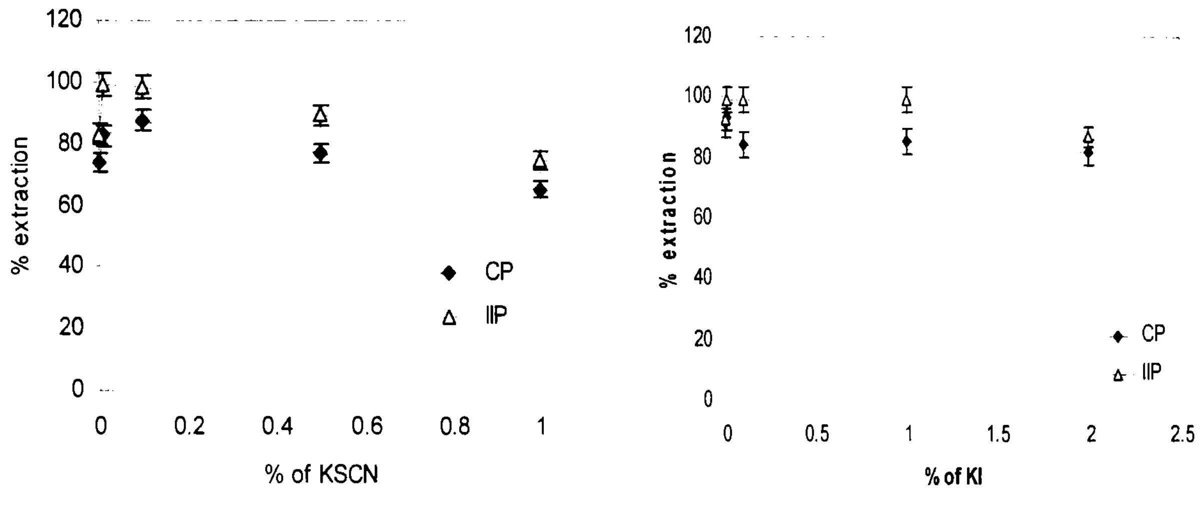
Fig.5.1: Scheme for the synthesis of palladium (II) ion imprinted polymer.

5.3 OPTIMIZATION OF EXPERIMENTAL CONDITIONS

The ion imprinted polymers synthesized using the ternary ion association complex templates were tested for the preconcentration as well as the selective separation of palladium(II) from dilute aqueous solution containing selected inorganics. The polymer particles having ion association complexes of palladium(II) with potassium iodide / potassium thiocyanate together with the vinyl pyridinium ion were synthesized and their analytical performances were evaluated and compared. Various parameters like the effect of pH, weight of the polymer particles, preconcentration and elution times and the concentration of the KI or KSCN on the percent extraction were optimized.

5.3.1 Effect of variation in the concentration of KSCN & KI

The concentration of KSCN and KI were varied from 0.001 – 2% (i.e. 10^{-5} M – 0.02 M). The results obtained are given in *Fig.5.2.* From the figure, one can notice the imprinting effect with both the systems. But this effect is more pronounced in the case of the thiocyanate system compared to the iodide system. Also in both the systems, we can see that at higher and lower concentration of KI or KSCN, the quantitative recovery of palladium from aqueous solution is not possible, i.e. an optimum concentration of these reagents during preconcentration is essential for the quantitative extraction. In the case of thiocyanate / iodide system, the concentration of KSCN / KI was found to be 0.01 / 0.1% respectively. The lower recoveries at concentrations below the optimum concentration is due to the insufficient formation of the $[PdI_4]^{2-}$ or $[Pd(SCN)_4]^{2-}$ and at concentration above the optimum, complexes of palladium other than the above mentioned complexes are formed resulting in decrease in percent extraction .



(a) (b)

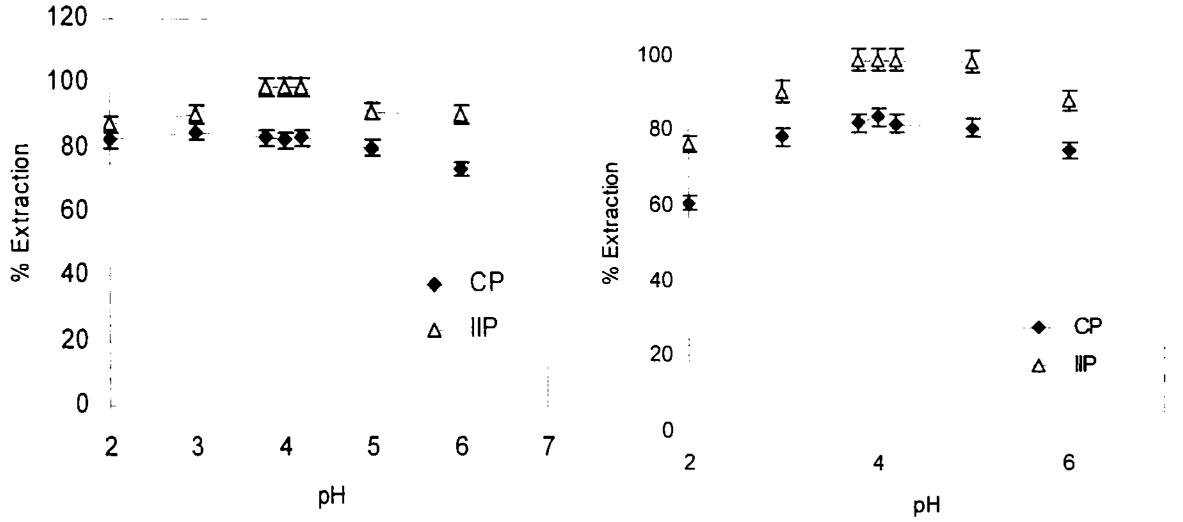
Fig.5.2: Effect of % of KSCN (a) / KI (b) on the percentage extraction of palladium(II)

5.3.2 Effect of pH

The effect of pH on the percent recovery of palladium(II) under the optimal concentrations of KI and KSCN are systematically investigated and is shown in *Fig.5.3*. Here also the imprinting effect is noticed in both the systems at all pH values. But the quantitative recovery of palladium(II) from aqueous solution is possible only at pH 4.0±0.2 for both the systems. The decrease in percentage extraction at lower and higher pH values may be explained as due to the dissociation of the required template species during preconcentration at lower pH values and the formation of the $Pd(OH)_2$ at higher pHs.

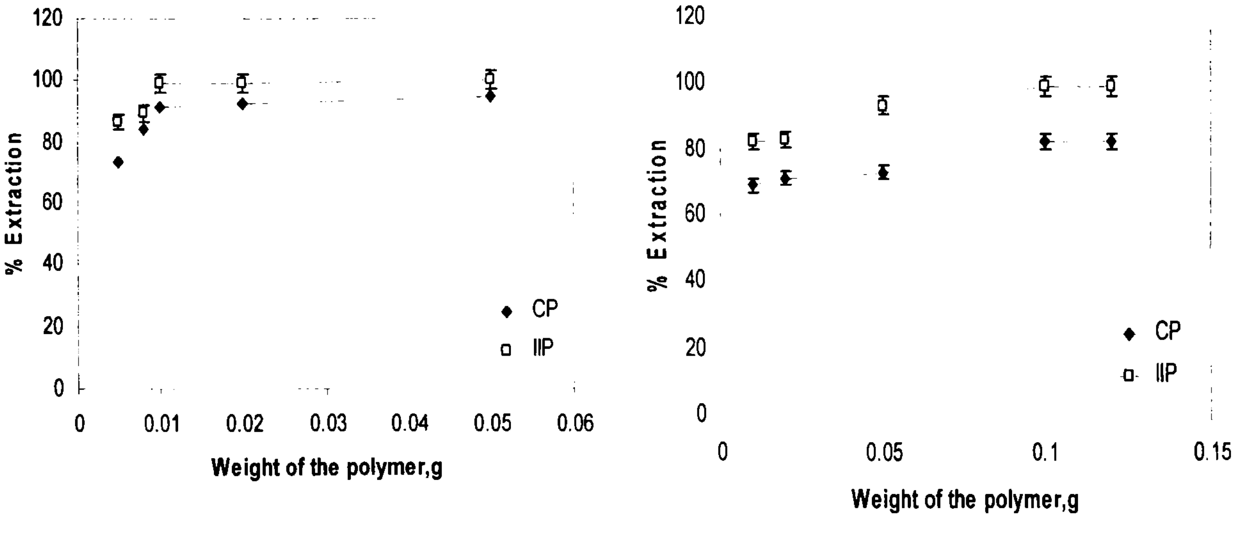
5.3.3 Effect of weight of the polymer particles

The influence of weight of the polymer particles under the above optimized conditions was evaluated and the results obtained are shown in *Fig.5.4*. It can be seen from the figure that even with 0.01 g of the polymeric material, the quantitative recovery of palladium(II) is possible in the case of the thiocyanate system, while for the iodide system the quantitative recovery is possible only when the polymer weight is increased up to 0.1 g. This may be due to the higher number of homogenous and high affinity binding sites in the case of the thiocyanate system compared to the iodide system.



