PRECONCENTRATIVE SEPARATION, REMOVAL AND SENSING OF SELECTED INORGANIC TOXINS

THESIS SUBMITTED TO
THE UNIVERSITY OF KERALA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY
UNDER THE FACULTY OF SCIENCE

By

DHANYA JAMES

CHEMICAL SCIENCES AND TECHNOLOGY DIVISION
NATIONAL INSTITUTE FOR INTERDISCIPLINARY SCIENCE AND TECHNOLOGY
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
TRIVANDRUM – 695 019
KERALA, INDIA

2011

Dedicated to the soul of my Achaachan,

For his lively and courageous styles…

For the inspirations, I got from the hard times of his life…

With a note of prayer, for his endless care and guidance from the top….

To my Amma,

The living motivation with me …

For her prayers, to survive and succeed….

DECLARATION

I hereby declare that the Ph.D. thesis entitled "**PRECONCENTRATIVE SEPARATION, REMOVAL AND SENSING OF SELECTED INORGANIC TOXINS**" is an independent work carried out by me at the Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum, under the supervision of Dr. T. Prasada Rao and the same has not been submitted elsewhere for any other degree, diploma or title.

In keeping with the general practice of reporting the scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Dhanya James

Trivandrum
18th April, 2011

NATIONAL INSTITUTE FOR INTERDISCIPLINARY SCIENCE AND TECHNOLOGY (NIIST)
(*Formerly Regional Research Laboratory*)
Council of Scientific & Industrial Research (CSIR)
Industrial Estate P O Trivandrum – 695 019, Kerala, INDIA.

ISO 9001 REGISTERED
DNV
MGMT. SYS.
RvA C 024
DNV Certification B.V., The Netherlands

Dr. T. Prasada Rao
Scientist G
Chemical Sciences & Technology Division

Tel: 91 471 2515317
Fax: +91 471 2491 712
E-mail: *tprasadarao@rediffmail.com*

18th April, 2011

CERTIFICATE

This is to certify that the work embodied in the thesis entitled **"PRECONCENTRATIVE SEPARATION, REMOVAL AND SENSING OF SELECTED INORGANIC TOXINS"** has been carried out by Ms. Dhanya James under my supervision and guidance at the Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum and the same has not been submitted elsewhere for a degree.

T. Prasada Rao
(Thesis Supervisor)

ACKNOWLEDGEMENTS

It gives me immense pleasure to place on record my deep sense of respect and gratitude to my thesis supervisor Dr. T. Prasada Rao for his encouraging guidance, practical advices, and constant motivation throughout the course of this work. His genuine attitudes and attentions were much inspiring and reassuring.

I would like to express my sincere thanks to Dr. Suresh Das, present director of NIIST; Professor T. K. Chandrasekhar and Dr. B. C. Pai, former directors, for their inspiring ideas and fruitful suggestions on this work and also for providing the necessary facilities and infrastructure of the institute to carry out my research work.

I express my sincere thanks to Dr. G. Venkateswaran, BARC, Mumbai, who was the collaborator for BRNS project and Dr. S. Bera, BARC facilities, Kalpakkam for XPS studies. I extend my warm gratitude to Dr. K. G. K. Warrier and Mr. Mukundan for their help in IR Spectroscopy and Surface area analysis. Thanks are also due to Dr. U. Syamaprasad and Mr. P. Gurusamy for XRD analysis, Mr. P. Prabhakara Rao and Mr. Chandran for SEM and EDS analysis and Mrs. Saumini Mathew for NMR and Ms. S. Viji for CHN analysis.

Financial assistances from the Board of Research in Nuclear Sciences, Bombay and the Council of Scientific and Industrial Research, New Delhi in the form of research fellowships are gratefully acknowledged.

I thank all the staff members of NIIST, Trivandrum who bid official support at various stages during my stay at NIIST.

It is with great most cheer I express my heartfelt thanks to my colleagues in the group

- *Dr. A. M. Starvin, Dr. J. Mary Gladis, Dr. V. M. Biju, Dr. C. R. Preetha, Dr. Sobhi Daniel, Dr. R. Kala, Dr. R. S. Praveen and Mrs. P. Metilda, my seniors during the initial stages of the research, with all support and encouragement.*
- *Mr. K. P. Prathish, Mr. Aneesh P. K., Dr. K. Prasad, Dr. Vishnu Vardhan and Mrs. Sumi. V. S, Mrs. Jaisy Joy, Mrs. Subha S. Kumar and Ms. Saritha S., as my co-workers, lending good suggestions and joyous company.*

- *Ms. Milja T. Elias, Ms. Dhanya S., Ms. Sindhu R., Mrs. Saumya Varghese, Mr. G. Karthik and Ms. Subha P. V., who joined to cheer up the days towards the end of my tenure and here I wish them good luck.*

I would like to thank the student community at NIIST who has been so friendly and supportive.

In this auspicious moment, I remember all my teachers with much gratitude for their affection and encouragement, from my schooling to masters.

Words are inadequate to express my gratitude to my beloved family members who supported me with good wishes throughout my student life. Finally my profound thoughts of gratitude towards my life partner, Mr. Jino George (SRF, NIIST) for his sharp and systematic styles and also to the budding life along with me, who will be joining us shortly.

Bowing my head in front of God Almighty for his finest care in each and every footsteps of my life. Trusting his endless blessings ahead….

Dhanya James

CONTENTS

CHAPTER 3: AMIDOXIME FUNCTIONALIZED IMPRINTED POLYMERS FOR URANIUM REMOVAL

CHAPTER 4: OPTICAL & ELECTROCHEMICAL SENSORS: AN OVERVIEW

List of Tables

List of Figures

List of Abbreviations

AA	Acrylic Acid
AIBN	2,2'-Azobisisobutyronitrile
AN	Acrylonitrile
CWE	Coated Wire Electrode
DCQ	5,7-Dichloro-8-hydroxy quinoline
DMSO	Dimethyl Sulphoxide
DOP	Dioctylphthalate
DVB	Divinylbenzene

EDS	Energy Dispersive X-ray Spectroscopy
EDTA	Ethylene Diamine Tetra Acetic Acid
EGDMA	Ethyleneglycol Dimethacrylate
FAAS	Flame Atomic Absorption Spectrometry
FET	Field Effect Transistor
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
HEMA	2-Hydroxy Ethyl Methacrylate
HLW	High-Level Radioactive Waste
IIP	Ion Imprinted Polymer
IIP_d	Dummy Templated Ion Imprinted Polymer
IPIM	Ion Imprinted Polymer Inclusion Membrane
ISE	Ion-Selective Electrode
ISFET	Ion-Selective Field Effect Transistor
IUPAC	International Union of Pure and Applied Chemistry
JAERI	Japan Atomic Energy Research Institute
LLE	Liquid-Liquid Extraction
M	Molar
MAGA	Methacryloylamidoglutamic Acid
MCL	Maximum Contaminant Level
MIP	Molecularly Imprinted Polymer
MMA	Methylmethacrylic Acid
NIP	Non Imprinted Polymer

NMR	Nuclear Magnetic Resonance
OFS	Optic Fibre Sensor
p (AA-co-AN)	poly (Acrylic Acid-Acrylonitrile) Copolymer
p (AA-co-AX)	Poly (Acrylic Acid-Amidoxime) Copolymer
PIM	Polymer Inclusion Membrane
PMMA	Poly Methylmethacrylate
PVC	Poly Vinylchloride
SA	Salicylaldehyde
SALO	Salicylaldoxime
SEM	Scanning Electron Microscopy
SPE	Solid Phase Extraction
TACN	N-[4-Vinylbenzyl]-1,4,7-Triazacyclononane
UCIL	Uranium Corporation of India Ltd.
USEPA	United States Environmental Protection Agency
UV	Ultra Violet
VP	4-Vinyl Pyridine
VPAN	4-Vinyl Phenylazo-2-Naphthol
WHO	World Health Organization
XPS	X-ray Photon Spectroscopy

PREFACE

Various types of natural and manmade processes increased our environmental pollution level colossally, which became a major issue where human struggles in many ways to survive. Among the different type of pollutants exist, inorganic pollutants need special attention because of their non-biodegradability unlike organics, i.e., they persist and build up in the environment. Certain inorganic species are well-known for their lethal toxicity when present in excess of their threshold concentrations. In recent past, uranium and its compounds are recognized as highly toxic like heavy metals (maximum permissible level in drinking water is 30 ppb) causing progressive or irreversible renal injury which may lead to kidney failure and death. Another inorganic specie, iodide also exerts harmful effects on health when present in excess (adjusted acceptable daily intake of iodine/iodide is 1.19 ppm). This has awakened the mankind to think about the importance of sensing, separation and removal strategies for inorganic toxins.

Researchers across the world have developed several techniques for treating the hazardous environmental samples in view of green science and technology. Advances in the analytical chemistry enabled scientists for the trace/ultratrace analysis of contaminants even in the parts-per billion (ppb) levels either directly or in conjunction with preconcentrative separation techniques like liquid-liquid extraction (LLE), ion exchange, nano/ultrafiltration, biosorption, coprecipitation, electrodeposition and solid phase extraction (SPE). SPE is currently being used widely for the selective preconcentrative separation or removal of toxic inorganics and is having many advantages over LLE technique. Among various sorbent materials employed in SPE, imprinted polymers have made a promising pathway for preparing materials with spatial recognition towards a target toxic molecule/ion through 'lock and key' mechanism. Metal ion imprinted polymer materials (IIPs), with similar recognition capacity as that of molecular imprinted polymers, can selectively rebind the template ion in presence of other inorganic ions. They find applications in selective separation, removal or sensing of target toxic inorganics present in aqueous solutions or contaminated natural waters, mining or industrial effluents, radioactive/nuclear wastes etc. **Chapter 1** deals with all these aspects of ion imprinted polymers as an efficient SPE sorbent.

Chapter 2 describes the synthesis of ion imprinted polymer for uranium using 5, 7-dichloro-8-hydroxy quinoline as uranophile. Various bivalent transition metal ions were screened as 'dummy template' for the preparation of uranyl imprinted polymer and nickel(II) templated IIP was found to have maximum affinity for uranium in styrene-divinyl benzene imprinted matrix. Imprinting effect was clearly explained in optimization studies with respect to non-imprinted polymer (NIP). The superior selectivity of IIP material for uranium over NIP among other inorganic ions was explained by the size and shape specific cavities created inside IIP. Use of low cost and less toxic nickel(II) salt as a substitute to uranyl nitrate enabled the synthesize of environmentally more benign imprinted materials, free from hitches like bleeding of original template, and ensure high sorption capacity and better separation characteristics. Effect of neutral electrolytes and metal ion mixtures on selective separation of uranium was studied to demonstrate the capability of dummy templated IIP for the preconcentrative separation of lower (ppb) concentrations of uranium present in complex matrices like seawater and nuclear reactor effluents.

Chapter 3 elucidates the synthesis of two sets of uranyl ion imprinted polymers using different amidoxime functionalities as uranophiles viz. i) a non-vinylated uranophile, formamidoxime (set I) and ii) a copolymer carrying both substrate anchoring carboxylic group and highly specific uranyl binding amidoxime functionality, namely (acrylic acid-amidoxime) copolymer (set II). Preparation of both sets of polymers was explained from binary and ternary complex mixtures of uranium followed by thermal copolymerization with 2-hydroxy ethylmethacrylate and ethylene glycol dimethacrylate as the polymer matrix. Extensive characterization of IIP & NIP materials and optimization of different experimental parameters were included in this work. Imprinted polymers prepared from ternary uranium complex mixtures showed high surface area and retention capacity than those formed from binary, which resulted in faster kinetics and high or comparable sorption capacities compared to existing uranium extractants. The applicability of the above prepared imprinted polymers for the removal of uranium from mining industry feed simulant solutions (using set-I polymers) and from simulated high level nuclear waste solutions (using set-II polymers) were successfully demonstrated.

An introduction to different types of sensors used in pollution monitoring is given in **Chapter 4.** It gives an overview of imprinted polymer based sensing platforms as well as potentiometric sensors using conductive materials. **Chapter 5** explains the fabrication of a two dimensional biomimetic IIP optode for the detection and quantification of uranium. Synthesis of a vinylated ligand, 4-Vinyl Phenylazo-2-Naphthol (VPAN) is highlighted and has been used as uranophile for the preparation of uranyl IIP. The sensing element was designed by the inclusion of uranyl IIP particles into polymethyl methacrylate followed by casting thin films on glass plates without any plasticizer. This imprinted polymer based optode exhibit superior selectivity over NIP optode. The applicability of the designed optode for analyzing ground, lake and tap-water samples collected in the vicinity of uranium deposits is successfully demonstrated in this chapter.

Microwave chemistry has its own impact in preparing novel inorganic materials with interesting physical properties. **Chapter 6** deals with the preparation of stable and conductive β-AgI using microwaves under pressurized conditions, followed by the fabrication of a simple and low cost heterogeneous iodide ion selective electrode (ISE). The developed ISE could respond to lower and wider range of iodide concentrations within 2 minutes with high selectivity towards iodide in the presence of interfering ions and has a lower detection limit of $1\text{x}10^{-8}$ M. Performance of this laboratory made ISE in the analysis of natural and sea water samples are quite encouraging on comparison with other ionophore based iodide ISEs and commercially available iodide ISEs.

In summary the thesis describes preconcentrative separation, removal and sensing of toxic uranium using imprinted polymers and also the potentiometric sensing of iodide using MW treated, highly stable β-AgI with their applications in various natural and simulant environmental samples. The whole work is well concluded in **Chapter 7**.

Chapter 1

INTRODUCTION:
Separation and Removal of Toxic Uranium

1.1 Introduction

Developments in science & technology brought out many advantages to the human society for a secure day to day life. But these advancements revealed a different facet of our mother earth where the natural environment is totally changed by the increasing level of pollution. It becomes much worse by various types of natural and man made processes, warning the existence of life on earth by causing terrible hazards towards public health and development. Pollutants come from different sources, enter into air, water and land in a variety of ways. Natural deposits of metals in earth crest also aggravate the accumulation of the respective metal contents in soil and water sources. But the amounts of various toxic chemicals disposed to environment from industries are high in the populated/industrial areas compared to the above mentioned natural deposits. All these toxic species finally target and accumulate inside the human body. The World Health Organization (WHO) estimates about a quarter of diseases that human beings face today occurs due to prolonged exposure to environmental pollution. So the United States Environmental Protection Agency (USEPA) has implemented various pollution monitoring & control methodologies to protect plants, animals, humans, wildlife, aquatic life, and the environment from the negative effects of pollutants and toxic substances.

Environmental pollutants are widely classified based on their nature and action on different parts of the environment. Among these classifications, chemical pollutants invite special attention because of their superior affinity towards many biological molecules which may lead to lethal toxicity. A general classification of chemical pollutants based on their chemical structure includes organic and inorganic chemical pollutants. Organic pollutants are those chemicals of organic origin or that could be produced by living organisms or are based on matter formed by living organisms. Common organic chemical pollutants include chlorinated solvents, polyaromatic hydrocarbons, polychlorinated biphenyl ethers, alcohols, trihalomethanes, phenols, plastics, pesticides/insecticides/herbicides, detergents, organo-metallic compounds etc. Inorganic chemical pollutants are mineral in origin and are not produced by any living organisms. Common inorganic chemical pollutants include metals and their salts originated from mining and smelting activities, as well as from disposed mining wastes, inorganic fertilizers (e.g., nitrates, phosphates) used in agriculture and gardening, sulfides (such as pyrite), ammonia, oxides of nitrogen and sulfur, acids and bases used in industrial applications, perchlorate etc. The wide spread use of all these chemicals in large amounts may pose a threat to environment and human health. This has awakened the mankind to think about the importance of separation of these pollutants from various environments and to develop removal strategies or sensor devices for these toxins to assure a green environment for life in addition to quality. In this chapter an overview of inorganic toxins and their separation or removal strategies using imprinted polymers are given as an introduction to the first part of the thesis where the separation and removal of toxic uranium is discussed.

1.2 Inorganic Toxins

Inorganic toxic substances in the environment are classified and ranked using their hazard measures. Compared to organic toxins, the range of inorganic toxins is rather limited and comprises about 100 elements together with organometallic compounds and the common anions. But these inorganic toxins are more alarmed for toxicity as they cannot be degraded or readily detoxified like organic toxins and gradually build up in the environment. The presence of metals in the environment can cause long-term environmental hazards. But all species of a particular inorganic toxin are not equally lethal while mostly depends on the nature of the specie in which it exists.

Among various inorganic elements present, elements such as iron, manganese, molybdenum, selenium, chromium, cobalt and iodine are identified as vital for growth and survival of both plants and animals. Several others like fluorine, nickel, tin and vanadium have shown to produce beneficial effects to health. They referred to as trace elements since they are required in only small quantities, unlike major nutrients such as N, P and K. However, excess dietary amounts of fluorine, iodine, molybdenum, selenium, vanadium etc. have high toxic effects and at the same time their deficiency can also result in health hazards. Important trace elements in the environment include As, Ag, B, Ba, Be, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V and Zn. Thirteen trace metals and metalloids are considered as priority pollutants, derived from both natural (geogenic) and anthropogenic sources and are listed in Table 1.1 [Adriano, 2001; Mandarino and Back, 2004]. Interrelation of two or more trace elements is important in some cases, like the well-established reciprocal antagonism of molybdenum and copper in many animal species. Regional geochemical reconnaissance surveys revealed that hyper cuprosis (copper deficiency) in cattle was linked with the presence of high molybdenum contents in stream sediments.