(a) *(b)*

Fig.5.3: Effect of pH on the % extraction of palladium(II) using KSCN (a) / KI (b) based polymers



(a) *(b)*

Fig.5.4: Effect of weight of polymers on the % extraction of palladium (II) imprinted polymers using KSCN (a) / KI (b) based polymers

5.3.4 Eluent variation

The anionic binary complexes viz $[PdI_4]^{2-}$ or $[Pd(SCN)_4]^{2-}$ were eluted from the polymer with various eluting agents. It can be seen from the *Table 5.1* that the complete elution of palladium(II) was possible only with acidified methanol (0.1N HCl).

Table 5.1: Nature of eluent on the percent extraction of Pd(II)

Eluents	% Extraction
5% thiourea	8.0 ± 0.02
10% thiourea	25.1 ± 0.05
5% citric acid	20.2 ± 0.04
6 M HCl	11.0 ± 0.02
0.1% DMG	20.1 ± 0.04
0.1% 8-aminoquinoline	69.6 ± 0.03
Methanol (0.01 M HCl)	73.2 ± 0.14
Methanol (0.1 M HCl)	> 99.9

5.3.5 Optimization of the other experimental parameters

From the above discussion, it is very clear that the ion-imprinted polymer particles synthesized via the ion association complex of palladium(II) with the thiocyanate system gave better results in comparison to the iodide system with respect to weight of the polymer particles. Hence, other experimental parameters such as preconcentration time, elution time and aqueous phase volume were optimized only for the thiocyanate system based polymers. The results obtained are compiled in *Table 5.2.* It can be seen from the Table that for the quantitative enrichment of palladium(II), the optimum time required for the preconcentration is 30 min. Also the complete elution of the palladium(II)with acidified methanol from the IIP particles is possible only with an elution time of 2 x 30 min and an eluent volume of 2 x 5 ml. The aqueous phase volume during the preconcentration was also varied from 25-500 ml and the quantitative enrichment was found to be possible only up to an aqueous phase volume of 250 ml.

Table 5.2: Influence of various parameters on the percent enrichment/ extraction of palladium(II) on to thiocyanate based CP and IIP particles

Parameters	% Extraction	
	CP	IIP
Preconcentration time (min)		
1x10	57.8 ± 0.10	62.5 ± 0.09
1x20	67.5± 0.12	76.2 ± 0.15
1x30	82.4 ± 0.16	>99.9
Elution time (min)		
1x10	36.8 ± 0.06	42.5 ± 0.09
2x10	46.9 ± 0.09	52.9 ± 0.08
1x30	65.4 ± 0.08	71.8 ± 0.14
2x30	81.6 ± 0.16	>99.9
Eluent volume (ml)		
1x5	55.8 ± 0.08	72.9 ± 0.10
1x10	74.2 ± 0.11	86.7 ± 0.13
2x5	82.5 ± 0.17	>99.9
Aqueous phase volume (ml)		
25	82.5 ± 0.17	>99.9
50	82.1 ± 0.12	>99.9
100	80.1 ± 0.16	> 99.9
250	80.0 ± 0.14	> 99.9
500	76.9 ± 0.15	92.5 ± 0.19

5.4 RETENTION CAPACITY

The retention capacity or the maximum amount of the palladium(II) ion preconcentrated per gram of control or ion imprinted polymer particles of both the systems were determined by saturating 0.02 g of polymer present in 25 ml of solution with 1 mg of palladium (II) under the optimal conditions. The results obtained are shown in *Table5.3*, from which it is clear that the retention capacities of the IIPs were found to be higher compared to the corresponding CPs (imprinting effect) and also the retention capacity of the IIPs of thiocyanate based system was higher than iodide system.

Table 5.3. Retention capacities of the polymer particles

IIPs	Retention capacity (mg/g)	
	CP	IIP
Thiocyanate system	29.00 ± 0.06	41.60 ± 0.08
Iodide system	18.51 ± 0.04	32.40 ± 0.06

5.5 CALIBRATION GRAPH AND DETECTION LIMIT

Under the optimal conditions described above, the calibration curve was linear over the concentration range of 2.5 -100 μg of palladium(II) present in 250 ml of solution based on the two systems. Five replicate determinations of 25 μg of palladium(II) in 250 ml of solution gave a mean absorbance of 0.052 and 0.050 with relative standard deviations of 2.0 and 2.2 % for the thiocyanate and the iodide system respectively. The detection limits corresponding to three times the standard deviation of the blanks were found to be 10 ppb for both systems. The linear equations with regression are as follows:

$$A_{SCN^-} = 2.3 \times 10^{-5} + 0.002 \times C$$

$$A_{I^-} = 1.7 \times 10^{-4} + 0.002 \times C$$

and the correlation coefficients are 0.9999 and 0.9994 for the thiocyanate based IIP and iodide based IIPs. A is the absorbance and C is the amount of palladium in micrograms per 250 ml of aqueous solution. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

5.6 SELECTIVITY STUDIES

The selectivity characteristics of control and palladium(II) IIPs prepared via the use of templates $[Pd(SCN)_4]^{2-}$ $(VP^+)_2$ and $[PdI_4]^{2-}$ $(VP^+)_2$ were systematically studied for palladium and other selected inorganics. *Figure 5.5* shows the percent extraction data, which clearly depicts the imprinting effect, i.e. increase in percent extraction of palladium with IIP over CP and decrease in percent extraction with IIP over CP in case of other inorganics for both the systems. The distribution ratio (D) and selectivity coefficients (S) calculated based on the above percent extraction data are shown in *Table 5.4*. From the *Table 5.4*, it is clear that D and S values are higher for palladium over platinum and gold incase of $[Pd(SCN)_4]^{2-}$ system compared to $[PdI_4]^{2-}$ system and the reverse is true for other elements viz. ruthenium, rhodium, copper, zinc & nickel. As the quantitative recovery of palladium(II) was possible even with 0.01 g of the polymer with the thiocyanate based system compared to 0.1 g needed for the iodide based system and also higher retention capacities were obtained with the former system, thiocyanate based polymers were selected for the subsequent analytical application studies.