Table 1.1 *Natural and anthropogenic sources and common forms in wastes of trace metals on the priority pollutant list*

Element	Natural sources	Anthropogenic sources	Common forms
As	Metal arsenides and arsenates, arsenolite, volcanic gases, geothermal springs	Pyrometallurgical industry, smelting, wood preserving, fossil fuel combustion, poultry manure, pesticides, landfills	oxides,organo-metallic forms, arsinic acids
Cd	Zinc carbonate and sulphide ores, Cu-carbonate and sulfide	Mining and smelting, plastic industry, microelectronics, battery industry, fertilizer, sewage	halides and oxides, Cd-CN, $Cd(OH)_2$
Cr	Chromite, eskolaite(Cr_2O_3)	Metal finishing, plastic industry, wood treatment refineries, pyrometallurgical industry, landfills	Cr metal, oxides, Cr-ligand complexes
Cu	Native metal (Cu), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$)	Mining and smelting, metal finishing, microelectronics, wood treatment, refuse disposal, pyrometallurgical industry, swine manure, pesticides	Cu metal, Cu^{2+} ions, Cu oxides, Cu humic complexes, alloys,
Hg	Native metal (Hg), cinnabar (HgS), gaseous form	Mining and smelting, electrolysis industry, plastic industry, landfills, paper/pulp industry, fungicides	Hg^{2+}, Hg_2^{2+}, halides, oxides,complexes(org)
Pb	Galena (PbS)	Mining and smelting, iron and steel industry, paint and battery industries, automobile exhaust, pesticides	oxides & carbonates, oxyanion complexes
Se	Free element (Se), $FeSe_2$	Smelting, fossil fuel combustion, irrigation waters	oxides, complexes
Zn	Sphalerite (ZnS), Zn_2SiO4, $ZnCO_3$, sewage, pesticides	Mining and smelting, metal finishing, microelectronics, refuse disposal and landfills, pyrometallurgical industry	Zn metal, ions, oxides and carbonates, alloys

Major inorganic chemical pollutants include mineral acids, toxic metals such as lead, cadmium, mercury, hexavalent chromium etc. and mineral salts present in aqua systems. They are also found in industrial discharge, household wastewater, and seepage from municipal dumps and landfills. As the concentration of metals exceeds the ability of the soil to retain them, the metals will percolate in to ground waters or travel along with the leaching waters and finally reaches the surface waters. A number of elements and their compounds discharged in gaseous, liquid and solid forms have now been identified as responsible for various occupational and cognate diseases. Inorganic pollutants present in water can render it undrinkable, as well as cause cancer and birth defects. In addition, sufficient concentrations of these chemicals in aqua system can kill fish and other aquatic life, cause lower crop yields due to plant damage, and corrode metals.

The presence of excess of arsenic, mercury and cadmium in human being result in blackfoot [Friberg and Vostal, 1972], minimata [Tsuhiya and Keijo, 1969] and itai-itai [Jacobs, 1967] diseases respectively. The presence of excess asbestos and silica dusts cause specific lung diseases such as asbestosis and silicosis respectively. Considering this health hazard, the safe threshold values given for asbestos and silica dusts are 5 million particles per cubic foot for each [Cannon and Hopps, 1971]. In view of this, different national governments and pollution control agencies have put forward the maximum contaminant/ permissible levels for selected important inorganic toxins in drinking water, industrial effluent and sludge as given in Table 1.2. [Sharpe, 2001].

Table 1.2 *Potential toxic effects and maximum contaminant/permissible levels in drinking water, industrial effluent and sludge for some important toxic inorganics*

Pollutant	**Potential health effects**	**Maximum contaminant level (µg/ml)**			**Sewage sludge (mg/g)**	
		Drinking water (USEPA)	**Industrial effluents (Indian standards)**			
			Inland surface waters	**Public sewers**	**EU**	**USEPA**
Arsenic	Skin damage & increased risk of cancer	0.01	0.2	0.2	-	41
Cadmium	Kidney damage	0.005	2	1	20 - 40	39
Chromium	Allergic dermatitis	0.1	0.1	2	-	-
Copper	Gastrointestinal distress, Liver or Kidney damage	1.3	3	3	1000 - 1750	1500
Lead	Kidney problems and high blood pressure	0.015	0.1	1	750 - 1200	300
Mercury	Kidney damage	0.002	0.01	0.01	16 - 25	17
Nickel	Decreased body weight, heart and liver damage & skin irritation	-	3	3	300 - 400	420
Uranium	Increased risk of cancer, kidney toxicity	0.03	-	-	-	-
Zinc	-	5	5	15	2500 - 4000	2800

Two inorganic pollutants which will be dealt in this thesis are, i) uranium as UO_2^{2+} ions, which is well known for its chemical toxicity than its radiation hazards and occur naturally in mine deposits and used widely in nuclear industries. From both sources it may enter the surface waters and cause health hazards leading to death. Other pollutant of concern is ii) iodine as iodide (I^-), which is an essential nutrient for health but its excess dosages may cause severe dangers to human health. The thesis is compiled into two parts, where separation and removal of uranium from various environmental simulant samples are described in the first part and the sensing of uranium and iodide is dealt in the second part.

1.3 Uranium as an Emerging Toxic Pollutant

Amongst various toxic inorganic pollutants existing in the environment; uranium is a recently emerged pollutant as a persistent inorganic toxin. Toxicity of uranium was well known to humans before Becquerel discovered its radioactivity in 1896. Industrial activities and mining operations have exposed man to the toxic effects of uranium rather than natural uranium deposits and thus give an important share in environmental pollution. But uranium mining operations contaminate both groundwater and surface water as the uranium get seeped from milling and mining discharges, and general run-off from mining sites. The general population may be exposed to low levels of uranium by inhalation or through the diet. Uranium 238 is the most dangerous form to the human body and has the longest half-life of about 4.4 billion years. Uranium is having enough energy to break chemical bonds and therefore can destroy living cells. Its biological effects are very similar to other heavy metals like Pb, Hg, Cd etc. and has been identified as a nephrotoxine. The nephrotoxic effects of uranium are more likely due to its chemical properties rather than its radioactivity [Zamora *et al.*, 1998].

Biokinetics, metabolism and chemical toxicity of uranium, including its toxic effects on kidney function, are well established, there is a lack of published observations regarding uranium-induced reproductive and developmental toxic effects [Domingo, 1995]. The latest experimental studies in mammals have demonstrated that during pregnancy, maternal stress may enhance the metal-induced adverse effects on embryo/fetal and postnatal development [Domingo *et al.*, 2004]. Even if the kidney is a critical organ for uranium toxicity, the brain could also be a target organ after uranium exposure. Central effects were observed, even though uranium brain levels were very low [Linares *et al.*, 2007]. Many isolated studies were published on the mechanism for the toxic effects of uranium at moderate to high acute doses on experimental animals. However, from the ethical point of view, only a few works were done on the biological effects of chronic uranium intakes by humans [Blantz *et al.*, 1985]. Depleted uranium is a low-level radioactive waste product of natural uranium enrichment with ^{235}U for reactor fuels or nuclear weapons. The radiological hazard of depleted uranium is less than that from natural or enriched uranium. However, depleted uranium is also a heavy metal, its toxicity being a function of route of exposure, particle solubility, contact time and route of elimination. Consequently, depleted uranium exposure can result in both chemical toxicity and toxicity from radioactivity. Chemical toxicity (mainly on kidney) occurs in general at lower exposure levels than the radiological toxic effects. In contrast, insoluble compounds are poorly absorbed from the gastrointestinal tract and generally have low toxicity [Cantaluppi *et al.*, 2000; Domingo, 2001]. Irreversible renal injury caused by uranium may lead even to death which concerned the USEPA to set the safe limit of uranium as 30 ppb in drinking water. The EPA estimates that more than 500 community water systems nationwide in USA have uranium levels in the water greater than 30 ppb.

Nuclear energy is indispensable in future world energy scenario due to the scarcity of fossil fuels and the given inconsistency in hydro-power generation. Nuclear power provides over 16% of the world's electricity, almost 24% of electricity in OECD countries, and 34% in the EU. The world will need greatly increased energy supply in the next 20 years, especially cleanly-generated electricity. But the price of uranium is nearly tripled, in the last few years and the existing uranium resources are adequate up to 2030, if not 2050. So everybody is looking for advanced exploration techniques to discover more uranium deposits like new mines and mills and novel nuclear reactor technologies. Of course these are really needed to meet our energy requirements, but again the toxic nature of uranium is extending towards the environment both from natural resources and nuclear industries. At this juncture, the removal of uranium from these discharges (which may acidic, alkaline or neutral) is essentially required in view of its extreme toxicity and environmental aggressiveness.

The toxic properties and bio affinity of uranium invites attention for continuous monitoring of the toxic effects through various control measures followed by trace level detection in the environment. While executing these control measures, it is necessary to identify and assess the extent of pollution, in order to determine the degree and type of treatment required to render different wastes harmless particularly in view of the increasing demand for "Green science and technology".

Improvement of living standards without disturbing the environment is indeed a global challenge in the present scenario of population growth. Researchers across the world have developed several removal strategies for treating hazardous materials and thereby bring down toxin concentrations below their maximum permissible levels. As an introduction to the first part of the thesis we will be looking into various preconcentrative separation techniques for uranium (if economical) or removal of toxic uranium (down to ppb level) from various environmental samples.

1.4 Preconcentrative Separation Techniques for Recovery or Removal of Uranium

Detailed literature survey shows that the uranium recovery studies were conducted with various adsorbent materials which include both organic and inorganic supports. The removal of toxic inorganic species from complex matrices was made possible over the past few decades by several preconcentration techniques like (a) liquid-liquid extraction, (b) ion exchange, (c) nano/ultra filtration, (d) biosorption, (e) coprecipitation, (f) electrodeposition and (g) solid phase extraction [Rao *et al.*, 2001; 2006]. A bird's eye view of different methods used for the separation/removal of uranium is discussed below.

1.4.1 Ion Exchange

Ion exchange has been regarded as one of the traditional methods for the recovery of uranium. It allows the exchange of ions of like sign between an aqueous solution of contaminants and a resin of highly insoluble body in contact with it. Ion exchange resins consist of a positive or negative surplus charge which is compensated by mobile counter ionic species which is passed through a column of ion exchange resin and the exchangeable ionic species will get exchanged. Subsequently, the exchanged toxic ionic species can be removed from the resin by washing with a suitable solvent. The capacity of ion-exchangers relies upon the number of exchangeable counter ions in the resin [Hellferich, 1962]. But the selectivity of the exchange resins were often inferior in presence of other metal ions as in the case of Zeo Karb 226 resin, which cannot be used for the extraction of uranium from seawater as it contains various coexisting metal ions. Other resins containing uranophiles such as 8-hydroxyquinoline or resorcinol arsenic acid formaldehyde show a very good uptake of uranium, but were suspected for rapid deterioration with aging [Kanno, 1984]. This demands frequent replacement of resins thus resulting in tedious and time consuming operations. Some macrocyclic polydentate ligands like polymer-bound macrocyclic hexaketone were used to improve the selectivity [Tabushi *et al.*, 1979] but have shown slow kinetics and potential loss of the chelating agent after various cycles of usages which precluded its further development.

1.4.2 Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) is a technique based on the distribution of species of interest between two immiscible solvents. The proper choice of extractant, pH or acidity of the aqueous phase, immiscible solvent, masking and salting out agents and modifiers are important in LLE of inorganics [Morrison and Freiser, 1957; Ashbrook, 1984]. Ion exchange has been replaced by LLE in view of its simplicity, rapidity and ready adaptability to scale up. However, in the past few years, researchers are looking for innovative separation technologies to replace LLE in order to avoid the use of toxic and environmentally hazardous solvents and reagents leading to disposal problems and low enrichment factors (arising out of the mutual solubility of two immiscible phases).

1.4.3 Foam Separation

Surface-active agents are used to make foams to collect metal ions by separation. Lauryl amine ($CH_3(CH_2)_{11}NH_2$) and alkybenzyl ammonium chloride ($CH_3(CH_2)_{13}NH_2(CH_2C_6H_5)Cl$) were used for the effective separation of uranium from sea water. Another example where uranium is adsorbed on a positively charged ferric hydroxide collector and an anionic surfactant, sodium dodecyl sulfate was used to make foam by bubbling of air though the seawater [Kim and Zeitlin, 1971]. Ferric hydroxide enriched with uranium was floated in the surface as a stable froth and could be easily removed. Even though the method offer 82% uranium recovery, the surface-active agents cannot be recovered which make the method more expensive.

1.4.4 Co-precipitation

Coagulation and co-precipitation methods were also reported for uranium extraction by using precipitation agents like $Fe(OH)_3$, $Al(OH)_3$, $Ti(OH)_4$ and $Ca_3(PO_4)_2$ [Berg, 1963]. It requires very long operation times as the precipitation takes place slowly which make the process impractical with large volumes of samples.

1.4.5 Biological Separation

Living cells are known to concentrate cations from their aqueous environments. Microbial biomass has been documented to exhibit a selective retention of heavy metal ions. Polikarpov [1966] pointed out that radio-nuclides present in an aquatic environment are accumulated by marine micro-organisms through direct adsorption which is independent of the life functions of the microbial cells since dead cells also exhibited this property as well as or better than live ones, supporting the hypothesis of physical and chemical retention of uranium ions by the microbial cells. The phenomenon of retention of cations from solution by dead microbial cells has been termed “biosorption” [Tsezos and Volesky, 1981]. Several types of biomasses have been reported to be used for uranium adsorption like algae, fungi, bacteria, actinomycetes etc. and other biological substances including acid polysaccharides and phosphorylated polysaccharides (chitin phosphate, chitosan phosphate, cellulose phosphate). Lyophilized biomass shows higher uranium sorption. The maximum loading obtained in the case of Pseudomonas sp. was 24.5% (245 mg-U/g dry biomass) dry weight of the biomass at pH 3.5 and for Talaromyces mersonii CBS 814.70 it was 323 mg-U/g dry biomass [Bengtsson *et al.*, 1995]. Streptomyces viridochromogenes and Chlorella regularis cells immobilized in polyacrylamide gel was used for uranium recovery from sea water because of its good mechanical properties and applicability in a column system. The immobilized cells can repeatedly recover uranium almost quantitatively from both fresh and sea water containing uranium. The major advantages of biosorption over conventional methods include low cost, high efficiency, minimization of chemical or biological sludge, and regeneration of biosorbent and possibility of metal recovery. But, low adsorption capacities and problems of making contact with microorganism in sample matrices are the disadvantages of bioseparation.

1.4.6 Filtration Techniques

Nanofiltration is a form of filtration process to separate and remove the toxic metal ions by using filter membranes. It is a pressure driven separation process with performance characteristics between reverse osmosis and ultrafiltration and takes place on a selective separation layer formed by an organic semi-permeable membrane. Nanofiltration membranes show a high selectivity for uranium illustrating the advantageous use of nanofiltration for the concentration of uranium from sea water. Ultrafiltration, another filtration process also uses a membrane that is partially permeable to perform separation, but the membrane pores are typically much larger than that are used in nanofiltration [Schaefer *et al.*, 1994].

1.4.7 Electrodeposition

Electrodeposition becomes a useful separation method when the product of an electrochemical reaction is insoluble in the solution phase and deposits on an electrode. The electrodeposition is usually carried out in an electrolysis cell, which essentially consists of two or three electrodes immersed in the electrolytic solution. Diffusion, convection and electrolytic migration are the three processes which regulate the movement of toxic inorganic species to the electrode [Vogel, 1989].

1.4.8 Solid Phase Extraction (SPE)

Solid phase extraction is currently being widely used for the separation or removal of toxic inorganic species. It has been well established as a versatile preconcentrative separation method over the past 2 to 3 decades in view of high enrichment factors, low reagent consumption, and reusability. SPE as an enrichment technique deserves much significance where low concentration of analytes has to be detected and removed selectively from complex matrices.

The basic principle of SPE is the transfer of toxic inorganic species from the aqueous phase to the active sites of the adjacent solid phase; it can also be termed as solid-liquid extraction. The transfer is simulated by the selection of appropriate optimal conditions in the system of 3 major components - water (liquid phase), target metal ion and sorbent [Junker-Bucheit and Witzenbacher, 1996]. The sorbed metal is then removed from sorbent with a suitable eluent (See Figure1.1). The mechanism involved in SPE depends on the nature of the sorbent and toxic species to be removed. SPE can be carried out by means of adsorption, ion exchange, chelation, ion pair formation etc.

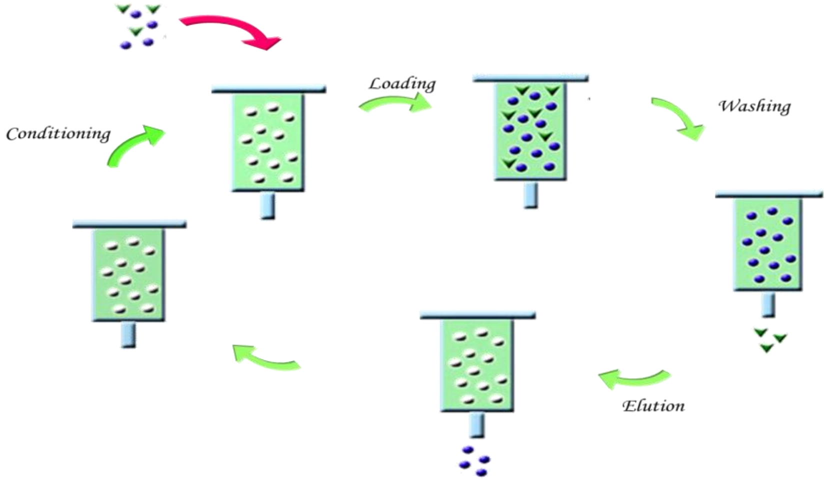


Figure1.1 *Steps involved in solid phase extraction process*

Hitherto, LLE was most often used for separation or removal of various toxic inorganic species in view of its simplicity, rapidity, ready adaptability for scale up studies, easy removal of toxic metal species and recycling of extractant. SPE offers several advantages over LLE [Thuman and Mills, 1998; Simpson, 2000]. These include

(a) flexibility

(b) absence of emulsion

(c) low cost because of lower consumption of reagents and

(d) environmental friendly.

The sorbents employed in SPE can be broadly classified into inorganic based (inorganic oxides) and organic based (natural and synthetic polymer) sorbents (See Figure 1.2). The most important inorganic based sorbents are silica gel, C18 bonded silica gel, modified silicas, alumina, florisil, diatomaceous earth, titania and zirconia. However, these inorganic based sorbents are beset with an additional problem due to the formation of suspensions. Hence, organic based sorbents are more popular and have been divided into polymeric and non-polymeric sorbents.

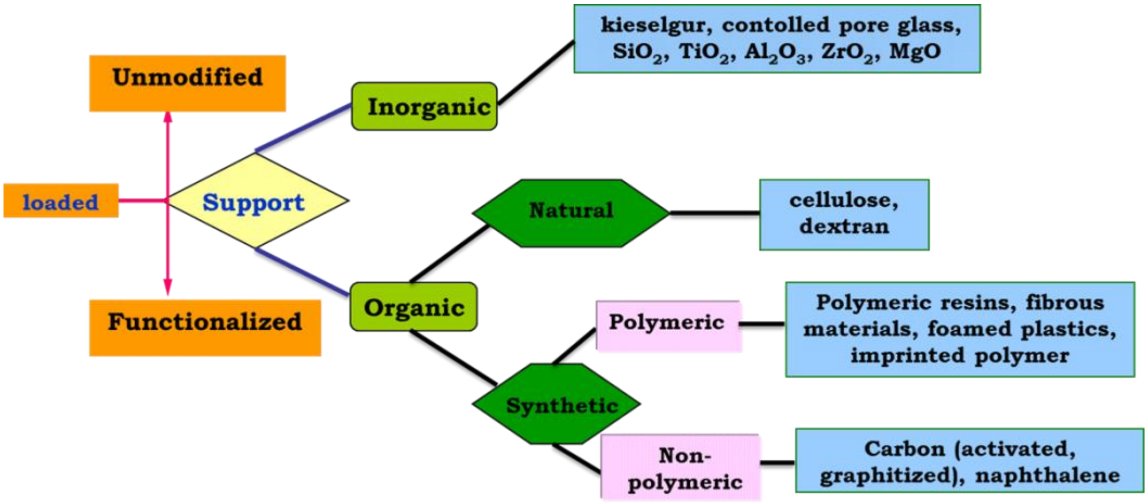


Figure 1.2 *Various sorbents used for solid phase extraction*

1.4.8.1 Solid Phase Extraction of Uranium

The concentration of uranium in many of the environmental and nuclear waste samples is very low to develop any commercial process for the economic recovery or selective removal. This demands stringent requirements on the properties of the adsorbent selected for uranium separation. Several SPE sorbents were reported for uranium extraction from dilute aqueous solutions by mechanisms like co-precipitation, sorption, chemical immobilization and polymer inclusion. Both unmodified and functionalized materials were used as extractants in SPE including natural polymers as well as synthetic polymers.

Hydrous TiO_2 was used as a promising inorganic SPE adsorbent since 1960's in UK, France, Germany and Japan for the collection of uranium from seawater. The adsorption ability of the hydrous titanium oxide reported by the Agency for Natural Resource and Energy (ANRE), MITI, and Metal Mining Agency of Japan was 0.1g-U/kg-adsorbent, which was too low for practical applications [Saito, 1980]. The adsorbent was mechanically not strong enough for seawater applications. Degradation of TiO_2 was reported by the usage of acidic eluents. Longer elution step makes this adsorbent a time consuming one. Activated carbon has also been used as an inorganic support for the absorption of uranium from seawater with a capacity of 500 $\mu g\ g^{-1}$ of carbon. But the adsorption rate highly depends upon the type of the carbon source used [Gregg and Folkendt, 1982]. Another inorganic material used for the purpose is Galena (PbS) and showed better adsorption properties (1100 μg/g PbS) compared to hydrous TiO_2 [Yun, 1982]. Galena can be used for several cycles and regenerated. Granulated lignite (brown coal) is used to provide an adsorption matrix with which sea water is brought into contact enough to reach a substantially maximum adsorption of uranium. Eventhough, about 3 mg of uranium per kg of dry granular (0.5-2.0 mm) lignite is adsorbed, the adsorption falls off when there is a substantially greater concentration of foreign ions like calcium, magnesium and sulphate. Wagener and Heitkamp [1980] have described an economical recovery of uranium ions utilizing an adsorbent matrix which comprises of biologically recent humic acids (found as recently as several thousand years ago) and natural black peat as the carrier material. The present status of all such research has been subsequent stoppage due to low recovery efficiency.

1.4.8.2 Use of Polymers as Adsorbents for Uranium

Micro and macroporous polymers containing various functionalities like N, N-dimetholacrylamide modified dihydroxamic acid polymer, amino acids and/or polyamino acid modified poly (2-hydroxyethyl methacrylate) beds etc. were used for uranium extraction. The higher flexibility and durability of these metal-chelating ligands as well as significantly lower material consumption and manufacturing costs are also very promising for applications.

Polymers, copolymers and fibres containing amidoxime as suitable uranium ligands (uranophiles) have been used for the selective separation of uranium from aqueous solutions [Güler *et al.,* 1997; Şahiner *et al.*, 1998; 1999; 2000; Pekel, *et al.*, 2000] and sea water [Kabei, 1994; Okamoto *et al.*, 1985; Omichi *et al.*, 1986] due to the efficient binding of amidoxime groups with uranium and the rapid kinetics offered by this uranophile at neutral or weakly alkaline conditions. Sugo *et al.* [2005] from Japan Atomic Energy Research Institute (JAERI) have patented a process for the recovery of uranium from sea water culminating in production of yellow U_3O_8 utilizing amidoxime fibre. They have used fibres of a polyolefin such as polyethylene or polypropylene which are grafted to the substrate polymer by radiation-initiated graft polymerization, and then amidoxime and a hydrophilic group are introduced into the same grafted side chains (See Figure 1.3 for synthesis scheme). Sugo and his coworkers [2005] were successful in producing 2 g of yellow uranium oxide cake employing 1 Kg of radiation grafted amidoxime functionalized polyethylene fibre from seawater in ~ 60 days (See Figure 1.4). However, it is reported that the uranium so produced contains 30% and 150% amounts of nickel and vanadium(V) compared to uranium itself and requires further purification. Moreover, it is also observed that a 20% decline in sorption capacity occurs after 5 uses.

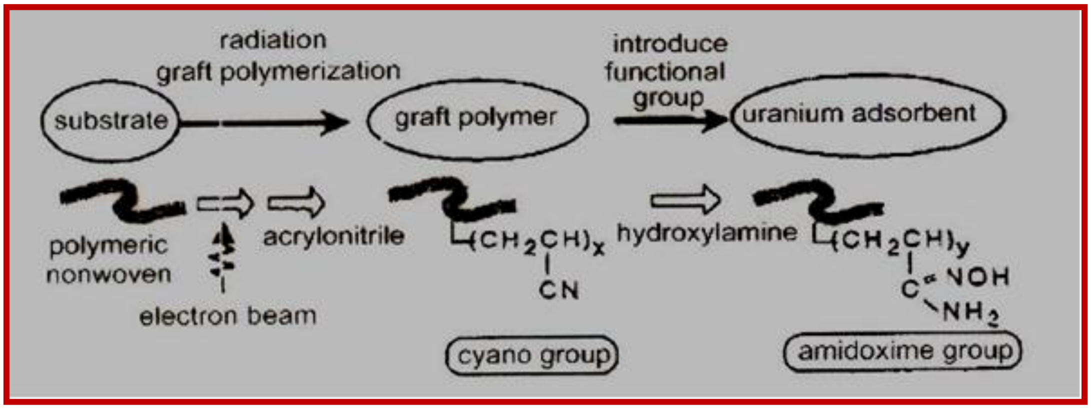


Figure 1.3 *Adsorbent production process by radiation induced graft polymerization*

The cost of uranium recovered from seawater was estimated to extract the technical problems in the practical application of the fibrous amidoxime adsorbent synthesized by radiation graft polymerization. The cost of the adsorbent production, the dipping in seawater for uranium adsorption and the uranium elution from the adsorbent were estimated in three different mooring systems of a buoy, floating body and chain binding system was estimated to be 5-10 times of that from uranium mining. The cost can be reduced to half by the reduction of the equipment weight and also by looking for better adsorbents.

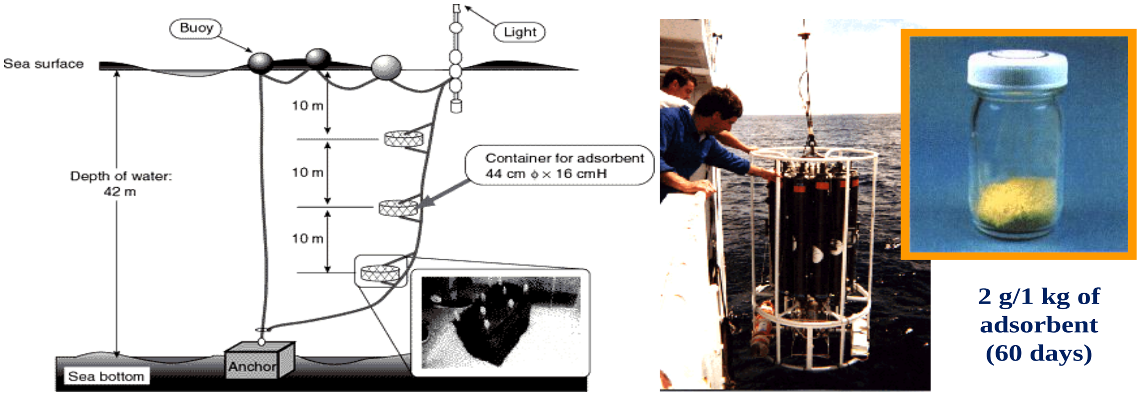


Figure 1.4 *Process of recovery of uranium from seawater by JAERI and the uranium recovered from sea water*

1.4.8.3 Developing New Materials to Improve Selectivity and Sorption Kinetics of Uranium Extractants

Enormous studies have been carried out to supersede the drawbacks of the existing adsorbents for uranium. Selectivity is the most important criteria in uranium separation or removal because in almost all the cases whether it is seawater or nuclear waste, uranium coexists with a number of other interfering metal ion species. So treatment of complex environmental samples became great challenge to the researchers in order to develop efficient absorbents with high selectivity for uranium in addition to high sorption capacities. The sorbents must be chemically very stable and durable during repeated sorption/elution cycles in order to make the process economically competitive.

TiO_2 sorption systems for uranium were failed mainly due to the large loss of the material during uranium collection process. The performance of the amidoxime-based sorbents was also found to deteriorate after repeated usages. Eventhough the current pre-concentration methods based on SPE are very fast but not selective and economical and usually not suitable for harsh environments. Most of these sorbents used in SPE are non-selective like ion exchange and are not that popular as of now for separation of uranium from various complex sample matrices. Improved synthetic routes have to be implemented for the preparation of uranium sorbents with specific ligands which can offer improved selectivities. High stability of the adsorbent backbone can help the functionalities from breaking down in acidic sorption/elution steps and thus significant reusability can be achieved. Suitable functionalization can improve the hydrophilic nature of the adsorbent which may increase the sorption rate of uranium ionic species. By the introduction of imprinted polymer technology, a new platform has been introduced for polymer based solid phase extraction. They are more advantageous with high sorption capacity and shows very good selectivity towards the imprinted analyte when coexist with several interfering species. The novelty of imprinted polymers as efficient solid phase extractants followed by their application for the removal or separation of toxic inorganics is described below.

1.5 Molecularly Imprinted Polymers (MIP) as Novel Solid Phase Extractants

A new era of solid phase extraction has been initiated by the introduction of molecularly imprinted polymers (MIP), without any vices remain with the existing adsorbents. Imprinting is a versatile technique for creating macromolecular matrices that display selective recognition behaviors. This has shown remarkable promise as a technique for preparing materials with spatial recognition towards a target toxin by mimicking the “key” and “lock” principle. Imprinted polymers are prepared by the copolymerization of functional and crosslinking monomers in presence of template which may be an ion or a molecule. Essentially three steps are involved in the preparation of an imprinted polymer. The functional monomers are allowed to self-assemble with the imprint ion to form the complex in the first step, followed by a second step where polymerization occurs in presence of a crosslinker by which the functional groups are held intact inside the highly crosslinked polymeric matrix. Subsequent leaching of template in the third step generates binding sites that are complimentary in size and shape to the template [Sellergren, 2000; Yilmaz *et al.*, 2000]. Thus, memory sites are introduced into the polymer, which are now capable of rebinding the imprint template selectively [Haupt, 2001]. The concept of molecular imprinting technology is described in Figure 1.5.

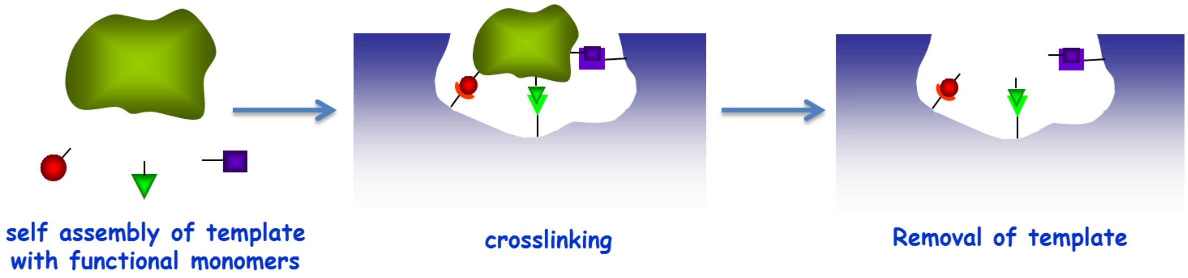


Figure 1.5 *Schematic representation of the imprinting process*

Two fundamental approaches of molecular imprinting are covalent or preorganized approach [Wulff and Sarhan, 1972] and the non-covalent imprinting or self-assembly approach [Mosbach *et al*., 1981]. In covalent imprinting the template and monomer interact via reversible covalent bonds in the pre-polymerization mixture and the rebinding of the template is dependent on the formation and cleavage of these bonds. The non-covalent approach explains the template - monomer interactions via non-covalent bonding and the subsequent rebinding also. Another strategy, named semi-covalent approach was also used [Whitcombe *et al.*, 1995] which takes the advantages of the combination of covalent and non-covalent approaches, where covalent bonds being used in the imprinting step followed by non-covalent interactions in the rebinding step after the leaching of template from the polymer matrix.

An especially appealing feature of the imprinted polymers is their potential to have the affinity and selectivity analogous to antibodies, while offering several benefits including greater stability in harsh environments such as acids, bases, organic solvents in addition to their ability to withstand high temperatures and pressures. The trends in synthetic approaches of MIPs opens up possibilities for newer preconcentrative separations, sensing and membrane based technologies [Uezu *et al.*, 1997].

1.6 Metal Ion Imprinting

Ion imprinted polymers (IIPs) are synthetic materials similar to MIPs but selectively recognizes ionic templates provided with selective binding sites. These materials are obtained by polymerization around a template ion with functional and cross-linking monomers chosen, taking into account their ability to interact with the functional groups of the template. A highly cross-linked three-dimensional network polymer is formed of binding sites with size, shape and functionalities complementary to the template. These imprinted materials possess remarkable features such as large number of binding sites, high surface area and porosity, faster binding and rebinding kinetics, selective affinity, thermal/mechanical/chemical robustness and stability which made them better candidates for the selective removal of toxic metals from hazardous complex matrices.