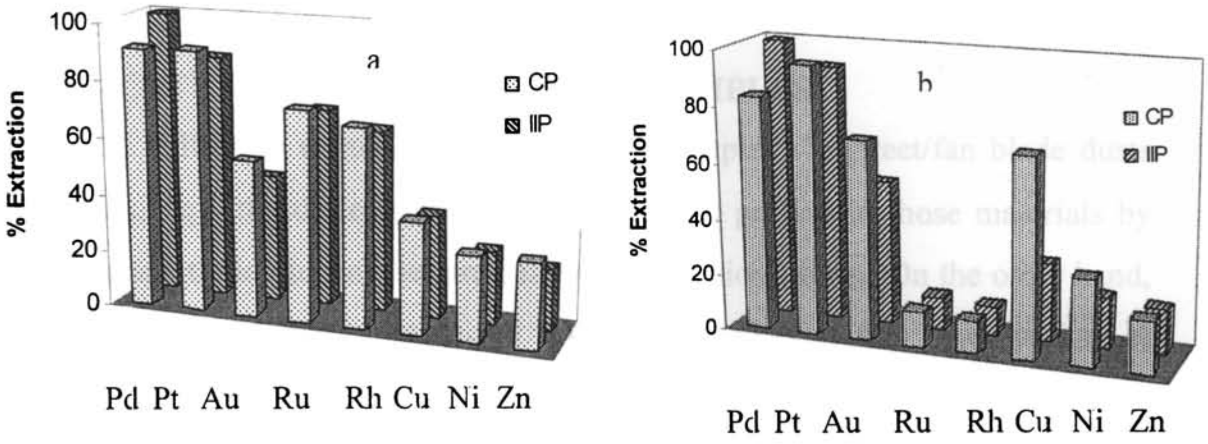


Fig.5.5: Percentage extraction of palladium(II) and other co existing elements using Pd (II) imprinted polymers using KSCN (a) / KI (b) based polymers.

*Table 5.4: Selectivity data of CP and palladium(II) IIP particles**

Metal ion	Thiocyanate system**				Iodide system***			
	D		S		D		S	
	CP	IIP	CP	IIP	CP	IIP	CP	IIP
Pd(II)	13	> 99.9	-	-	5.15	> 99.9	-	-
Pt(IV)	11.18	8.40	1.2	11.8	23.93	11.19	0.2	8.8
Rh(III)	2.27	1.78	5.7	55.7	0.14	0.12	37.9	842.0
Ru(III)	2.83	2.33	4.6	42.5	0.15	0.13	35.5	740.0
Au(III)	1.21	0.79	10.7	124.7	2.4	1.07	2.1	93.0
Cu(II)	0.65	0.56	19.9	176.8	2.40	0.39	2.2	251.0
Zn(II)	0.27	0.43	48.0	230.0	0.23	0.19	22.1	504.0
Ni(II)	0.43	0.34	29.7	288.0	0.45	0.25	11.5	440.0

** D and S values are computed from the threee successive experimental values.*

***0.02 g polymer particles for the thiocyanate system.*

****0.1 g polymer particles for the iodide system.*

5.7 APPLICATION TO DUST / FAN BLADE SAMPLES

Since palladium content in the geological samples viz street/fan blade dusts were ~ 0.4 μg g^{-1}, the determination of palladium(II) present in those materials by batch preconcentration techniques are below the detection limits. On the other hand, the ion imprinted polymers synthesized via the thiocyanate system when packed in home made microcolumn for the FI-FAAS experiment resulted in 60 fold enhancement in sensitivity compared to 25 fold for batch systems. Other advantages of on-line technique over offline include high sample throughput, improved precision as it is computer controlled, low sample and reagent consumption, ease of automation, reuse capability and also it is well suited to low volume samples.

5.8 OPTIMIZATION OF ON-LINE FIA CONDITIONS

5.8.1 Flow conditions

High sample loading flow rates are important for efficient preconcentration and high sample throughput. In general, FI sample flow rates are limited by the back pressure produced by the column and or sorption efficiency, which decreases the flow rate. No degradation of sorption efficiency was observed up to loading flow rate of 5 ml min^{-1} for palladium(II). The reagent flow rate adds to the total loading flow rate and hence calls for a proportional decrease in the sample flow rate. The reagent flow rate should not be too low so as to ensure good mixing of the reagent and sample solution. An optimum sample and reagent flow rates of 5.0 and 3.0 was used in the subsequent studies.

An elution flow rate of 4.0 ml min^{-1} provided optimum sensitivity and elution peaks with minimum tailing. No provision was made to compensate for the lower flow rates delivered by the FI system; however the transfer capillary to the nebulizer (PTFE 0.3 mm i.d) restricted the uptake rate to values closer to the flow rate provided by the system. Operating the nebulizer at this flow rate does not lower the sensitivity in proportion to the decrease in flow rate because of the potential improvements in the nebulizer efficiency under starved conditions. The lower flow rate in the FI mode in comparison with conventional free uptake of the nebulizer is also beneficial for the droplet diameter distribution, which is shifted to smaller droplets and is therefore less prone to vapourization interferences.

5.8.2 Calibration Graph

Fig.5.6 shows the calibration plots for palladium(II) concentration in the range 0-0.2 mg l^{-1}. The detection limits corresponding to 3 times the standard deviation of the blank were found to be 1.5 μg l^{-1} for palladium(II). The linear equation with regression was as follows.

$$A = 1.244 \times C + 0.0028$$

The correlation coefficient is 0.9948 .where A is the absorbance and C is the concentration of palladium(II) in mg l^{-1}. All statistical calculations were based on average of triplicate readings for each standard solution in the given range. Furthermore, a 1 min loading / preconcentration time allows a sample frequency of 30 h^{-1}. Higher sensitivities can be obtained by modifying the method, i.e. using longer preconcentration period of 2 min at the expense of lower sample throughput.

The characteristic data for the performance of on-line preconcentration system are summarized in *Table5.5.*

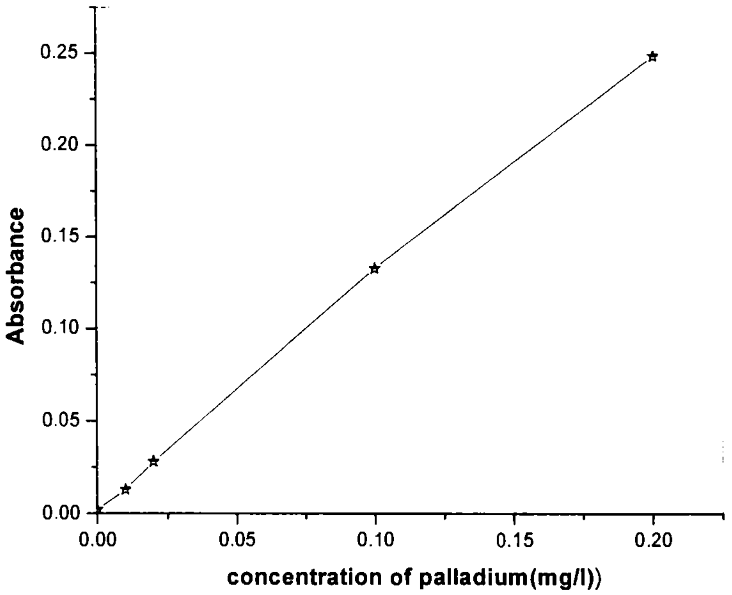


Fig.5.6: Calibration plot

Table 5.5: Analytical performance data for FI on-line preconcentration by FAAS method for palladium(II) determination.

Analytical parameters	Palladium(II)
Linear range (μg l^{-1})	0-200
Sensitivity enhancement	60
Precision (RSD) (at 100 μg l^{-1})	2.4
Sample consumption (ml)	5
Loading time (min)	1
Sample frequency	30 h^{-1}
Detection limit (3σ) (μg l^{-1})	1.5

5.9 EFFECT OF MATRIX ELEMENTS PRESENT IN DUST SAMPLES

The FAAS analysis data of dust samples is given in *Table5.6*. It is clear from this table that these samples essentially contain iron (III), magnesium(II), calcium (II), copper(II), zinc(II), lead(II) and nickel(II) in major amounts (i.e., matrix elements) compared to palladium. According to the literature [17, 18] many elements especially iron, depresses the AAS signal of palladium. For this reason the concentration of matrix elements in 3 street and 1 fan blade dust samples were determined after passing through a micro column packed with palladium (II) IIP particles. The results obtained are shown in *Table 5.6.*

Table 5.6: Concentration of elements determined in street dust/domestic fan blade samples by FAAS (n=3) ($\mu g/g$)*

Ion	Street dust						Fan blade	
	Chennai		Tirupati		Trivandrum		Chennai	
	a	b	a	b	a	b	a	b
Fe (III)	5955	31.75	9155	57.14	2311	35.29	2222	27.4
Zn (II)	295.5	<0.48	425	<0.48	3730	15.8	2149	4.87
Ca (II)	6563	2.22	3906	<2.1	6563	<2.1	7656	<2.1
Mg (II)	75.9	0.53	176.6	0.484	179.9	<0.48	183.3	1.82
Cu (II)	6.32	<2.05	172.1	<2.05	158.1	<12.0	232.6	27.9
Pb (II)	139.5	<12.0	46.5	<12.0	46.5	<2.05	186.1	<12.0

a) Before passing through microcolumn packed with IIP particles

b) After passing through microlumn packed with IIP particles

**Average of 3 determinations.*

It is clear from the table that the concentrations of matrix ions are very low in the eluent due to selective enrichment of palladium (II) during loading mode (arising out the imprinting effect). This observation clearly shows that the palladium (II) can be selectively enriched on to palladium (II) IIP particles, thus enabling reliable determination of palladium (II) in real dust samples.