Metal ion imprinted polymers were historically introduced by Nishide *et al.* [1976] on the lines of Prof. Wulff’s [1995] and Prof. Mosbach’s [1994] strategies of covalent and non-covalent molecular imprinting. They have prepared IIPs for Cu(II), Zn(II), Co(II), Ni(II), Hg(II), Cd(II) etc. using a complexing agent 1,4-dibromobutane followed by cross-linking with poly(4-vinylpyridine) as shown in Figure 1.6. Each IIP showed selectivity towards its own template rather than other metal ions. Later copolymer of diethylvinylphosphonate and acrylic acid was used to complex metal ions by Kabanov *et al.* [1979] and cross-linking was carried out using N, N'-methylene diacrylamide. Further the area has grown into fully developed technology by numerous ion imprinted polymers and their potential applications especially in the removal of inorganic toxins from the environment.

A survey on the synthesis of metal ion imprinted polymers show that they may be roughly classified by the following four approaches based on the way of incorporation of ligands in the polymer matrix viz. (i) linear chain polymers carrying metal-binding groups being cross linked with a bifunctional reagent (Figure 1.6) [Nishide and Tsuchida, 1976], (ii) chemical immobilization by preparation of binary complexes of metal ions with ligands having vinyl groups, isolation and then polymerization with matrix-forming monomers (Figure 1.7) [Bae *et al.*, 1999], (iii) surface imprinting conducted on aqueous-organic interface and (Figure 1.8) [Yu *et al.*, 1992],

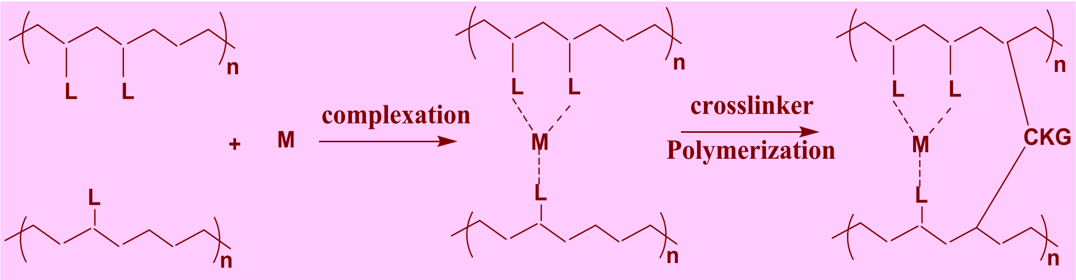


Figure 1.6 *Linear chain polymers bearing metal-binding ligands*

(iv) double template imprinting (Figure 1.9) [Dai *et al.*, 1997], (v) trapping of non-vinylated chelating ligand via imprinting of binary/ternary mixed ligand complexes of metal ions with non-vinylated chelating agent and vinyl ligand (Figure 1.10) [Prasada Rao *et al.*, 2006] and (vi) ion association based imprinting (Figure 1.11) [Daniel *et al.*, 2006].

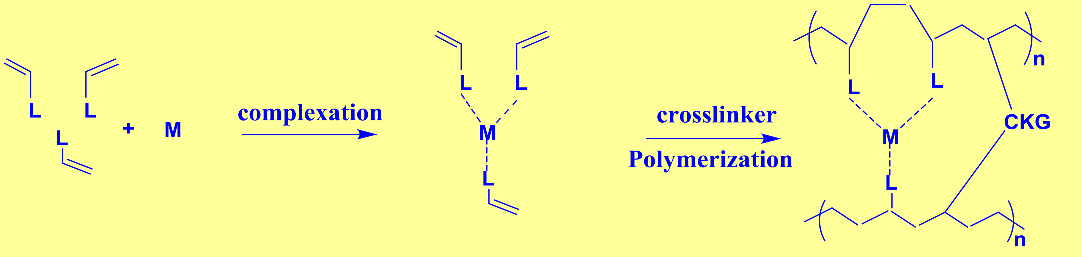


Figure 1.7 *Polymerizable metal-binding ligands having vinyl groups*

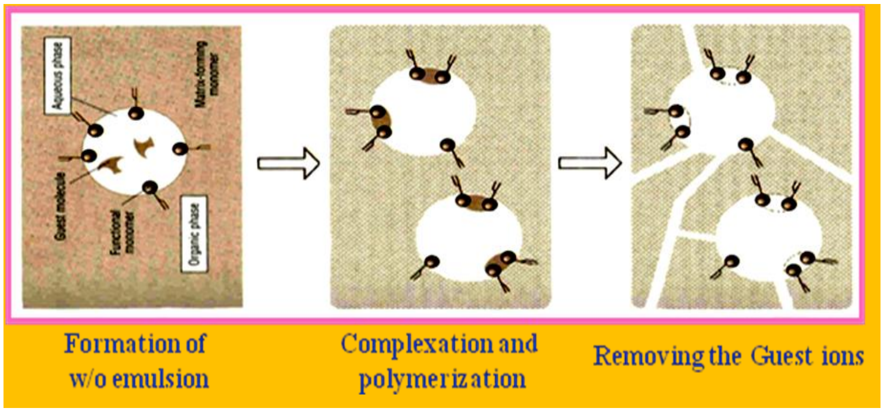


Figure 1.8 *Surface imprinting*

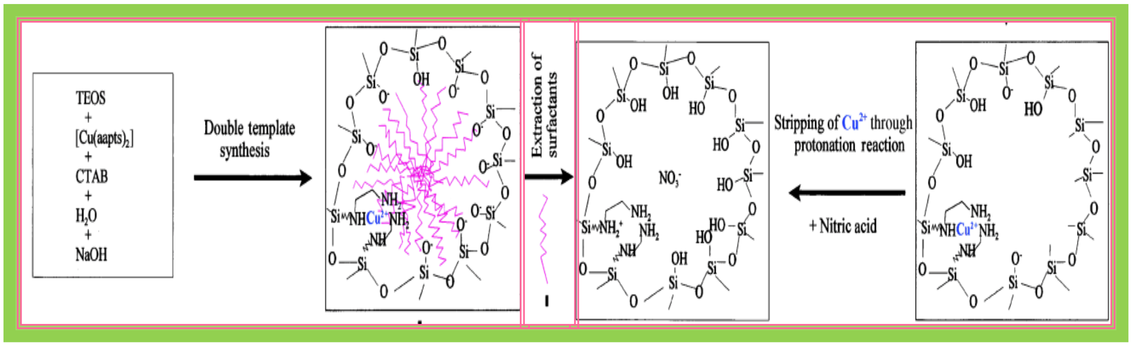


Figure 1.9 *Double template synthesis*

The last two approaches developed Rao *et al.*, in which the one involving trapping of non-vinylated chelating ligand have shown to possess several advantages over other approaches of metal ion imprinting in terms of higher retention capacity and selectivity in addition to the use of simple, low cost (as they do not require vinylation of chelating ligand) and commonly available ligands. The synthesis of metal ion imprinted polymers can be performed either via one-pot synthesis of the imprinted polymer where metal specific ligand, metal salt, other functional monomers and cross-linker are taken together and subjected to polymerization, [Vigneau *et al.*, 2001; 2003] or by a two-step process where the metal-ligand complex is isolated in the first step and then it is used for the polymerization with the crosslinker [Kuchen and Schram, 1988; Bae *et al.*, 1999].

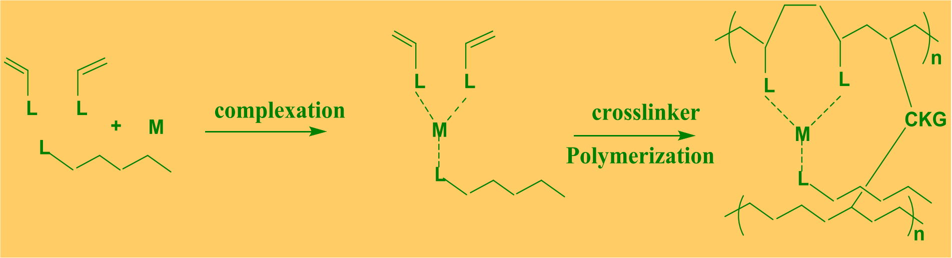


Figure 1.10 *Trapping of non-polymerisable metal-binding ligands*

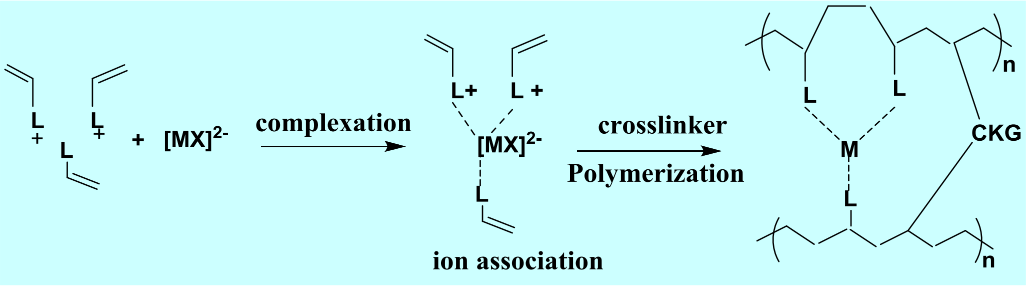


Figure 1.11 *Polymerizable metal binding ionic ligand*

Apart from the above discussed approaches a variety of imprinting polymerization methods like bulk, precipitation and suspension exist and found applicable in various fields

[Daniel *et al.*, 2005]. Majority of metal ion imprinted polymer were synthesised by bulk and surface imprinting, which exhibit prominent selectivity for particular metal ions [Prasada Rao *et al.*, 2006].

Various factors are believed to be crucial in determining the high performance and selectivity of these polymers. Multiple site interactions of template ions with the functional monomers yield high binding strength to polymer and reliable recognition for metal ions depending on the number and type of interaction sites. Shape and size of each template as well as the specific geometry of the template-monomer (ligand) complex play a unique role in achieving quantitative rebinding for specific metal templates. A better fit between the site and the template lead to less entropy loss due to the conformational changes in the binding site as well as in the template upon rebinding causing an increase in the affinity and selectivity during recognition. Kinetic considerations on template rebinding are due to the formation constants of metal ion with specific ligand which can predict the selectivity of a chosen IIP for its template when present with similar ionic interferents. Cross linking density of the polymer matrix offer a rigid seating to the functional monomers/ligands in order to hold them tightly in their exact positions without any relaxations even after leaching with mineral acids. Lower crosslinking may allow the functional ligands to relax upon the removal of templates during leaching. So proper crosslinking is essential for the preparation of each ion imprinted polymer in order to facilitate the reorientation of the ligand functionalities on approach of template during rebinding. Various polymerization methods allow different formats for imprinted polymers viz. particles, beads or micro/nano spheres [Sellergren 2001; Perez-Moral and Mayes, 2003]. Nature of porogens, polymerization methods and temperature needed for polymerization etc. also have definite responsibilities in defining the nature and characteristics of ion imprinted polymers. These features enable IIPs to find many applications like separation, removal and sensing of inorganic toxins.

1.7 Ion Imprinted Polymers for Uranium

Ion-imprinted polymer based SPE became a most popular technique for preconcentration and removal of trace uranium. Their remarkable features such as large number of binding sites, high surface area and porosity, faster binding and rebinding kinetics, selective affinity, thermal/mechanical/chemical robustness and stability which make them better adsorbents for the selective separation or removal of uranium from various environmental samples. Many IIPs were reported for the selective removal of uranium as this technique provides higher enrichment factors and selectivity coefficients compared to non-imprinted polymers [Rao *et al.*, 2004]. They could successfully implement for applications in uranium extraction and treatment of nuclear effluents [Bae *et al.*, 1999; Saunders *et al.*, 2000; Preetha *et al.*, 2006].

1.7.1 International Scenario

The invention by John *et al.* [1999] describe the detection and extraction of uranyl ions by polymer imprinting, wherein the complexable functionality used was halogen-substituted carboxylic acids. The preparation of mesoporous sorbent materials were described by Dai *et al.* [2001] via embedding binary complex templates of uranyl ion with bifunctional ligands such as amines, sulphonic acids and phosphonic acids. But these inventions do not describe the extraction characteristics of other competitor metal ions. Saunders *et al.* [Saunders *et al.*, 2000] reported a modified method for the preparation of uranyl IIP material by copolymerizing chloroacrylic acid and EGDMA, which after removal of template selectively extracts uranium from dilute aqueous solutions containing +2, +3 and +4 competitor metal ions. Bae *et al.* [1999] have synthesized IIP resins for uranyl ion based on the isolation of binary uranium-vinyl benzoic acid complex and copolymerizing in presence of styrene and DVB. These resins were used for enriching of uranyl ion from aqueous and sea water solutions prior to its quantification. The authors have not studied the extraction ability of non-imprinted polymeric resins, i.e. imprinting effect has not been demonstrated. Dai and coworkers [2001] investigated the properties of sol-gel glasses templated with uranyl ions. They observed a significant increase in affinity and selectivity of the imprinted sol-gel sorbents over non-imprinted polymer based sorbents, while the surface areas remained equal. An IIP material was prepared with methacryloyl amidoglutamic acid (MAGA) and ethylene glycol dimethacrylic acid (EGDMA) and was used for selective separation of uranyl ions from aqueous solutions [Gladis and Prasada Rao, 2003]. MAGA was chosen by these authors as the glutamic acid molecules are linked to the polymer backbone through primary amine groups and the pendant carboxyl groups are responsible for complexation of uranyl ion. Murray *et al.* [Kimaro *et al.*, 2001] have developed ionically permeable imprinted membranes for uranyl ion using vinylbenzoic acid and vinylsalicyladoxime.

1.7.2 National Scenario

Gladis *et al.* [2003] have prepared uranyl ion-imprinted polymer particles using 5, 7 dichloro 8-hydroxy quinoline (DCQ) as the uranophile. Uranyl IIPs were prepared by copolymerizing ternary mixed ligand complex UO_2^{2+}-$(DCQ)_2$-$(VP)_2$ with styrene (monomer) and divinyl benzene (DVB, cross-linking monomer) in presence of 2,2'-azobisisobutyronitrile (initiator) via thermal polymerization. The uranyl imprinted ions are leached by subjecting to 6.0 M HCl. The leached IIP particles will now rebind selectively the uranyl ion from dilute aqueous solutions containing several inorganic species including alkali and alkaline earth salts thus enabling a selective chemical winning of uranium from aqueous solutions and synthetic seawater [Gladis and Prasada Rao, 2003]. Various porogens employed during polymer synthesis were investigated for pre-concentrative separation of uranium from several inorganic species [Gladis and Prasada Rao, 2004]. Of these, materials that prepared using 2-methoxyethanol as porogen gave a higher retention/sorption capacity for uranium and better selectivity for uranium over thorium. The percent chemical winning 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) complexes have been studied [Metilda *et al.*, 2004]. These studies show the significant imprinting effect, i.e. higher percent extraction, selectivity coefficients and retention capacity in all cases compared to corresponding non-imprinted polymers (NIPs). However, the percent enrichment of uranium is maximum with ternary mixed ligand complex. Another uranophiles were also employed for preparing uranyl IIPs by Rao's group [Metilda *et al.*, 2007] which include succinic acid (SA), salicylaldoxime (SALO) in presence of 2-hydroxyethyl methacrylate (functional monomer), EGDMA (crosslinking monomer) and AIBN (initiator). Of these, ternary complex based imprinted resins with SA and DCQ as one of the ligand alone gave quantitative recovery of uranium from synthetic sea water solutions. However, experiments with real sea water showed that the UO_2^{2+} - DCQ-VP based imprinted resin alone recover ~

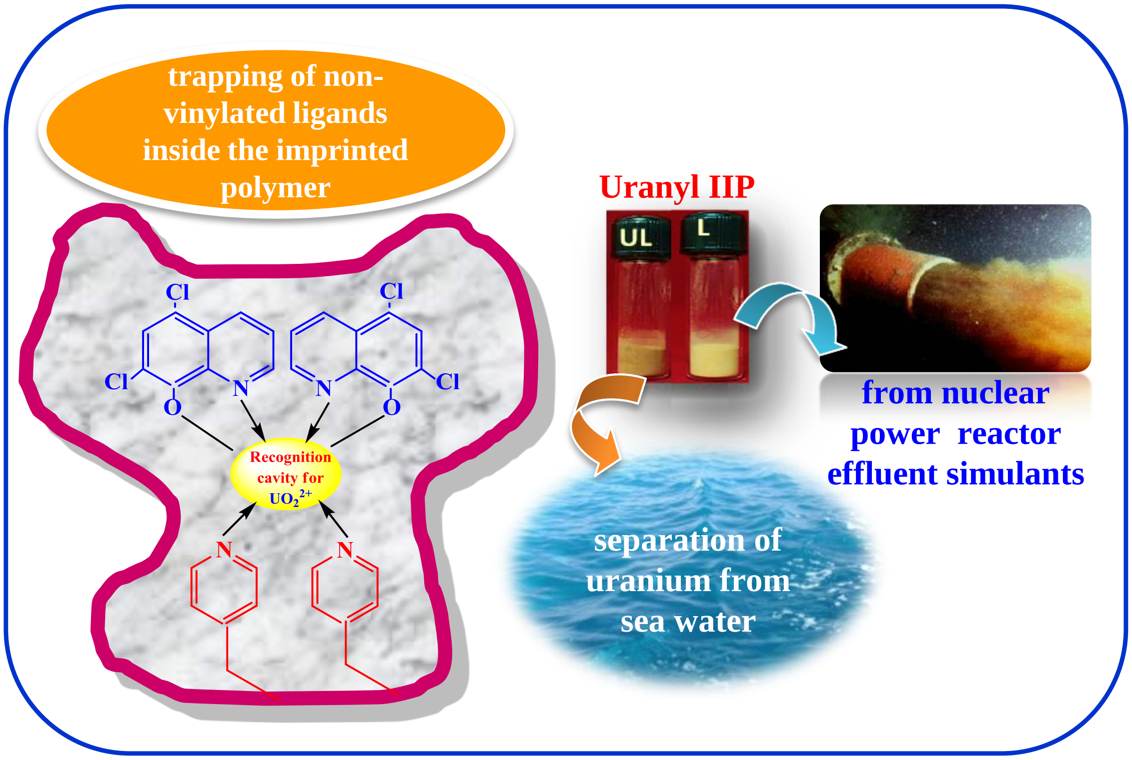
80% of uranium in offline batch mode of operation. It is pertinent to mention here that unlike amidoxime functionalized polymeric resins; imprinted polymers selectively adsorb uranium from sea water excluding heavy metals. This eliminates an additional purification step with phosphino- or phosphono-group modified resins required in the case of amidoxime resins. Preetha *et al.* [2006] have prepared uranyl IIP for the removal of uranium from synthetic nuclear power reactor effluents. All these uranyl imprinted polymers were applied for the separation or removal of uranium from various environmental samples. Shamsipur *et al.* [2007] have reported the preparation of surface imprinted polymer for uranium. Recently surface imprinted polymer nanospheres using quinoline-8-ol functionalized silica nanoparticles were used for the selective removal of uranium from simulants of Sambhar salt lake and ground water [Milja *et al.*, 2011].

1.8 Scope of the Work

Potentials of ion imprinted polymers are very wide for the separation and removal of toxic uranium from natural drinking water sources to nuclear industry wastes. Researchers are trying various imprinting strategies to develop more efficient IIPs which can be applied under various pH conditions. Design of ligands with specific functionalities and bifunctional ligands may help in improving the selectivity and also the hydrophilicity of the imprinted polymers. In view of this, the scope of the present work is to prepare uranyl imprinted polymers consuming various uranophiles for the selective preconcentrative separation and removal of uranium and to check the feasibility of these IIPs for various analytical applications. The studies carried out on the above lines and the results obtained are described in the subsequent chapters.

Chapter 2

DUMMY TEMPLATED ION IMPRINTED POLYMERS FOR PRECONCENTRATIVE SEPARATION OF URANIUM



2.1 *Abstract*

Synthetic polymer receptors selective for uranium have been prepared by ion imprinting technique using 5, 7-dichloro-8-hydroxyquinoline as the uranophile. Concept of 'dummy template' was introduced in ion imprinting through this study by using various bivalent transition metal ions in place of toxic and costly uranium. Of these, ion imprinted polymers (IIP) prepared using nickel(II) ion template offer highest affinity for uranyl ions inside styrene-divinylbenzene copolymer matrix. The selectivity coefficients obtained using imprinted polymers with nickel(II) dummy template were comparable to that of the original uranyl ion imprinted polymers. Use of nickel(II) salt which is less toxic and more cost-effective as a substitute to uranyl nitrate has facilitated the synthesize of ion imprinted polymers free from problems like bleeding of original template. They have presented highly precise, reliable and sensitive (due to low blank values) analytical data in addition to environmental benevolence and economic viability. Thus, nickel(II) dummy templated polymer as a suitable sorbent for pre-concentrative separation exhibit selective binding properties for uranyl ion facilitating its separation as well as quantification from various complex matrices including sea water and nuclear reactor effluents.

2.2 Introduction

Uranium and its compounds are well-known for their toxicity due to the severe chemical damages caused by them than the radioactive damages. The U.S. Environmental Protection Agency (USEPA) has set a Maximum Contaminant Level (MCL) for uranium of 30 $\mu g\ L^{-1}$ in the Safe Drinking Water Limits. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 mg Kg^{-1} of body weight per day [Gilman *et al.*, 1998]. The indispensable use of uranium as a nuclear fuel in nuclear power reactors and its extreme toxicity warns the urgent requisite for routine monitoring of uranium in a variety of environmental samples such as surface or ground waters, sea water, soils, sediments, mining and power reactor effluents.

Various pre-concentrative separation techniques were developed because of the low concentrations of uranium present in potentially interfering sample matrices and found promising but, have been stopped due to low recovery efficiency. But the significant contribution of imprinted polymer technology was much advantageous not only for the efficient recovery of uranium but also in terms of reusability of adsorbents. There are few reports [Bae *et al.*, 1999; Preetha *et al.*, 2003; Dai *et al.*, 2001; John *et al.*, 1999; Gladis *et al.*, 2003; Gladis and Rao, 2004; Metilda *et al.*, 2004; Say *et al.*, 2003; Saunders *et al.*, 2000] on uranium IIPs as well for pre-concentrative separation and determination of uranium. Of these, only Bae *et al.* [1999], Preetha *et al.* [2006] and Gladis *et al.* [2003] have used uranyl IIP materials for the analysis of synthetic sea water, nuclear power reactor effluents and real soil and sediment samples respectively. However, in all these reports IIPs have been prepared using costly and toxic uranyl salts. In both MIP-SPE and IIP-SPE, it is of great concern to analytical chemists that the toxic templates being remained in the washed or leached polymer material against the environmental benevolence of imprinted polymers. Later they may seep out and deteriorate the sensitive detection of the template [Matsui *et al.*, 2000]. Severe safety problems exist with such templates due to their extreme toxicity. In certain cases, templates are very expensive and the synthesis will not be economical along with the toxic effects of templates. In such situations the synthesis experts are compelled to think about substituents for original templates. An elegant solution to these twin problems is the utilization of a template analogue, i.e. "pseudo template" or "dummy template" of the original template, which is non-toxic and cheaper. With this approach, any leakage of the "dummy template" will not interfere with the quantitation of template analyte in the chosen analytical procedure. Thus, there are few reports on MIPs, which employ the so-called "dummy template" for certain organic molecules [Theodoridis *et al.*, 2003; Hosoya *et al.*, 2004; Wang *et al.*, 2005] but none for metal ion imprinted polymers.

Uranyl IIP materials prepared by different research groups essentially utilize costlier uranyl nitrate for imprinting. To cite one example, almost 1.0 g of uranyl nitrate is used for obtaining ~8 g of leached uranyl IIP material which have been used for selective rebinding of uranyl ion [Gladis and Rao, 2003]. In the economical, green chemistry and analytical utility points of view, it is felt worthwhile to identify a valid "dummy template" for uranyl ion in IIP-SPE studies. To our knowledge, there are no reports so far on the use of "dummy template" concept in IIPs. It is not out of context to state here that the rational design and concepts involved in dummy template selection in case of IIPs are radically different from MIPs. For example, the cavities in IIPs are equipped with complexing groups arranged to match the charge, coordination number, coordination geometry in addition to the size of template ion. Formation constants of specific metal complexes and thermodynamic effects are important factors which can influence the rebinding kinetics of IIPs. In this paper, we explore the possible use of bivalent transition metal ions as “dummy templates” for uranyl ion, which are more economical and harmless, compared to uranyl salts and the use of dummy templated IIP materials for uranium separation from certain environmental samples.

2.3 Preparation of “Dummy Templated” IIP Material (IIP_d)

Bivalent metal ions having almost similar ionic radii as that of uranium(VI) like Ni(II), Cu(II), Mn(II), Zn(II), Co(II) etc. were screened for the selection of a suitable ‘dummy template’ for uranium. Even though uranium(VI) exists as UO_2^{2+} in aqueous solution with linear O-U-O bond, the similarity can be explained by visualizing that two oxygen atoms to be perpendicular to the plane where uranium centre is bridged to chelating ligands during complex formation as shown by Saunders *et al.* [2000] so that uranium(VI) only reoccupies the position of the cavity created by the dummy template. Again, considering the lesser toxicity and low cost of selected bivalent metal ions, studies were undertaken to investigate whether any of these metal ions can substitute uranium template i.e. to function as a ‘pseudo’ or ‘dummy’ template.

The synthesis of IIP material was carried out in two steps (i) isolation of metal -5, 7-dichloro-8-hydroxyquinoline (DCQ) binary complexes, and (ii) conversion of binary metal-DCQ complex into ternary complex by mixing with 4-vinyl pyridine (VP) in 2-methoxyethanol (porogen) followed by thermal copolymerization with styrene and DVB.

The binary nickel-DCQ complex (1:2) was prepared by stirring 0.56 g (2 mmol) of nickel sulphate ($NiSO_4.7H_2O$) dissolved in 5 mL of water with 4 mmol of DCQ (0.88 g in 100 mL of acetone) for 2 h. A yellow coloured complex is precipitated which is filtered and washed with water to remove uncomplexed nickel and dried in hot air oven at 45 °C. This product is characterized by absorption studies.

UV-visible absorption spectra of individual monomers and uranyl complexes in 2-methoxy ethanol are shown in Figure 2.1. On examination of various absorption bands, one can clearly notice the formation of nickel-DCQ complex as seen by a broad band in the wavelength range 390-420 nm. The ternary complex was formed by dissolving 1 mmol of nickel-DCQ in 10 mL of 2-methoxy ethanol and stirring for 2 h after mixing with 2.0 mmol of VP. The proof for the formation of ternary complex can be gauged by comparing the spectrum corresponding to it with that of the ligands (DCQ and VP) and binary complexes (Ni-DCQ and Ni-VP). The high intensity band corresponding to Ni-DCQ-VP complex explains the formation of a stable ternary complex which remains stable in the styrene-DVB polymerization mixture.

The ternary complex thus prepared was polymerized using styrene and DVB. For polymerization, 20 mmol of styrene (2.1g), 20 mmol of DVB (2.6 g) and 50 mg of AIBN were added to the ternary mixture and stirred until a homogenous solution was obtained. The polymerization mixture was cooled to 0 °C and purged with N_2 for 10 min, sealed and heated in an oil bath at 80 °C with stirring for 3 h. The preparation of dummy templated IIPs is described in Figure 2.2. The bulk polymer material formed was ground into fine particles using a mortar and dried in hot air oven for 2 h followed by sieving to get uniform sized polymer particles lower than 45 μm. The other bivalent metal ion (Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}) imprinted polymers were prepared on similar lines as described above for nickel

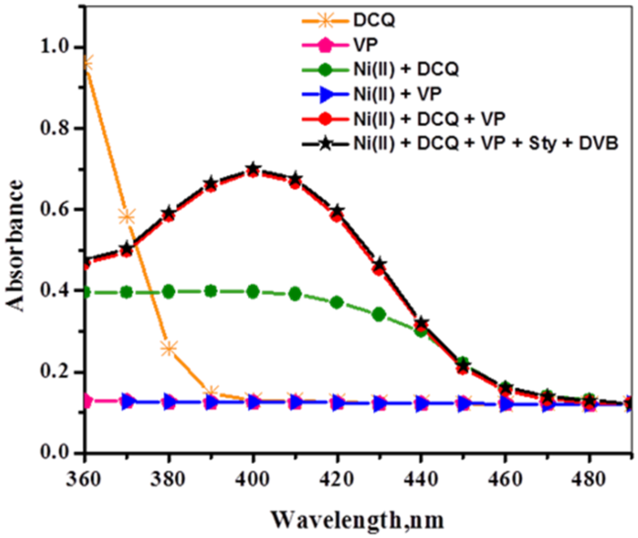


Figure 2.1 *UV-visible absorption spectra of DCQ, 4-vinyl pyridine (VP), Ni(II)+DCQ (binary complex mixture), Ni(II)+VP, Ni(II)+DCQ+VP (ternary complex mixture) and Ni(II)+DCQ +VP+styrene+DVB (imprinting recipe) in 2-methoxy ethanol*

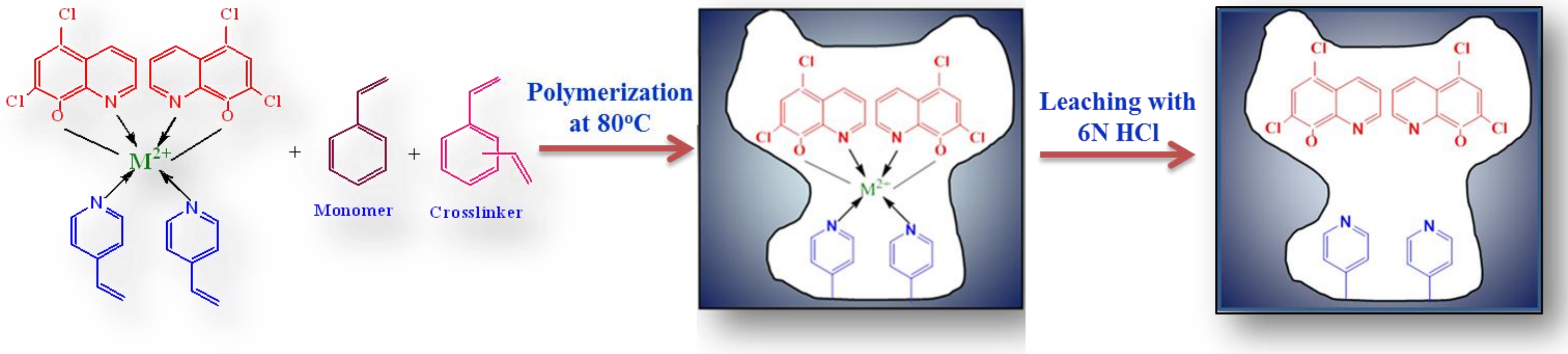


Figure 2.2 *Schematic diagram for the general preparation of dummy templated IIP materials using ternary complex of bivalent metal ion with DCQ and VP*

dummy templated IIP (Ni-IIP$_d$). The respective M^{n+} - DCQ binary complexes were prepared in 1:2 ratio and used for imprinted polymerization.

2.4 Preparation of “Non Imprinted” Polymer (NIP) Material

Non imprinted polymer materials were prepared in a similar way as that of IIPs but, by omitting the corresponding “dummy template” ions. The composition and ratio of DCQ, VP, styrene and crosslinker were kept same as that of imprinted polymer recipe. NIP prepared in bulk format was also processed like IIP to get uniform sized particles.

2.5 Leaching Studies

Leaching of dummy templates from imprinted polymer matrix was ensured by using different mineral acids and the optimized leaching parameters are listed in Table 2.1. Experiments were carried out with Ni-IIP$_d$ by leaching 0.5 g of the material with 25 mL of various leachants like HCl, H_2SO_4, HNO_3 etc. The results obtained on the selection of leachant showed that the use of HCl resulted in quantitative removal of bivalent nickel ions. The effect of leachant (HCl) concentration (1.0-10.0 M) and leaching time (5-8 h) for removal of nickel dummy template ions were also studied. The complete removal of nickel ions was quantitative in the leachant (HCl) concentration range 6.0-8.0 M within a leaching time of 6-8 h. Hence, nickel(II) template from unleached IIP materials was leached by using 6.0 M HCl for a leaching time of about 6 h. The same leaching procedure was applied to all other dummy templated IIPs and the removal of corresponding dummy templates has been carried out successfully. The complete leaching of dummy template metal ions was verified by flame atomic absorption spectrometric studies of leachant solutions. It was again confirmed by performing EDS and XPS analysis as described in section 2.6. Since Ni-IIP$_d$ showed the highest percent rebinding for uranium, subsequent optimization studies are restricted to nickel-dummy templated IIP (Ni-IIP$_d$) and NIP materials only, for uranyl rebinding experiments.

Table 2.1 *Optimization of various leaching parameters for of Ni-IIP$_d$*

Leaching parameters	Percent rebinding of uranium	
	NIP	**Ni-IIP$_d$**
1. Nature of leachant		
6.0M HCl	77.8 ± 0.8	> 99
6.0M HNO_3	78.3 ± 0.7	86.4 ± 0.8
3.0M H_2SO_4	82.2 ± 0.8	90.7 ± 0.9
2. Leachant (HCl) concentration, M		
1.0	74.4 ± 0.7	81.8 ± 0.8
3.0	76.2 ± 0.7	85.7 ± 0.8
5.0	77.3 ± 0.8	88.6 ± 0.9
6.0	77.7 ± 0.8	> 99
8.0	77.8 ± 0.8	> 99
3. Leaching time (h)		
5.0	64.3 ± 0.6	81.5 ± 0.8
6.0	77.8 ± 0.8	> 99
8.0	81.4 ± 0.8	> 99

2.6 Characterization Studies

The Ni-IIP$_d$ and NIP materials were characterized by FTIR, EDS, XPS and FAAS studies.