5.10 ANALYTICAL APPLICATION

The ion imprinted polymers synthesized via the thiocyanate system packed in home made microcolumn for the FI-FAAS experiment resulted in 60 fold enhancement in sensitivity compared to 25 fold for batch systems. The matrix elements that usually present in geological samples (see section 5.9) can be removed by passing the digested samples through the microcolumn. In addition to higher enrichment, as the on-line FI-FAAS allow better precision, selectivity and can analyse more samples for a given time compared to batch "Static" method, the former procedure is preferred for the analysis of palladium present in the street/fan blade dust samples collected from busy cities. The results obtained are shown in *Table 5.7.* The results are quite comparable with the standard ICPMS measurements indicating the possible use of FI-FAAS for routine monitoring of palladium in dust samples.

Table 5.7: Analysis of street/fan blade dust samples

Sample	Palladium(II) found (μg/g)	
	Present method*	ICPMS
Street dust		
Chennai	0.50 ± 0.05	0.50 ± 0.01
Tirupati	0.45 ± 0.05	0.44 ± 0.01
Trivandrum	< 0.05	< 0.01
Fan blade dust		
Chennai	0.45 ± 0.05	0.42 ± 0.01

**Average of three determinations*

5.11 EXPERIMENTAL

5.11.1 Instrumentation

The Perkin-Elmer® model A Analyst^{TM} 100 flame atomic absorption spectrometer (Perkin Elmer Life and Analytical Sciences, Shelton, CT, USA) along with FIAS-400 flow injection analyzer equipped with deuterium background correction was used. Perkin-Elmer Lumina® palladium hollow cathode lamp was used. The above lamp was operated at 30 mA using 0.2 nm slit width. The wavelength used was 244.8 nm. A standard air-acetylene stainless steel burner and 10 cm path length system were operated at an air flow rate of 4.0 ml min^{-1} and an acetylene flow rate of 1.0 ml min^{-1}. The burner height was adjusted to about 30mm from base for optimum sensitivity. The nebulizer uptake was adjusted to provide optimum response for conventional sample aspiration.

5.11.2 Reagents and standard solutions

All reagents used were of Analytical reagent grade. A stock solution (1 mg ml^{-1}) of palladium(II) was prepared by dissolving 0.1666 g of palladium chloride (Loba Chemie, India) in 10ml of 6 M HCl and diluted to 100 ml with deionized water. Stock solution (1 mg ml^{-1}) of platinum, ruthenium, rhodium and gold were prepared by dissolving 0.1000 g of platinum foil, 0.2053 g $RuCl_3$, 0.2035 g of $RhCl_3$ and 0.1541 g of $AuCl_3$ in 100 ml of distilled water. KI and KSCN were obtained from E-merck, India. 4-Vinyl pyridine (VP), 2-hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA), methanol, dimethyl sulphoxide, 2,2'-azobisisobutryonitrile (AIBN), acetyl chloride were obtained from Aldrich (Milwauke, USA).

5.11.3 General procedure for preconcentration / separation of palladium

A portion of the solution containing 2.5-100 μg of palladium(II) and 0.1% KI or 0.01% KSCN was taken in 500 ml beaker and diluted to 250 ml and the pH was adjusted to 4.0±0.2. The palladium IIP particles prepared using $[PdI_4]^{2-}(VP^+)_2$ (0.1 g) or $[Pd(SCN)_4]^{2-}$ $(VP^+)_2$ (0.02 g) ion association complexes were added to the above solution and stirred for 30 min. The palladium (II) ions preconcentrated on to above IIP particles were eluted with 2 x 5 ml of acidified methanol (0.1M HCl) for 30 min and analyzed by flame atomic absorption spectrometry.

The selectivity of palladium(II) over other precious metal ions like platinum(IV), ruthenium(III), rhodium(III) and gold(III) and selected transition elements viz copper(II), nickel(II) and zinc(II) were evaluated using the synthesized IIPs. The platinum(IV) concentration was established by employing iodide-rhodamine 6G procedure [19].The ruthenium(III) [20] and rhodium(III) [21] concentrations were established by thiocyanate-rhodamine 6G procedures reported elsewhere. The concentrations of gold and other transition elements were determined by flame atomic absorption spectrometry.

5.11.4 Flow injection (FI)-flame atomic absorption spectrometric (FAAS) procedure

Standard palladium(II) solutions (adjusted to pH of 4.0 ± 0.2 in presence of 0.01% KSCN) were pumped through a home-made microcolumn packed with palladium(II) IIP particles via a peristaltic pump P_1 for 1 min during the loading mode. The enriched palladium(II) was eluted with acidified methanol (0.1 M) at a flow rate of 4 ml min^{-1} using peristaltic pump P_2 and subjected to FAAS determination. Both loading and elution steps (See *Fig.5.7 & 5.8*) were computer controlled using Perkin-Elmer AA Winlab^{TM} V 3.0 spectrometric software. The programme for the injection valve in load (fill) and elute (inject) positions are given in *Table 5.8.*

Calibration graphs were constructed by pumping standard palladium(II) solutions in the concentration range 0 - 200 μg l^{-1} of palladium(II). Unknown sample solutions were similarly subjected to FI-FAAS procedure described above after the addition of requisite amount of KSCN and the palladium(II) content was established by reference to calibration graph.