2.6.1 FTIR Studies

The nature of FTIR spectra of NIP and unleached and leached Ni-IIP$_d$ materials are similar, which indicate that these polymers have same polymer backbone. The absence of peaks in the region 1648-1638 cm^{-1} corresponding to C=C stretching vibration in all the polymers suggest that both VP and DVB are completely polymerized. Significantly, the presence of strong peak at ~ 758 cm^{-1} corresponding to υC-Cl in the spectra of both leached and unleached Ni-IIP$_d$ materials shows that DCQ is intact or trapped in polymeric matrix even after leaching with mineral acid.

2.6.2 EDS Analysis

The EDS spectra of unleached and leached Ni-IIP$_d$ materials are shown in Figure 2.3. As seen from the figure, the peak corresponding to nickel appearing at 0.85 KeV in the case of unleached material is absent in the leached material, indicating the complete removal of nickel ion dummy template by leaching with 6M HCl. On the other hand, the significant presence of peak corresponding to Cl at 2.60 KeV in unleached and leached (after thorough washing) IIP material indicate that DCQ is intact even after leaching, substantiating the results obtained from FTIR studies.

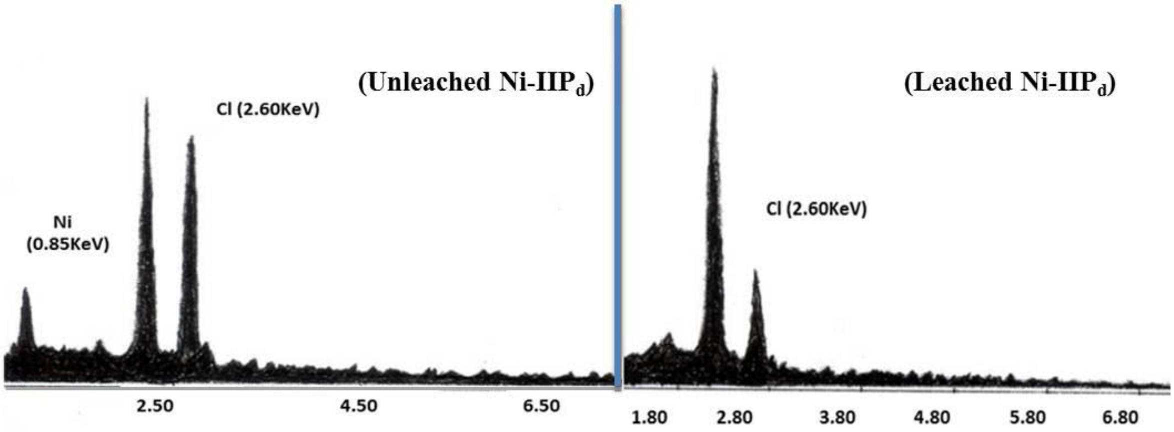


Figure 2.3 *EDS spectra of the unleached and leached Ni-IIP$_d$ materials*

2.6.3 XPS Analysis

The XPS spectra obtained for unleached and leached Ni-IIP$_d$ materials are depicted in Figure 2.4. Again, the presence of peak corresponding to Cl at 200.5 eV in the unleached and leached IIP material conclusively proves that DCQ is trapped inside the polymer matrix and is intact without any relaxation even after leaching. Furthermore, the absence of peak corresponding to nickel at 855.9 eV in leached IIP material provides an additional evidence for complete leaching of nickel ion dummy template.

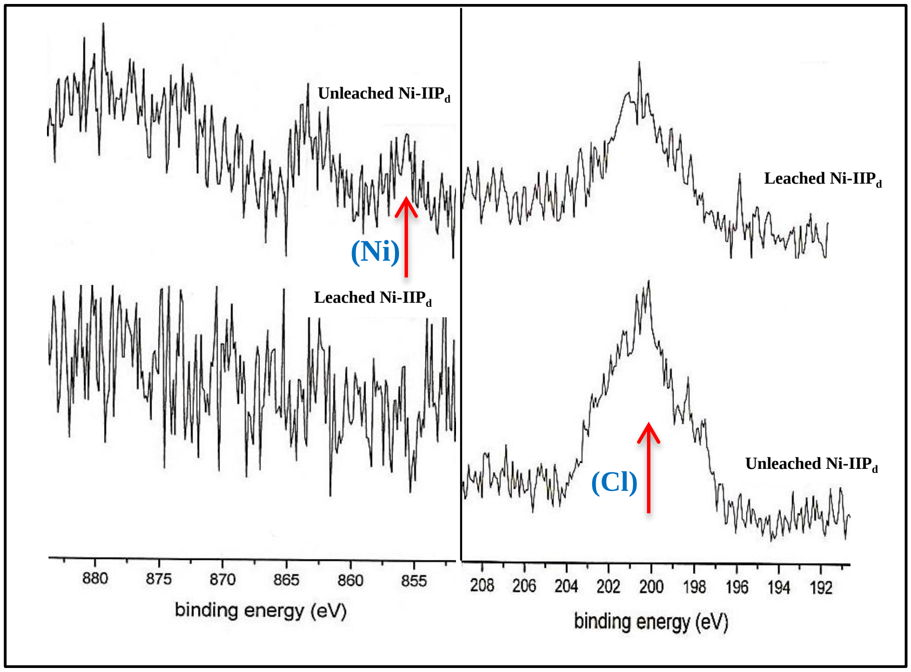


Figure 2.4 *XPS spectra corresponding to Ni (A) and Cl (B) of the unleached and leached Ni-IIP$_d$ materials*

2.6.4 FAAS Studies

Flame AAS determination of leachant solution for nickel ions shows the complete removal of templates during the leaching of Ni-IIP$_d$ material with 6M HCl for 6 h. This observation again confirms the removal of nickel from IIP material on leaching, as indicated in EDS and XPS studies.

2.7 Procedures for Uranium Rebinding and Determination

Test solutions of various uranium concentrations (100 mL) were taken in 250 mL beaker and pH was adjusted to 6.0±1.0 by using 0.1 M sodium acetate-acetic acid buffer. Ni-

IIP_d material was added to the above solution and stirred well. The preconcentrated uranyl ions were stripped with 1.0 M HCl and determined spectrophotometrically using Arsenazo III method as described in section 2.15.3 [Snell, 1978].

2.8 Optimization Studies

The effect of pH (4.0-8.5), weight of polymer material (0.02-0.1 g), time of stirring (5-30 min) during preconcentration and stripping of uranium, aqueous phase volume (25-1000 mL), nature of stripping agent (1M HCl, 1M HNO_3, 0.5M H_2SO_4 and 0.25M EDTA), stripping agent concentration (0.1-1.0 M HCl), and volume (5-20 mL) were studied by checking the percent rebinding of 25 µg of uranium present in 500 mL of aqueous solution by stirring with imprinted materials. Non imprinted polymer was also tested for all variable parameters to evaluate the effect of imprinting.

2.8.1 Effect of pH

The percent rebinding of uranyl ions onto Ni-IIP_d material was constant and maximum in the pH range 5.0-7.0 (See Figure 2.5). The comparison of percent rebinding of uranium with Ni-IIP_d and corresponding NIP material at different pH values clearly indicates the imprinting effect. The decrease in percent rebinding of uranyl ion at $pH < 5.0$ for Ni-IIP_d material is attributed to the competition of H^+ ions with uranyl ions to bind with DCQ and also due to an increase in the ratio of protonated DCQ to free DCQ. As the pH goes above 7.0, the competitive equilibrium between the formation of uranyl hydroxide (solubility product, $Ksp = 1.1x\ 10^{-22}$) and uranium-DCQ complex ($K_2 = 1.29x10^{21}$) [Sillen and Martell, 1964] increases and thereby reducing the percent rebinding uranyl ions. Therefore, an optimum pH of 6 was selected for uranium separation with maximum imprinting effect.

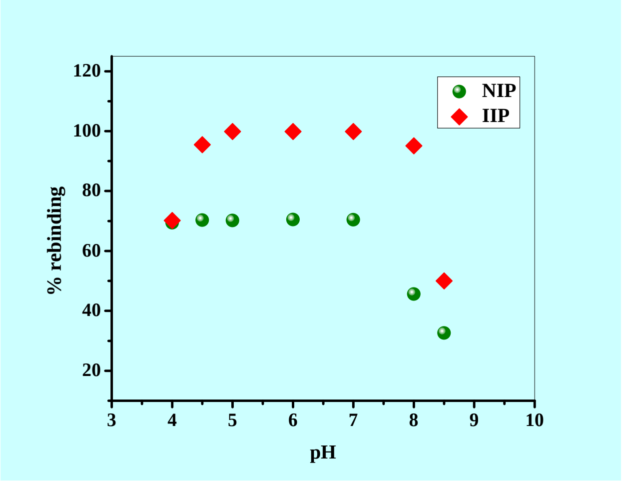


Figure 2.5 *Effect of pH on the rebinding of uranyl ions using leached Ni-IIP$_d$ and NIP materials*

2.8.2 Effect of Weight of Polymeric Materials

The percent rebinding efficiency of Ni-IIP$_d$ was tested with different weights of Ni-IIP$_d$ and NIP materials. Again, as in the case of pH studies imprinting effect was noticed in all cases (See Figure 2.6). A minimum of 75 mg of Ni-IIP$_d$ material was found to be necessary for quantitative rebinding of uranyl ion.

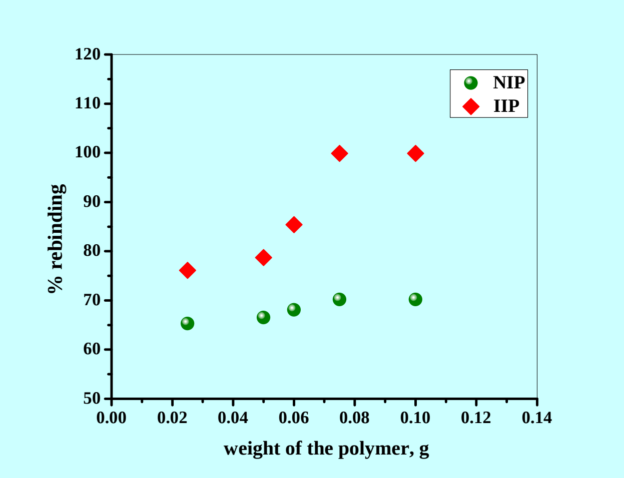


Figure 2.6 *Effect of weight of leached Ni-IIP$_d$ and NIP materials on rebinding of uranyl ions*

2.8.3 Optimization of other Experimental Variables

Studies conducted for understanding the effect of preconcentration time for quantitative rebinding of uranyl ions at pH ~ 6.0 using 75 mg of Ni-IIP$_d$ or NIP show that a minimum of 30 min (See Table 2.2) is required as against 10 min. of time required by original uranyl IIP material. This can be attributed to the possible realignment of DCQ and VP ligands towards uranium in the vacant sites of Ni-IIP$_d$ created by nickel(II) dummy templates. As expected, the stripping of bound uranyl ions was possible in 10 min of stirring time with Ni-IIP$_d$ materials. Once again, the imprinting effect was noticed in these cases, as the rebinding efficiency of uranium with Ni-IIP$_d$ material is higher than that of NIP material in all experiments performed. The increase of aqueous phase volume upto 500 mL did not affect the quantitative rebinding of uranyl ions by 75 mg of Ni-IIP$_d$ material (See Table 2.2). Subsequent uranyl ion rebinding studies were carried out from 500 mL of solutions. Of the various mineral acids evaluated as stripping agents or eluents, hydrochloric acid was the most efficient eluent for quantitative elution of uranium bound to Ni-IIP$_d$ material. The effect of concentration and volume of HCl eluent required for stripping of uranyl ion bound to Ni-IIP$_d$ or NIP materials are shown in Table 2.2. A minimum concentration of 1.0 M HCl is required for the elution and is recommended for subsequent studies. Again, single stripping with 5 mL of 1M HCl is optimized for quantitative rebinding of uranyl ion enriched from a 500 mL of aqueous solution, thus enabling quantitative rebinding factor.

Table 2.2 *Influence of various parameters on the percent rebinding of uranium with 75 mg of Ni-IIP$_d$ and NIP materials (pH 6.0)*

Parameters	Percent rebinding	
	NIP	Ni-IIP$_d$
1. Preconcentratin time (min)		
5	68.8 ± 0.7	70.2 ± 0.7
20	68.0 ± 0.7	79.1 ± 0.8
30	77.8 ± 0.8	> 99
2. Stripping time (min)		
5	63.8 ± 0.6	70.2 ± 0.7
10	78.3 ± 0.8	> 99
20	77.8 ± 0.8	> 99
30	77.9 ± 0.8	> 99
3. Aqueous phase volume (mL)		
25	77.7 ± 0.8	> 99
100	77.8 ± 0.8	> 99
500	77.8 ± 0.7	> 99
4. Nature of stripping agent		
1M HCl	77.8 ± 0.8	> 99
1M HNO_3	75.5 ± 0.8	84.8 ± 0.9
0.5M H_2SO_4	55.3 ± 0.6	70.5 ± 0.7
5. Stripping agent concentration (M)		
0.1	69.0 ± 0.7	80.5 ± 0.8
0.3	70.0 ± 0.7	84.5 ± 0.8
0.5	71.4 ± 0.7	87.8 ± 0.8
1.0	77.7 ± 0.8	> 99

6. Stripping agent volume (mL)		
5	91.5 ± 0.9	> 99
10	77.8 ± 0.8	> 99
20	77.6 ± 0.8	> 99

2.9 Rebinding Procedure

Rebinding experiments for uranium using Ni-IIP$_d$ was carried out under the optimized conditions described above. Uranium containing solutions (upto 500 mL) were taken in 1.0 L beaker and pH was adjusted to 6.0±1.0 by adding 10 mL of 0.1 M sodium acetate-acetic acid buffer. Ni-IIP$_d$ material (75 mg) was added to the uranium solution and kept for preconcentration for 30 min. The uranyl ions preconcentrated on Ni-IIP$_d$ material were eluted with 5 mL of 1.0 M HCl for 10 min. The eluent was collected and the uranium concentration was determined spectrophotometrically using Arsenazo III method.

2.10 Retention Capacity of Nickel(II) Dummy Templated Polymer

The maximum amount of uranyl ion preconcentrated per gram of Ni-IIP$_d$ was determined by saturating 0.04 g of polymer material in 25 mL of solution containing 1.0 - 5.0 mg of initial uranium concentrations. The uranyl ion content retained on the polymer was eluted with 2x25 mL of 1.0 mol L^{-1} of HCl and determined spectrophotometrically using Arsenazo III method. The retention capacity experiments indicate that the quantity of uranium retained on Ni-IIP$_d$ material increases with increasing concentration of uranium(VI) taken initially and reached a plateau in the range 160 - 200 mg L^{-1}. The retention capacities of Ni-IIP$_d$ and corresponding NIP material for uranium was found to be 85.25 and 71.93 μmol g^{-1} respectively, with efficient imprinting effect.

2.11 Selectivity Studies

The selectivity of Ni-IIP$_d$ and NIP materials for uranium over other inorganic ions was determined by equilbrating to 10 µg of uranium with 100 µg each of Cu(II), Co(II), Mn(II), Zn(II), Cr(III) and Fe(III) present in 500 mL of deionized water with 75 mg polymeric material under optimal conditions. The concentrations of these elements in eluent solutions were determined by flame atomic absorption spectrometry after eluting with 10 mL of 1.0 M HCl. The selectivity coefficient $(\mathbf{S}_{\mathbf{UO_2^{2+}/M^{n+}}})$ is defined as

$$\mathbf{S}_{\mathbf{UO_2^{2+}/M^{n=}}} = \frac{\mathbf{D}_{\mathbf{UO_2^{2+}}}}{\mathbf{D}_{\mathbf{M^{n+}}}}$$

where, $D_{UO_2^{2+}}$ and D_M^{n+} are the distribution ratios of uranyl ion and other inorganic species, respectively, with polymeric materials (NIP or Ni-IIP$_d$). These distribution ratios were calculated using the formula,

$$\mathbf{D}_{\mathbf{M^{n+}}} = \frac{\mathbf{C}_{\mathbf{M^{m+}}} \quad \mathbf{C}}{\mathbf{C}_{\mathbf{M^{n+}}}} \times \frac{\mathbf{v}}{\mathbf{m}}$$

where, C_M^{n+} and C are the concentrations of metal ions in aqueous phase before and after extraction, v is the volume of the solution, and m is the mass of the polymeric material.

The percent extraction (% E) of metal ion is defined as

$$\mathbf{\%E} = \frac{\mathbf{C}_{\mathbf{M^{m+}}} \quad \mathbf{C}}{\mathbf{C}_{\mathbf{M^{n+}}}} \times \mathbf{100}$$

The percent extraction, distribution ratio and selectivity coefficients of uranyl ion with other metal ions using Ni-IIP$_d$ and NIP materials are shown in Table 2.3. The selectivity coefficients for Ni-IIP$_d$ materials were greater by several folds over NIP material owing to the rebinding kinetics of Ni(II) ions into specific cavities created in Ni-IIP$_d$ unlike NIP.

Table 2.3 *Percent extraction, distribution ratio and selectivity coefficients of Ni-IIP$_d$ and NIP materials*

Metal ion	**Percent extraction**		**Distribution ratio (D)**		**Selectivity coefficient** $(S_{UO_2^{2+}/M^{n+}})$	
	NIP	**Ni-IIP$_d$**	**NIP**	**Ni-IIP$_d$**	**NIP**	**Ni-IIP$_d$**
U(VI)	77.8	> 99	3.49	99	-	-
Cu(II)	84.4	73.9	5.40	2.80	0.7	35.4
Co(II)	31.2	51.9	0.04	1.08	87.3	91.7
Mn(II)	4.9	4.2	0.05	0.04	69.8	2.5×10^3
Zn(II)	25.1	45.7	0.34	0.84	10.3	1.2×10^2
Fe(III)	46.3	45.7	0.86	0.84	4.1	1.2×10^2

2.12 Uranium Rebinding Efficiency of Dummy Templated IIPs

Percent rebinding of uranium onto various IIP$_d$ materials was conducted after completely removing the respective dummy templates, and the results obtained are shown in Table 2.4. The percent rebinding of uranium by various dummy templated IIPs lies in the order Ni-IIP$_d$ > Cu-IIP$_d$ > Mn-IIP$_d$ > Zn-IIP$_d$ > Co-IIP$_d$. An attempt has been made to explain the sequence observed in uranium rebinding by Ni-IIP$_d$ by correlating with ionic radii of dummy templates and formation constants of Mn^{2+}-DCQ complexes. Size of the template is the prime determinant factor of selectivity as reported in the case of organic dummy templated MIPs. Copper and zinc ions were having closer ionic radii to uranyl ion than nickel and so the expected sequence for the percent rebinding of uranium with various dummy templates lie in the order Cu-IIP$_d$ > Zn-IIP$_d$ > Ni-IIP$_d$ > Mn-IIP$_d$ > Co-IIP$_d$. Here the ionic radii consideration may be worthwhile to explain the lower uranium rebinding in the case of Mn-IIP$_d$ and Co-IIP$_d$ compared to Ni-IIP$_d$. But the anomalous behavior of lower uranium rebinding with Cu-IIP$_d$ compared to Ni-IIP$_d$ in the present study has to be attributed to the incompatibility of the uranyl-DCQ complex formed inside the imprinted polymer matrix during uranium rebinding with the Cu^{2+}-DCQ complex which is formed during imprinting process. This happens by the difference in the orientation of these complexes inside the crosslinked polymer matrix due to their unique geometries. Similar explanation is applicable to Zn-IIP$_d$ for its lower uranium rebinding.

On the other hand, as per the formation constants of metal-DCQ complexes, the expected order for preferential uranium rebinding in binary mixtures should lie in the order Mn-IIP$_d$ > Zn-IIP$_d$ > Co-IIP$_d$ > Ni-IIP$_d$ > Cu-IIP$_d$. Hence the selectivity sequence of Ni-IIP$_d$ for uranyl ions over other metal ions has to be in the order $Mn^{2+} > Zn^{2+} > Co^{2+} > Cu^{2+}$. This is exactly matches with the experimentally obtained selectivity sequence for Ni-IIP$_d$ (see Table 2.3). Prof. Fish's group [Chen *et al.*, 1997] has reported that copper ions are favored in presence of Fe^{3+} ions by Zn-imprinted polymer.

A study by Gupta *et al.* [1970] showed that Cu^{2+}-DCQ complex has high formation constant as that of UO_2^{2+}-DCQ on comparison with other metal-DCQ complexes (see Table 2.4). Hence, the formation constant solely cannot form the basis for uranium rebinding by dummy templated IIPs. In those cases one has to consider the definite geometry orientations of the complexes formed even though similar metal to DCQ molar ratios are maintained in all dummy templated IIP preparations. The steric and geometric aspects of non-covalent imprinted polymers have been previously studied by Spivak's research group [2005]. Pre-organization of functional groups with templates and shape selective binding cavity that is complementary to the shape of the template were considered to be responsible for selectivity in imprinted polymers. But in the case of dummy ion templated imprinted polymers we can expect a rearrangement of the binding sites lined with DCQ ligands in Ni-IIP$_d$ which are specific to Ni^{2+} ions, during equilibration with uranyl ions.

Again, as per Fish's studies on Zn- N-[4-vinylbenzyl]-1,4,7-triazacyclononanes (TACN) based IIP, he could also observe a similar effect where the Zn specific IIP preferred Cu ions over Zn (157 copper ions for every ion of zinc) in a solution containing equal concentrations of both ion species. They believed that the thermodynamic effects are the overriding factor when these two metal ions have similar radii. The chemical combination of copper and TACN ligand has better thermodynamic stability despite the nice fit of the zinc ion in the polymer matrix where the imprinted shape does not have an important role. But in a separate test of the role of shape and ionic radius, divalent copper ions were favored by the zinc-imprinted polymer than the trivalent ions of iron (by a ratio of 44 to one) where the size of the hole in the polymer was expected to play the role even though zinc and copper ions have nearly similar radii, but the radius of the iron ions is significantly smaller. The current study also shows Ni-IIP$_d$ picks uranium in preference to Ni^{2+} when present in admixture. This can be explained on the basis of Fish's observations i.e. preference of Zn-IIP for Cu^{2+}. This visualization can be reinforced by implementing some theoretical models for dummy template complex formation with DCQ to shed more light on observed recognition behavior Ni-IIP$_d$ for uranium.

Table 2.4 *Correlation of percent rebinding of uranium by various dummy templated IIPs with template ionic radii and formation constants of respective* M^{n+}*-DCQ complexes*

Template used	Percent rebinding	Ionic radii of template (pm)	Formation constants of M^{n+}-DCQ complex (log β_2)
UO_2^{2+}	> 99	73	17.48 ± 0.07
Ni^{2+}	> 99	69	17.84 ± 0.12
Cu^{2+}	86.5	73	22.88 ± 0.07
Mn^{2+}	80.9	67	10.53 ± 0.13
Zn^{2+}	69.8	74	14.86 ± 0.06
Co^{2+}	69.8	65	16.22 ± 0.09

2.13 Effect of Various Complex Matrices on the Determination of Uranium

In view of the high selectivity coefficients offered by Ni-IIP_d materials, the separation of uranium is possible from various complex matrices. Synthetic solutions of neutral electrolytes, mixture of metal ions, seawater and nuclear power reactor effluents were prepared and used for the separation studies of specific amounts of uranium. Table 2.5 shows the results obtained on the determination of uranium(VI) using Arsenazo III method using 75 mg of Ni-IIP_d material from 500 mL of synthetic solutions after adjusting the pH to ~6.0 under other optimal conditions. The results show the feasibility of Ni-dummy templated IIP materials for the separation of uranium from various complex matrices containing potentially interfering ions. This study indicates that quantification of uranium when present in ng mL^{-1} level in seawater matrix is also possible on preconcentrative separation of uranium using Ni-IIP_d material. The effective separation of uranium from nuclear power reactor effluent simulant which is having a composition of La-263.8 mg L^{-1}, Ce-532.5 mg L^{-1}, Nd-862.5 mg L^{-1}, Sm-163.8 mg L^{-1}, Pr-243.8 mg L^{-1}, Gd-165.0 mg L^{-1}, Tb-5.0 mg L^{-1}, Dy-2.0 mg L^{-1}, Y-99.0 mg L^{-1}, Ru-463.8 mg L^{-1}, Pd-267.5 mg L^{-1}, Na-3000 mg L^{-1}, Ba-308.8 mg L^{-1}, Ni-100.0 mg L^{-1},Cr-100.0 mg L^{-1}, Mn-181.3 mg L^{-1}, Co-127.5 mg L^{-1}, Mo-731.3 mg L^{-1} and Zr-771.3 mg L^{-1} with 2000 mg $L^{-1}$of uranium [Preetha *et al.*, 2006] was also studied quantitatively as shown in the Table 2.5.

Table 2.5 *Separation of uranyl ions present in 500 mL sample solutions of electrolytes, metal mixtures and simulants of seawater and nuclear power reactor effluent (pH 6.0, weight of Ni-IIP$_d$ material = 75 mg)*

Sl. No.	Composition of the synthetic sample	Amount of Uranium (µg)*	
		Spiked	Recovered
1	None	10.0	10.0 ± 0.05
2	Neutral electrolytes (Na (1.07%), KCl (0.04%), $CaCl_2$ (0.0415%), $MgCl_2$ (1.28%)	20.0	19.8 ± 0.08
3	Mixture of metal ions (ng L^{-1}): Cr (330), Ni (480), Cu (120), Zn (390), Mn (10), Fe (40), Co (2)	5.0	5.0 ± 0.02
4	0.0023mmol L^{-1} Na_2CO_3	10.0	10.0 ± 0.04
5	Synthetic Seawater (composition 2+3)	5.0	4.9 ± 0.02
6	Nuclear power reactor effluent	10.0	4.9 ± 0.04

*Average of 3 successive determinations employing Arsenazo III method for quantification.

2.14 Experimental

2.14.1 Materials

Uranyl nitrate and bivalent metal salts were of analytical grade from Aldrich, Milwaukee, WI, USA. Chromogenic agent (Arsenazo-III) for spectrophotometric monitoring of uranium was obtained from Fluka, Buchs, Switzerland and used without further purification. 5, 7-dichloro-8-hydroxyquinoline (DCQ), 4-vinyl pyridine (VP), styrene, divinylbenzene (DVB), 2, 2’-azobisisobutyronitrile (AIBN) were also from Aldrich. All other chemicals used were also of Analytical Reagent Grade.

2.14.2 Instrumentation

A Shimadzu UV-2401 PC controlled UV visible spectrophotometer (Shimadzu, Kyoto, Japan) was used for the determination of uranium. Flame atomic Absorption spectrometric analyses were performed using a Perkin-Elmer Analyst 100 (Perkin Elmer, Shelton, CT, USA) during leaching and selectivity studies. FT-IR spectra were recorded in the frequency range 4000-400 cm^{-1} by KBr pellet method using Nicolet MAGNA FT-IR-560 spectrometer (Madison, WI, USA). Energy dispersive X-ray spectroscopic analyses (EDS) were carried out using EDAX (Mahwah, NJ, USA).

2.14.3 Arsenazo III Method

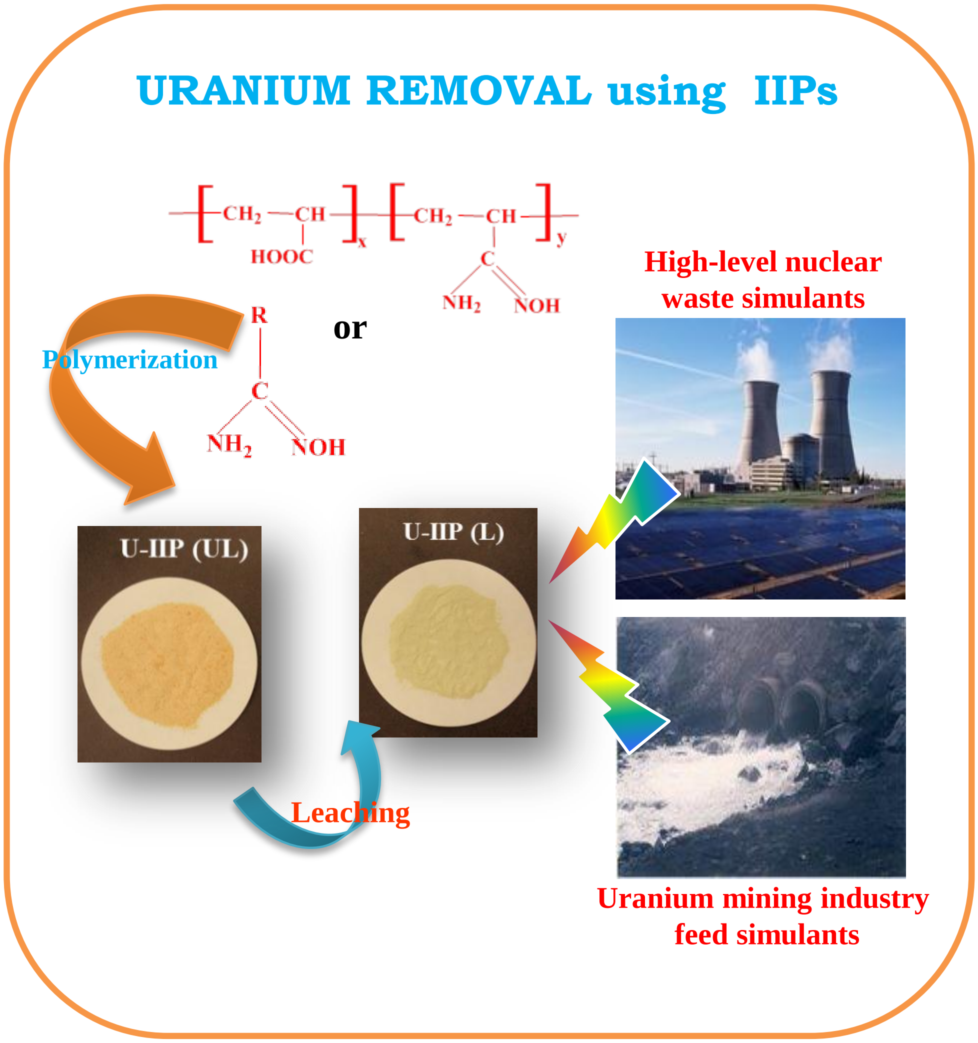
Arsenazo III reagent is widely used in industry and scientific research for the photometric determination of U, Th, Zr, Hf, Pd, Sc, Pa, Np, Pu, Am, Cm, rare earth elements, etc. A special feature of the analytical effect of Arsenazo III is the capability of forming stable complexes; thus, metal ions can be determined in strongly acid solutions. This fact is responsible for the good reproducibility of the results of determination and for convenience in operation. So the method is used as the best spectrophotometric method for uranium determination throughout our studies. Suitable aliquots of collected eluent solutions were treated with 5mL of 1:1 HCl and 2.5mL of 0.1% Arsenazo III solution. It is then diluted to 25mL with deionized water. The high intensity absorption of uranium–Arsenazo III complex was measured at a wavelength of 656 nm.

2.15 Conclusions

To summarize, the above investigations demonstrate the possible use of less toxic and low cost nickel(II) salt as a substituent for uranyl nitrate during the preparation of imprinted polymer. A comparison of the results obtained for Ni-IIP_d with corresponding NIP material indicates that there is a significant imprinting effect in pH, weight of polymeric material, aqueous phase volume, retention capacity, and selectivity coefficient (increase by 10-50 fold for uranyl ion with respect to other inorganic species) studies. The high selectivity coefficients achieved in this work enable complete separation of toxic uranium from various complex interfering matrices including sea water and nuclear power plants effluent.

Chapter 3

AMIDOXIME FUNCTIONALIZED IMPRINTED POLYMERS FOR URANIUM REMOVAL



3.1 *Abstract*

Ion imprinted polymers (IIP) were prepared for uranium in two sets using different amidoxime functionalities as uranophiles. In Set I, IIP was prepared by trapping of a non-vinylated uranophile, formamidoxime but in Set II, a copolymer which carries both substrate anchoring carboxylic group and highly specific uranyl binding amidoxime functionality was utilized. Another non-vinylated ligand 4-vinyl pyridine was used for preparing ternary complex mixtures of uranium which could also serve as an additional functional monomer for free radical initiated crosslinking. Two sets of polymers were prepared from both binary and ternary complex mixtures of uranium followed by thermally copolymerizing with 2-hydroxy ethyl methacrylate (HEMA) and cross linking with ethylene glycol dimethacrylate (EGDMA) in presence of 2, 2'-azobisisobutyronitrile as initiator. Corresponding non-imprinted polymers (NIP) were also prepared under the same conditions as that of IIP but in the absence of uranyl ion template. All the polymers formed were subsequently leached with 50% (v/v) HCl to form vacant imprinted sites which can be used for rebinding of uranyl ions selectively from aqueous solutions. Extensive characterization of polymers and optimization of different experimental parameters were included in this chapter. Imprinted polymers prepared from ternary uranium complex mixtures showed high surface area and retention capacity than those formed from binary which resulted in faster kinetics and high or comparable sorption capacities. The applicability of the above prepared imprinted polymers for the removal of uranium from mining industry feed simulant solution using Set I polymers and from simulated high-level nuclear waste solution using Set II polymers were successfully demonstrated.