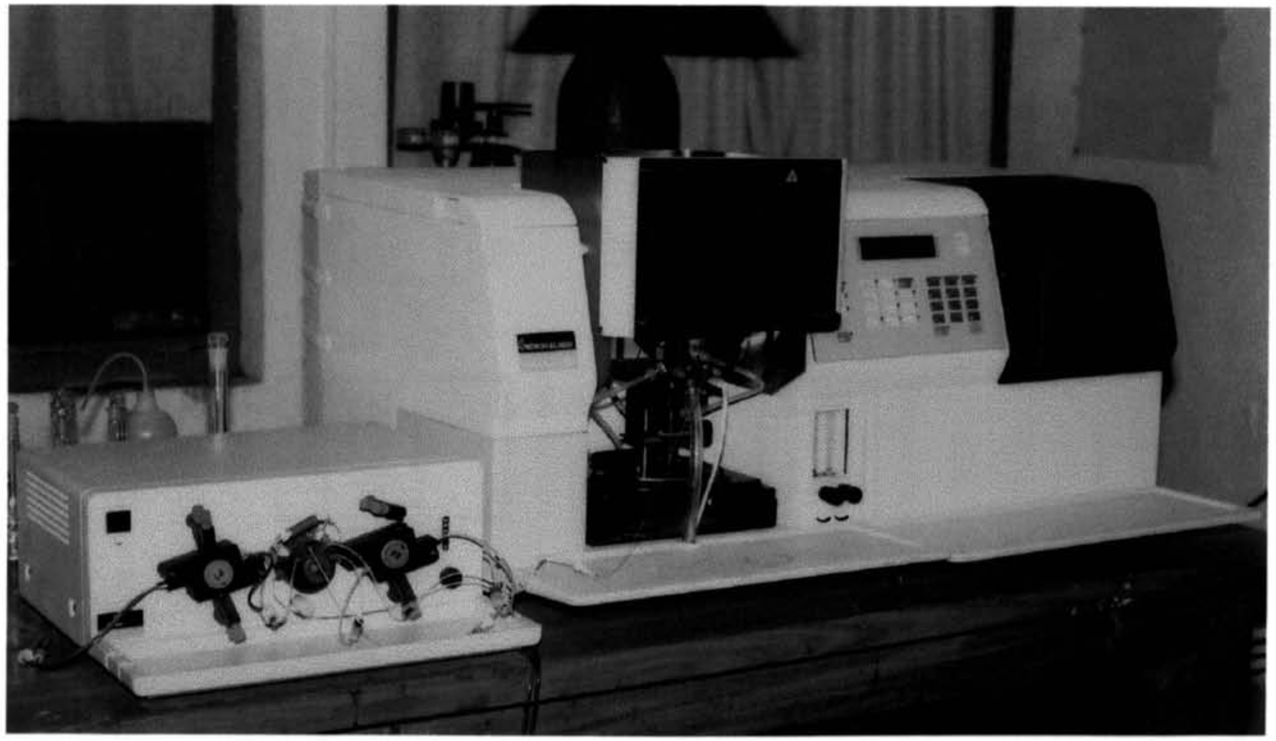


Fig.5.7: Flow Injection-FAAS for online preconcentration & determination

Table 5.8: Programme for the injection valve in loading (fill) and elution (inject) positions

FIAS Step	Time (sec)	Pump 1 (rpm)	Pump 2 (rpm)	Valve mode
Prefill	20	100	120	Elution
1	40	100	0	Loading
2	20	100	120	Loading
3	20	0	120	Elution

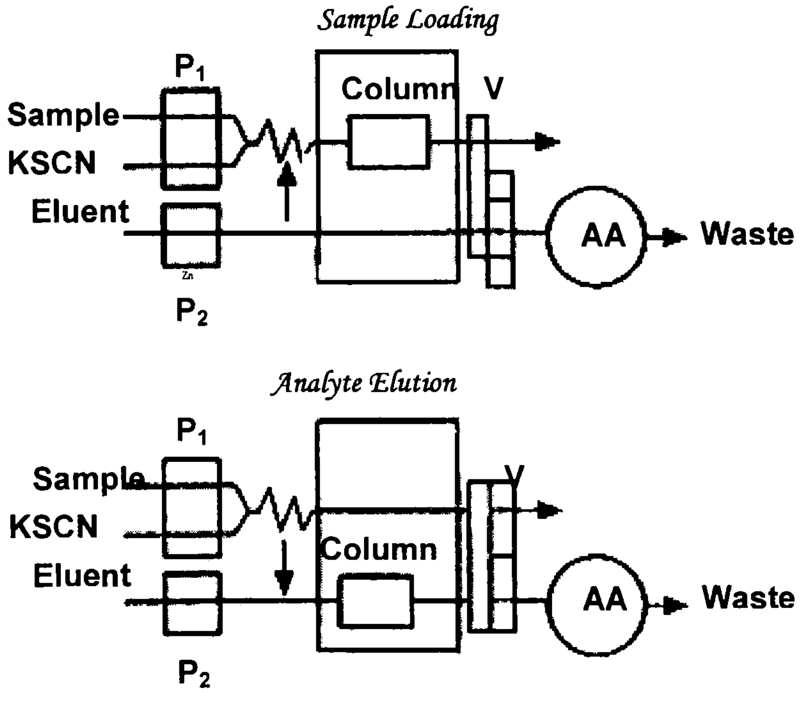


Fig.5.8: Flow injection manifold for on-line preconcentration. V: Injection valve, P1 & P_2: Peristaltic pumps with flow rates of 11.4 & 4.0 ml/ min respectively, AA: Atomic absorption spectrometer.

5.11.5 Analysis of street/fan blade dust samples

The dust samples were collected from different road sides having dense traffic or from the fan blades in houses located in dense traffic area in various cities of India. The samples were dried at 105°C for 2 h, ground, passed through a 200 mesh and then homogenized. 1.00 g specimen of each sample was weighed into a 100 ml beaker. In order to decompose it, 10 ml of conc. H_2SO_4 and 3 x 15 ml of conc. HNO_3 were added and heated on a hot plate at 120°C. After complete decomposition, the sample solution was evaporated to fumes of SO_3, cooled and diluted to ~20 ml and the pH of the solution was adjusted to 4.0 ± 0.2 and then made up to 25 ml. These solutions were then subjected to FI-FAAS quantization procedure described above after the addition of 1 ml of 0.01% KSCN. Furthermore, the samples were analyzed by standard ICP-MS technique for verifying the results obtained by the above mentioned FI-FAAS method.

5.12 CONCLUSIONS

The palladium(II) ion IIP were synthesized via a new strategy ie, by the use of ion association complexes of palladium(II) with thiocyanate / iodide with the vinyl pyridinium ion as templates. The synthesized IIPs based on two systems were compared and their analytical performances were evaluated systematically. The studies reveal that the thiocyanate system is superior to the iodide system based on the analytical studies viz percent extraction as well as retention capacity studies. Thus, IIPs based on thiocyanate were able to pick up palladium from very dilute aqueous solutions. Also the IIPs of thiocyanate system was used for the analysis of street/fan blade dust samples using FIA-AAS and the values obtained were quite comparable with the valued obtained with standard ICPMS.

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CHAPTER 6

ION ASSOCIATION COMPLEX OF PLATINUM AS A TEMPLATE FOR THE RECOVERY OF PLATINUM(IV)

6.1. INTRODUCTION

Since the extraction and production of platinum is a quite complex process, there is a wide scope for research and technological advances in this field. The efficiency of platinum extraction is low and any improvement in efficiency would end up with significant economic gains [1-4]. To our knowledge, platinum(IV) imprinted materials have not been synthesized for the SPE studies. However, a few reports on the synthesis of platinum imprinted polymers as catalysts were described by Gagne *et al* [5-6]. Here, we report the platinum metal ion imprinting by utilizing its ternary ion - association complex i.e., $[PtI_6]^{2-}$ $(VP^+)_2$ in presence of 2- hydroxyl ethyl methacrylate, HEMA (functional monomer) and ethylene glycol dimethacrylate, EGDMA (cross linking monomer) i.e., by using the similar strategy that was described in Chapter 5.

6.2 SYNTHESIS OF ION IMPRINTED POLMERS

6.2.1 Ion imprinted polymer (IIP) preparation

The synthesis of the ion imprinted polymers was carried out in two steps.

1. Ion association complex formation
2. Copolymerization of the ion association complex with functional and crosslinking monomers.

The ion association complex of platinum was prepared by adding excess of KI (5%) to the platinum solution followed by the addition of an aqueous solution of the vinyl pyridinium ion (synthesized by adding equivalent amounts of 4-vinyl pyridine and acetyl chloride in dichloromethane). The formation of the ion association complex was confirmed from the UV - Visible studies. The enhancement of absorption and shift in the absorption maximum in the spectrum of $[PtI_6]^{2-}$ and (VP^+) mixture compared to the spectra of $[PtI_6]^{2-}$ ensures the formation of ion association complex. Under these conditions VP^+ and (Pt - VP^+) do not absorb in the wavelength range 400 - 600nm. (*Fig.6.1*).The binary $[PtI_6]^{2-}$ absorbs maximally at 510 nm and on addition of (VP^+) to $[PtI_6]^{2-}$ results in increase in absorbance in the wavelength range confirming the formation of ternary ion - association complex. The UV -visible absorption spectrum of ternary ion -association complex is unaffected on addition of HEMA, EGDMA and AIBN indicating the absence of interaction of ternary ion association complex with combination of functional and crosslinking monomers and initiator at the room temperature.

The ternary complex formed was floated with cyclohexanol in a 60 ml separating funnel and then both the aqueous and organic layers were discarded. The ternary ion-association complex precipitate deposited on the walls of the separating funnel was dissolved in minimum amount of methanol and then imprinted with HEMA (6 mmoles) and EGDMA (30 mmoles) using 50 mg of AIBN as initiator at 60°C. The unleached polymer particles thus formed were ground, dried in vacuum oven, sieved and used for the various analytical studies.

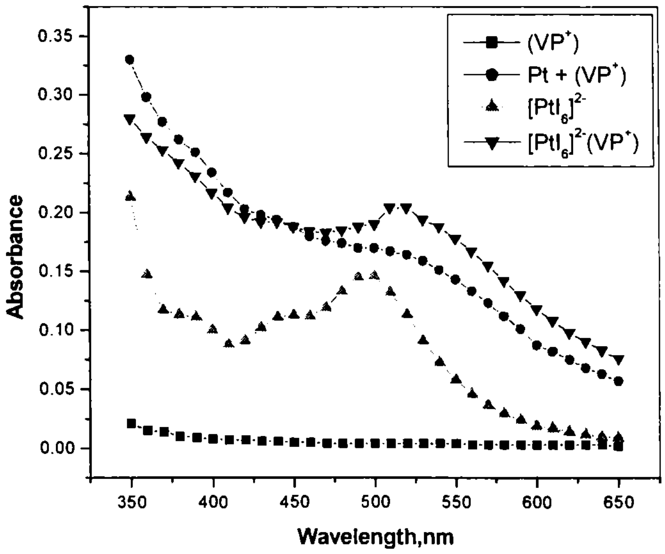

Fig. 6.1: UV -Visible spectra of aqueous solutions of (VP^+)*, Pt +* (VP^+)*,*$[PtI_6]^{2-}$*,* $[PtI_6]^{2-}(VP^+)_2$*.*

6.2.2 Pretreatment of IIPs

The IIP synthesized by the above procedure was leached with 6M HCI for 18 hrs inorder to selectively remove the template i.e., $[PtI_6]^{2-}$.The resultant polymer after filtration was dried at 80^0C to obtain leached polymer particles for possible recovery of platinum from dilute aqueous solutions.

6.2.3 Synthesis of the control polymer (CP)

CP particles were prepared in a similar fashion as that of leached IIP particles but without the platinum ion. The resulting CP materials were subjected to same pretreatment as in the case of IIPs to compare their performance (i) for recovery of platinum(IV) from dilute aqueous solutions and (ii) for separation of platinum(IV) from selected inorganics.

6.3 CHARACTERIZATION STUDIES

6.3.1 X-Ray diffraction analysis

The XRD patterns of control polymer (curve A), leached (curve B) and un leached (curves C) of ion imprinted polymeric materials are given in *Fig.6.2*.The peaks obtained at 2θ values 7.07, 14.42 and 18.42 in the unleached polymer particles were absent in the leached one indicating that the platinum(IV) is completely removed from the particles during leaching.

6.3.2 UV-Visible Spectrophotometry

UV visible spectrophotometric determination of platinum(IV) present in leached solution of IIP particles confirms the quantitative removal of platinum during leaching of unleached polymer with 2 x 50 ml of 6M HCI for 18 h. These observations also confirms the XRD observation that platinum(IV) ions were absent in leached IIP polymer particles.

6.3.3 Scanning electron microscopy

The surface morphology of the synthesized polymer particles were evaluated using SEM. *Fig.6.3* shows the SEM micrograph of leached IIP particles. It can be seen that the polymeric particles having almost spherical shape and uniform sizes were obtained by the present method.

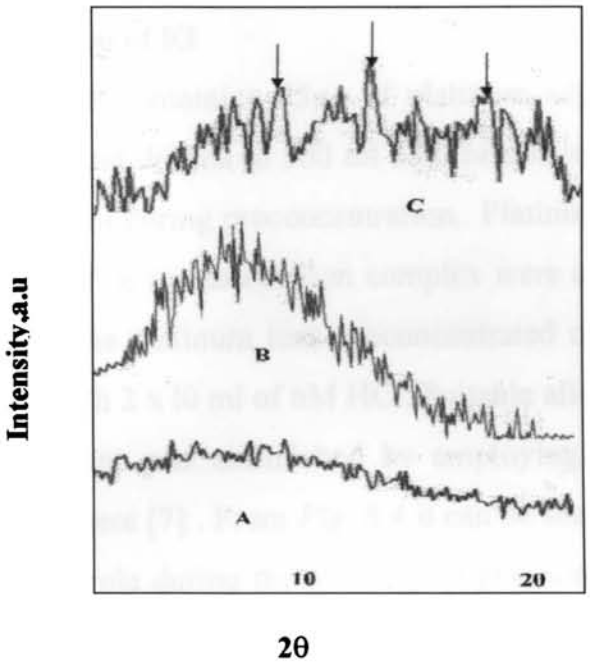

Fig.6.2: XRD patterns of Control (A), Leached (B) and Unleached (C) polymers

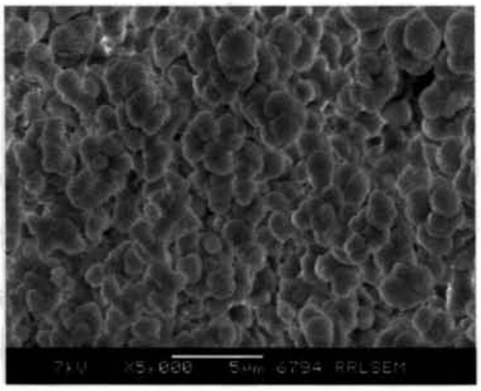

Fig.6.3: SEM micrograph of the leached IIP particles

6.4 OPTIMIZATION STUDIES

The influence of various parameters such as effect of acidity during preconcentration, weight of IIP particles, preconcentration time, elution time and the aqueous phase volume on the solid phase extractive preconcentration of platinum(IV) was studied using IIP particles.

6.4.1 Effect of concentration of KI

A portion of solution containing 25μg of platinum adjusted to pH 3.0 ± 0.2 taken in one litre beaker and diluted to 500 ml and the concentration of KI (0.01%) was varied from 0.1- 3.0 ml during preconcentration.. Platinum IIP particles (0.02 g) prepared using $[PtI_6]^{2-}$ $(VP^+)_2$ ion association complex were added to above solution and stirred for 30 min. The platinum ions preconcentrated onto above IIP particles were eluted for 30 min with 2 x 10 ml of 6M HCl. Suitable aliquots of the eluent were taken and platinum content was established by employing iodide-Rhodamine 6G procedure reported elsewhere [7] . From *Fig. 6.4* it can be seen that the concentration of KI plays an important role during the recovery of platinum. The lower recoveries at concentration below 0.30 ml are due to insufficient formation of $[PtI_6]^{2-}$ species. At I^- concentration > 1.0 ml of 0.01% KI is due to formation of iodo complexes of platinum other than $[PtI_6]^{2-}$. The percent extraction of platinum(IV) for IIP particles is higher at all concentrations of KI compared to CP particles indicating the imprinting effect.

6.4.2 Effect of pH

A set of solutions (volume = 500 ml) containing 25μg of platinum(IV) ions were taken and the pH of the solution was varied from 2-5 during the preconcentration. It can be seen from the *Fig 6.5* that an appreciable imprinting effect is noticed at all pHs in the case of IIPs compared to the CP. Also the optimum pH for the preconcentration was found to be 3.0±0.2.

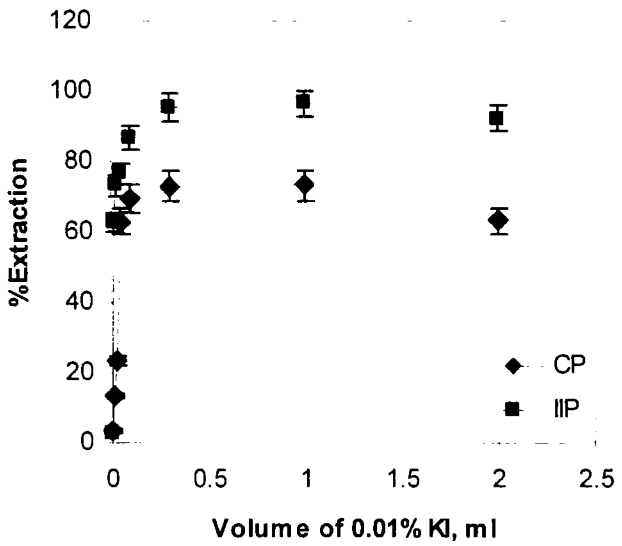

Fig.6.4: Variation of KI concentration on the percent extraction of platinum(IV)

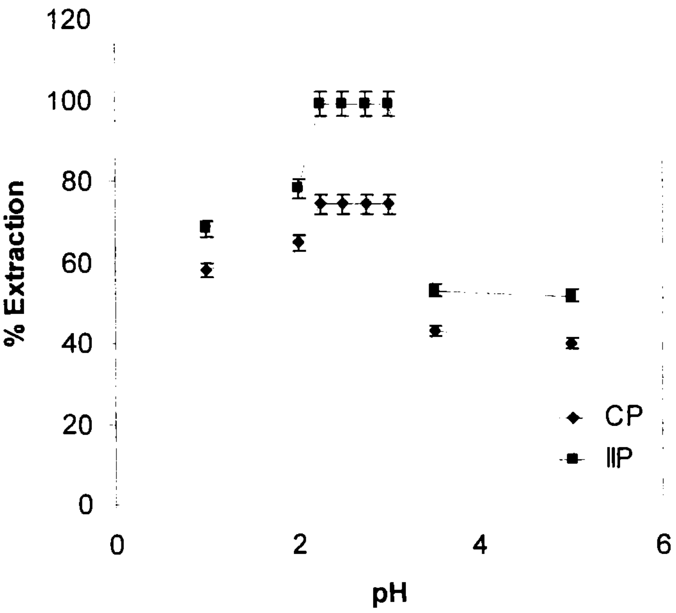

Fig.6.5: Effect of pH on the percent extraction of platinum(IV)

6.4.3 Effect of amount of polymer particles

The influence of weight of polymer particles (IIP or CP) on the percent enrichment of 25μg of platinum(IV) present in 500 ml of solution was systematically investigated. The results obtained are given in *Fig.6.6*, from which it is seen that (i) for quantitative preconcentration, a minimum of 0.020 g of platinum IIP particles are required and (ii) imprinting effect is noticed in all instances once again. Hence, 0.02 g of platinum IIP particles was used for subsequent preconcentration studies.

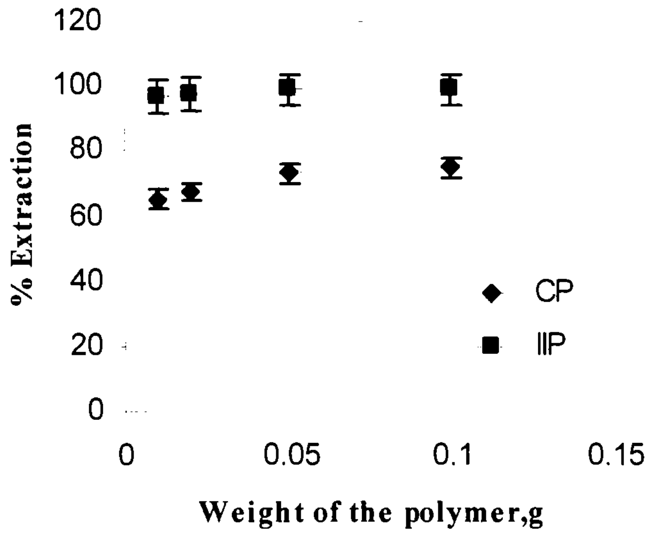

Fig.6.6: Influence of weight of the polymer on the percentage enrichment of platinum

6.4.4 Optimization of other experimental parameters

The other optimization studies carried out were compiled in *Table 6.1*. It can be seen from the table that 30min of stirring is necessary to quantitatively recover 25μg of platinum(IV) present in 500 ml of solution using 0.02 g of platinum IIP particles.

Further, it was established that stirring for 30 min with 2xl0 ml of 6M HCI is necessary for quantitative elution of platinum(IV) recovered with platinum IIP particles. The change of aqueous phase volume from 25 to 1000 ml indicates that the percent recovery of platinum (IV) was unaffected up to 500 ml.

Table. 6.1: Influence of other parameters on the percentage extraction of platinum

Parameters	Percentage recovery	
	IIP	CP
Preconcentration		
10	52.87 ± 1.0	52.0 ± 0.78
20	85.27± 1.2	68.5 ± 1.3
30	>99	73.0 ± 1.2
Elution time(min)		
10	52.8 ± 0.92	47.5 ± 0.95
20	85.24 ± 1.7	58.4 ± 0.87
30	>99	72.3
Aqueous phase volume(ml)		
250	>99	71.2 ± 1.0
500	>99	73.3 ± 1.3
1000	84.4 ± 1.6	52.1 ± 1.0

6.5 STATISTICAL AND CALIBRATION PARAMETERS

A set of solutions (volume1000 ml) containing platinum(IV) in the range 0-100 μg were adjusted to the pH 3.0 ± 1.0 after the addition of 0.4M citrate buffer and palladium content was established by as described in section 6.4.1 Under the optimum conditions described above, the calibration curve was linear over the concentration range of 0 -100 μg of platinum(IV) present in 0.5 litre of sample solution as evidenced from *Fig.6.7.* Five replicate determinations of 50 μg of platinum(IV) in 5.0 ml of solution gave a mean absorbance of 0.600 with a relative standard deviation of 2.50 %. The detection limit corresponding to 3 times the standard deviation blank was found to be 2.7μg l^{-1}.

The linear equation with regression is as follows.

$$A = 0.002 + 0.012C$$

Correlation coefficient = 0.9998

Where A is the absorbance and C is the amount of platinum in μg per 0.5litre of sample solution. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

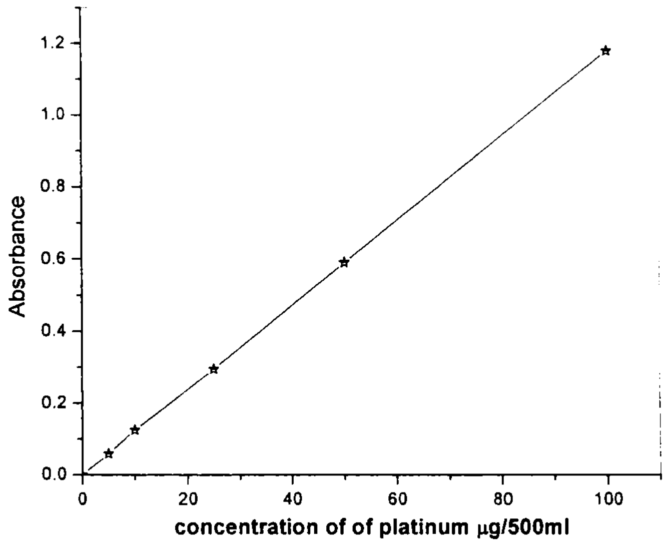

Fig.6.7: Calibration curve

6.6 RETENTION CAPACITY STUDIES

The retention/binding capacities of CP and IIP particles were determined by saturating 0.05g of polymer material present with 1mg of platinum(IV) under optimal conditions described above. The amount of platinum(IV) after saturation was determined spectrophotometrically after eluting with 2 x 10 ml of 6 M HCl. The retention/binding capacities of CP and IIP particles were found to be 20 and 27.5 mg per g of platinum polymer particles.

6.7 SELECTIVITY STUDIES

The percent extraction of platinum(IV), other noble metals viz. palladium(II), gold(III), ruthenium(III), rhodium(III), and the base metals were determined using both the CP and IIPs. The results obtained are given *Fig. 6.8* .The graph visually indicates the imprinting effect in favour of platinum on comparing i) increase in recovery of platinum with platinum IIP particles over CP particles and ii) decrease in recovery of other noble and base metals with platinum IIP particles compared to CP particles. The distribution ratio and selectivity coefficients of platinum over the other selected inorganics that coexists with platinum in its mineral deposits for CP and IIP particles were summarized in *Table 6.2*.

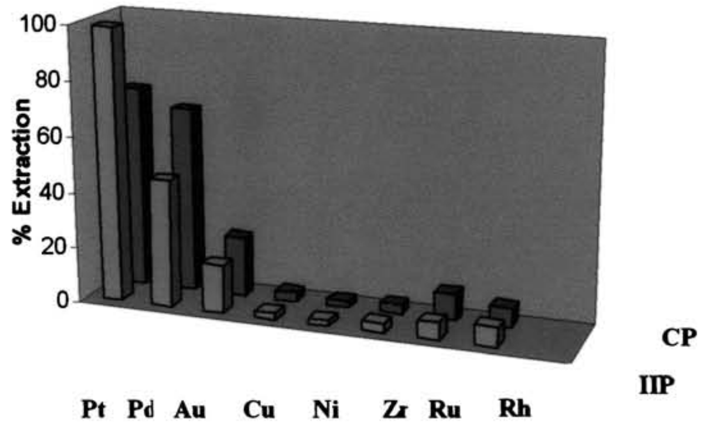

Fig.6.8: Percentage recovery of Pt and the coexisting ions using IIP and CPs

From *Table 6.2*, the following observations can be made,

1. The CP material shows minimal selectivity for platinum over precious as well as transition metals.

2. On imprinting, the selectivity coefficient $(S_{Pt}^{4+} /_{M}^{n+})$ increases, which indicate a reasonable preconcentrative separation of platinum(IV) from other metal ions that co exist along with platinum.

3. On imprinting , the % recovery and D values increase for platinum alone while lowering these parameters for other precious and base metals resulting in several fold increase in selectivity coefficients of platinum(IV) over other selected inorganics.

***Table.6.2*: Disrtibution ratio and selectivity coefficients of leched IIP and IRP particles**

Element	Distribution ratio(D)x 10^4		Selectivity coefficient (S)	
	CP	IIP	CP	IIP
Pt	6.82	247.5	-	-
Pd	5.10	2.17	1.4	113.7
Au	0.692	0.525	9.8	470.3
Cu	0.085	0.060	78.4	4125
Ni	0.0625	0.052	107.0	4690
Zn	0.0875	0.090	77.1	2690
Ru	0.272	0.170	25.0	1450
Rh	0.190	0.192	35.7	1295

6.8 EXPERIMENTAL

6.8.1 Reagents

A stock solution of 1000 μg $ml^{-1}$of platinum was prepared by dissolving 0.1g of platinum foil (99.99 %, Aldrich, USA) in 10 ml of aquaregia and diluted to 100 ml with deionized water. Rhodamine 6G (0.005% (w/v)) (Aldrich, USA) was prepared by dissolving 0.0125 g of reagent in 250 ml of deionized water. A 0.4 M citrate buffer (pH 4) was prepared by adjusting to 4.0±1.0 after dissolving 8.4 g of citric acid (E-Merck, India) and 11.8 g of trisodium citrate (E-Merck, India) in 100 ml of deionized water. Potassium iodide (E-Merck, India) (5%, w/v) was prepared by dissolving 5 g of KI in 100 ml of deionized water. 4-vinylpyridine (VP), 2-

hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Aldrich (Milwauke, USA). All other chemicals used were of analytical reagent grade.

6.8.2 Apparatus

A Shimadzu-UV-2401 PC controlled double beam spectrophotometer (Shimadzu, Japan) was used for preconcentration and separation studies. A Perkin-Elmer A Analyst 100 atomic absorption spectrometer (Perkin Elmer, USA) was used for measuring distribution ratios of copper, zinc and nickel during selectivity studies. A LI-120 digital pH meter (ELICO, India) was used for pH measurements.

6.8.3 General procedure for the preconcentration / separation of platinum

A portion of solution containing 25μg of platinum and 3ml of 0.01 % KI was taken in one litre beaker and diluted to 500 ml and the pH of the solution was adjusted to 3.0 ±0.2. Platinum IIP particles (0.02 g) prepared using $[PtI_6]^{2-}$ $(VP^+)_2$ ion association complex were added to above solution and stirred for 30 min. The platinum ions preconcentrated onto above IIP particles were eluted for 30 min with 2x10 ml of 6M HCl. Suitable aliquots of the eluent were taken and platinum content was established by employing iodide-Rhodamine 6G procedure reported elsewhere[7] .

6.9 CONCLUSIONS

The ion imprinted polymer particles of platinum(IV) was synthesized by making use of the ternary ion association complex template for the first time. The IIP particles showed significant imprinting effect on comparison with CP particles. As a result of imprinting, the distribution ratio as well as selectivity coefficients for platinum(IV) over the co-existing ions increase. This clearly establishes selective recovery of platinum from other noble and transition elements. The studies are in progress to evaluate a variety of ion association complexes of platinum as template for the recovery of not only platinum but also for other economically valuable metals and in the removal of toxic inorganics from wastes.

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CHAPTER 7

CONCLUSIONS

The concentration levels of platinum group metals (PGM) are very low in natural resources, metallurgical intermediates and environmental samples. Thus in recent years, the development of sensitive and reliable techniques for the preconcentration prior to determination of PGM has attracted great interest. It is envisaged that, the introduction of ion imprints on the lines of molecular imprinting provide vital breakthroughs in the preconcentration and / or separation of PGM. Studies carried out with this objective in mind are described below.

The introductory part of the thesis begins with the importance of platinum group metals (PGM) and a discussion on array of analytical techniques available for their quantization. The need for preconcentration prior to analytical determination is highlighted. Again, a summary of literature reports on such preconcentration procedures has been brought out. A curtain raiser to imprinting and detailed account of application of ion imprinting polymers in different areas has been brought out in this chapter. The chapter ends with a scope of proposed work in the area of ion imprinted polymer solid phase extraction of palladium(II) and platinum(IV).

Chapter 2 described the quantitative enrichment and selective separation of palladium(II) from dilute aqueous solution with palladium(II) IIP particles synthesized by using mixed ligand complex of palladium(II) as templates viz. palladium – dimethyl glyoxime – vinyl pyridine. Also the influence of post γ – irradiation of polymer particles revealed that even with half the amount of palladium(II) per g of unleached polymer, the quantitative enrichment was possible compared to unirradiated polymer particles.

In Chapter 3, the synthesis of palladium(II) IIPs using the ternary complex of palladium(II) with amino quinoline (AQ), hydroxyl quinoline (HQ) or mercapto quinoline (MQ) as one of the ligand and 4- vinyl pyridine as the other ligand was discussed. The imprinting effect was noticed in all cases but the AQ based IIP particles showed better preconcentration efficiency and higher selectivity coefficient compared to selected noble and other co- existing elements. The rebinding studies carried out also helped in the evaluation of binding parameters.

Chapter 4 described the three different polymerization methods viz. bulk, precipitation and suspension for the synthesis of palladium(II) ion imprinted polymers and the investigations of the analytical performances of the synthesized IIPs. The studies indicated the imprinting effect in all the three cases and the comparative account on the studies for palladium(II) regarding distribution coefficient, retention / binding capacity and selectivity (for palladium(II) over other selected inorganics) are in the order precipitation $\simeq$ bulk > suspension. Also the rebinding studies revealed that the binding capacities of the IIP materials obtained by bulk and precipitation method are almost same and for the beads obtained by suspension method have very low binding capacity compared to the other two IIPs, which is in tune with the analytical performance data of the three sets of polymers.

Chapter 5 described the synthesis of palladium(II) ion imprinted polymer via a new strategy i.e., the use of ion association complexes of palladium(II) as templates. The results obtained indicated that the thiocyante system is superior to the iodide system based on the analytical studies .The thiocyanate based IIP particles were used for the analysis of street / fan blade dust samples using FIA – AAS and the values obtained are quite comparable to the values obtained from standard ICPMS. Thus, the results obtained indicate the possible use of FIA – AAS for the routine monitoring of palladium(II) in environmental samples.

In Chapter 6 we described the synthesis, characterization and analytical application of platinum(IV) imprinted polymer prepared by using the ternary ion association complex of platinum as templates. As a result of imprinting, the distribution ratio as well as selectivity coefficients for platinum(IV) over the co-existing ions increase. This clearly establishes selective recovery of platinum from other noble and transition elements.

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