3.2 Introduction

Nuclear power is regarded as an indispensable energy resource in future world energy scenario; but the environmental impact of nuclear industries and uranium mining activities are severe and generates massive stockpiles of radioactive and toxic waste and tailings creating serious contamination to surface and ground waters. In uranium mining, up to 85 percent of the radiological elements contained in the original uranium ore end up in the tailings. Rain falls causes the overflow of tailings from the tailing ponds into village ponds, wells and fields. Nowadays the question of nuclear waste disposal is also becoming a major issue as that of mining tailings and became a major reason for the decline in nuclear power programs worldwide. High-Level Radioactive Waste (HLW) is the waste generated during reprocessing of spent nuclear fuel and its management or safe disposal has become a challenging task as majority of radioactivity in the entire nuclear fuel cycle is concentrated in high-level radioactive liquid waste [Duff *et al.*, 2004]. This waste, through contact by ground water, get leached into solution, travel through aquifers, and eventually reach surface waters from which they may enter into drinking water or food supplies. Uranium is a major constituent of nuclear power reactors effluents and mine leachants and well known for its chemical toxicity rather than radioactivity. In concern with the extreme toxicity (MPL in drinking water as per USEPA is 30 ppb) and environmental aggressiveness regarding uranium, detoxification of nuclear waste effluents and mine leachants are essential prior to discharge into environment.

Removal or separation of toxic uranium from various environments has been accomplished successfully by various pre-concentrative separation techniques as we have seen in section 1.4 of chapter 1. [Booking, 2007]. Methods like co-precipitation, ion exchange and solvent extraction have been reported for the detoxification of acidic nuclear wastes [Schulz *et al.*, 1987]. In view of the growing concerns for environmental protection, removal of emerging pollutant uranium has become a fertile and vital area for the present day research. A variety of solid phase extractants employed for the removal of uranyl ions have been reported, essentially from aqueous solutions. These include activated carbon [Abbasi and Streat, 1994], hydrogels [Karadag *et al.*, 1995], silica gels [Michard *et al.*, 1996], and hydrous oxides [Gupta and Venkataramani, 1988]. Titanate solids such as monosodium titanate and sodium nonatitanate are chemically stable at high pH and could be used for the removal of radio strontium and actinides [uranium (U), plutonium (Pu), and neptunium (Np)] from highly alkaline salt solutions [Behrens *et al.*, 1998; Hobbs *et al.*, 2000]. But specific chelating agents can achieve multiple applications such as selective removal, nuclear waste management and in vivo chelation therapy. A renewed interest is found in uranium chelation because the handling of uranium in the nuclear industry as well as for military purposes is increasing. The uranyl ion UO_2^{2+}, the most stable form of uranium is a hard Lewis acid and its particular coordination mode encouraged the design and synthesis of many uranyl ligands (i.e., uranophiles) useful for the selective detection [Lu *et al.*, 2000] or extraction of uranium from sea water or nuclear wastes [Shinkai *et al.*, 1987; Sessler *et al.*, 2001; I. Tabushi *et al.*, 1980]. In view of the theoretical aspects of the actinide complexation, atoms softer (less electronically dense) than oxygen tend to bind more strongly with minor actinides like U(VI) than the lanthanides. Among the various uranophiles synthesized for uranium, amidoxime functionality captured a good attention in the above perspective and has shown superior affinity towards uranyl ions [Zhang *et al.*, 2005; Nogami *et al.*, 2004]. Colella *et al.* [1980] have also demonstrated that poly (acrylamidoxime) can be successfully used for the preconcentration of trace metals from aqueous solutions. Sugo *et al.* [2005] have patented a process for the recovery of uranium from sea water culminating in production of yellow U_3O_8 utilizing amidoxime fiber. To attain this, the fiber of a polyolefin such as polyethylene or polypropylene are grafted to the substrate polymer by radiation-initiated graft polymerization, and then an amidoxime group and a hydrophilic group are introduced into the same graft side chains.

Amidoxime functionalized poly(propylene) fibrous and microporous sheets were studied for the uranium sorption kinetics from sea water by Das *et al.* [2009] and found that the density of amidoxime groups in the sorbents and their conditioning play major roles in the U(VI) sorption from seawater. Thus polymers, copolymers and fibers having amidoxime have been used as a suitable uranophile for the selective recovery of uranium from aqueous solutions [Sahiner *et al.*, 1998; 2000; Omichi *et al.*, 1986] due to the efficient binding of amidoxime groups with uranium and the rapid kinetics offered by this uranophile at neutral or weakly alkaline conditions. But these materials were of low sorption/retention capacity, lack in sufficient selectivity (resulting in poisoning of sorbents) and have shown incomplete removal (leaving traces of uranium). These hitches are mainly because of small and inaccessible pores with irregular pore sizes, low surface areas, poor selectivity and low sorption capacity of the adsorbents.

Historical introduction of ion imprinted polymers [Nishide *et al.*, 1976] had opened up a new era for solid phase extraction. These imprinted polymers (either ionic or molecular) are highly selective like biological antibodies, with higher thermal/mechanical/chemical stability, more easily prepared, and at a lower cost, which enable them to detect and selectively remove specific substances from the environment. In ion imprinting the ligand moiety is held around the template to preserve a specific geometry within the polymeric network which is responsible for rebinding the imprint ion. Imprinted polymers in SPE has gained extensive impetus during last decade for the selective recovery of lanthanides, actinides, and noble metals from dilute aqueous solutions as this technique provides higher enrichment factors and selectivity coefficients as compared to non-imprinted polymers. Combination of imprinting with highly specific amidoxime uranophile by incorporating the ligand moiety inside the crosslinked polymer can have better chances for detoxification of uranium from alkaline nuclear industry waste effluents.

Recently Bhaskarapillai *et al.* [2009] have reported significant reduction of radioactive waste generated during decontamination of nuclear reactors by removing cobalt(II) ions even when present in ppb levels using IIP from strong complexing medium against excess ferrous ions. But the first report on the selective removal of uranium from synthetic nuclear power reactor effluent solutions using IIPs was by Preetha *et al.* [2006] where they used salicylaldoxime (SALO) and 4-vinyl pyridine (VP) as non-vinylated and vinylated ligands respectively for complexing uranium using styrene and DVB as functional and cross-linking monomers respectvely. However, the usefulness of this material is limited to weakly acidic sample solutions i.e. in the pH range 3.5-5.0.

From the inclusive literature survey carried out, it is revealed that there are no reports for the preparation of ion imprinted polymers materials using "amidoxime chelating functionality”. The present work include the preparation of two sets of uranyl ion imprinted polymers via i) trapping of formamidoxime functionality as Set I and ii) incorporating amidoxime chelating functionality accommodated in a copolymer chain as Set II. The copolymer contains amidoxime functionality at one end for specific interactions with uranyl ion template through weak non-covalent interactions and a hydrophilic carboxylic moiety at the other end, which is not interacting with the template and can get anchored on to the rest of the polymer matrix during cross-linking. Both sets of polymers were prepared either alone or in presence of 4-vinyl pyridine, a vinylated chelating ligand which can function as an additional functional monomer during imprinting. Non imprinted polymers were also prepared as the control by omitting the uranyl ion template. The results obtained on comparison of imprinting effect which has been carried out for different imprinted polymers prepared from binary and ternary prepolymer complexes of Sets I & II polymers were explained. This chapter also describes an extensive characterization of imprinted (both unleached and leached) and non-imprinted polymer materials using IR, XPS, EDS SEM, and BET- surface area and pore size analysis and various sequential optimization studies. The work was extended towards the removal of uranyl ions from alkaline simulants of high-level nuclear waste and uranium mining industry feed solutions using the above amidoxime functionalized imprinted polymers.

3.3 Preparation of Uranyl Ion Imprinted (IIP) and Non-Imprinted Polymers (NIP) Using Amidoxime Uranophiles

Bulk polymerization method was employed for the preparation of uranyl ion imprinted polymers which is described as one of the successful molecular imprinting polymerization protocols by Takeuchi and Masque [Takeuchi *et al.*, 1999; Masque *et al.*, 2001]. Nature and composition of polymer matrix plays a major role in the imprinting effect [Spivak, 2005]. Cross linking density of the polymeric matrix was preferred in such a way that enough crosslinking is provided for retaining the structural integrity of the template even after its removal from the matrix. Normally, in metal-ion imprinting 50-80% of crosslinking is used which is having a dependency on the monomer composition. Commonly used functional and cross linking monomer combinations have been tested by Kala *et al.* [Kala *et al.*, 2005] during the preparation of erbium (III) ion imprinted polymer particles using trapped functionalities. They illustrated the imprinting effect of IIPs with different polymeric matrices like styrene -DVB, HEMA - EGDMA and MMA - EGDMA. Among these, HEMA - EGDMA offers more biocompatibility and biodegradability than other matrices with better selectivity coefficients, and was selected for the polymer preparations in this work. Porogens play a major responsibility for the mesoporous nature of imprinted polymers [Sellergren, 1999] and in effect the percent rebinding. Gladis *et al.* [2004] have investigated various porogens employed during synthesis of IIPs for the pre-concentrative separation of uranium from several inorganic species including thorium. Of these, 2-methoxyethanol gave a higher retention/sorption capacity for uranium and better selectivity for uranium over thorium. Hence, we have chosen 2-methoxyethanol as the porogen for polymerization in the present study. Prepolymerization mixtures for the imprinting process were prepared from ternary and binary complex mixtures of uranyl ions with amidoxime functionalities and with or without vinylated ligand, 4- vinyl pyridine respectively in a suitable porogen. Further these mixtures were mixed with functional and crosslinking monomers and initiator to initiate the polymerization.

3.3.1 Set I: Imprinted Polymers Using Formamidoxime as the Uranophile (IIP-I & NIP-I):

The stoichiometry of template-ligand complex in an imprinting polymerization mixture has a major impact on the quantity and quality of recognition sites in the resultant imprinted polymer [Andersson and Nicholls, 1997]. It can capably expose the selectivity of binding with relatively low non-specific binding. Uranyl nitrate was complexed with formamidoxime in a stoichiometric ratio of 1:2 using 2-methoxy ethanol as the porogen. For ternary complexation, an additional vinylated ligand 4- vinyl pyridine (2 mmoles) was also added into another set of binary complex mixture taken in a separate polymerization flask, maintaining a 1:2:2 stoichiometric ratio. The extent of self-assembly of chelating functionality and template ion in the prepolymerization mixture has been evaluated by UV-VIS spectrophotometry. Solutions of formamidoxime, UO_2^{2+}, UO_2^{2+}+ formamidoxime binary complex, UO_2^{2+} + formamidoxime + VP ternary complex, were prepared in 2-methoxy ethanol which was used as the porogen for polymerization. The ternary complex mixture (UO_2^{2+} + formamidoxime +VP) showed an increased absorption maximum over that of (UO_2^{2+}+ formamidoxime) binary complex at around 442 nm. This confirms the existence of a highly stable ternary complex than the binary in the pre-polymerization stage. VP acts not only as the ligand in the ternary complexation but also as an additional functional monomer during polymerization. Thus IIP could be prepared with ligands capable of strong and effective complex formation with uranyl ions and thus promise more defined recognition sites.

Binary and ternary complex mixtures prepared above were then copolymerized with functional monomer, 2-hydroxy ethyl methacrylate (HEMA-8 mmoles) followed by crosslinking with ethylene glycol dimethacrylate (EGDMA-32 mmoles) in presence of 2, 2'-azobisisobutyronitrile (AIBN-0.05 g) as the free radical initiator in 10 mL of porogen, 2-methoxy ethanol. The polymerization recipe was allowed to purge with N_2 in a closed flask for 10 min. and then sealed and thermally polymerized at 80 °C with continuous stirring. Both bulk polymers obtained from binary (IIP-I.a) and ternary (IIP-I.b) complexes of uranium were ground, sieved well and were dried overnight under vacuum at 55 °C allowing the excess porogen to evaporate off. The corresponding non-imprinted polymers were also prepared (NIP-I.a & NIP-I.b) but avoiding the uranyl cation template during the prepolymerization step.

3.3.2 Set II: Imprinted Polymers Using Poly (Acrylic Acid-Amidoxime) Copolymer, [P(AA-Co-AX)] as the Uranophile (IIP-II & NIP-II):

Bulk monolith preparation of IIP by thermal polymerization was performed from binary and ternary complex mixtures of uranium by preorganizing uranyl cation (1 mmoles) with 2 mmoles of poly (acrylic acid-amidoxime) copolymer having amidoxime groups as the chelating functionality (IIP-II.a) and another set with 2 mmoles 4-VP monomer in addition to copolymer, respectively (IIP-II.b) in 10 mL of porogen. Polymerization was followed in presence of HEMA, EGDMA & AIBN (similar molar ratios as described for Set

I polymers). Non-imprinted polymers (NIP-II.a & NIP-II.b) were also prepared. Grinding and sieving were done for all the polymers prepared to get uniformly sized particles.

Synthesis of poly (acrylic acid-acrylonitrile) copolymer, [p(AA-co-AN)] and its chemical modification into poly (acrylic acid-amidoxime) copolymer, [p(AA-co-AX)] is given below.

3.3.2.1 Synthesis of Poly (Acrylic Acid-Acrylonitrile) Copolymer, [p (AA-co-AN)]

Poly (acrylic acid-acrylonitrile) copolymer was synthesized by radical polymerization of monomers namely, acrylic acid (AA) and acrylonitrile (AN) in DMSO solution, as described elsewhere [Shan *et al.*, 2006]. In a reaction flask, 12.1 g of acrylonitrile and 1.34 g of acrylic acid were added to 47.3 g of DMSO, and 0.61 g of 2, 2'-azobisisobutyronitrile was also introduced as the free radical initiator. The reaction was carried out under inert atmosphere for 24 h Schematic representation of the synthesis is given in Figure 3.1. The resultant solution was cooled to RT and diluted by adding around 60 mL of DMSO. It was then slowly sprayed using a syringe into a beaker containing 500 ml of distilled water under constant stirring. The resultant low weight polymer formed was filtered and washed well with distilled water and ethanol and dried under vacuum at 40 °C.

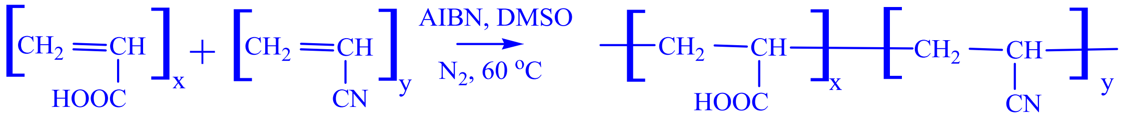


Figure 3.1 *Synthetic route for the preparation of Poly (Acrylic Acid-Acrylonitrile) copolymer, [p (AA-CO-AN)]*

3.3.2.2 Chemical Modification of Acrylonitrile Groups of the Copolymer into Amidoxime Functionality, [p (AA-co-AN)] into [p(AA-co-AX)]

[p(AA-co-AN)] was amidoximated using free hydroxylamine as given in the Figure 3.2. Neutralization of hydroxylamine hydrochloride was done with sodium carbonate in DMF which was then mixed with [p (AA-co-AN)] and kept for 16 h with constant stirring at RT. Conversion of -CN into –C(NOH)NH_2 was confirmed by FT-IR, H^1 and C^{13} NMR .

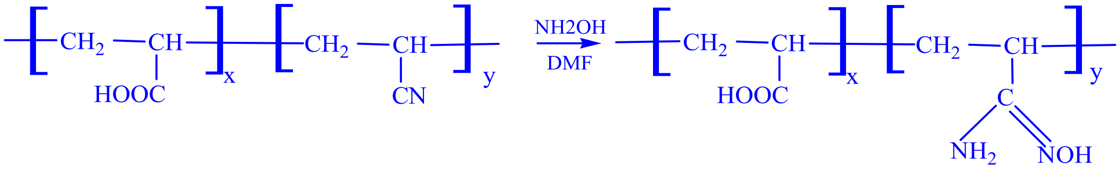


Figure 3.2 *Amidoximation of [p (AA-CO-AN)] into [p(AA-co-AX)]*

The synthesized copolymer contain amidoxime functionalities as highly selective functional sites for uranyl cation and an acrylic acid moiety as the hydrophilic anchor blocks inside the polymer matrix to facilitate the arrangement of the complex inside the imprinted polymer network. Here, self-assembly of uranyl ion template with amidoxime chelating functionality by using noncovalent interactions leads to the formation of a binary/ternary complex, which is then incorporated into the growing polymer network. Chances of multiple sites of interactions between copolymer and template in the pre-polymerization complex enhance the recognition ability of the imprinted polymer. Acrylic functionality in the copolymers facilitates the cross-linking and hydrogen bonding, during polymerization. Addition of vinylated ligand, 4-VP results in the formation of ternary complex in the pre-polymerization mixture (Figure 3.3). This was confirmed by increase in absorbance at 298 (λ_{max}) for ternary complex compared to binary complex. 4-VP can act both as chelating ligand for uranium and as an additional functional monomer resulting in the formation of a very stable ternary complex and get stabilized in the highly cross-linked polymer matrix.

Role of functional monomers and the stability of the ternary complex have a great deal in the imprinting effect, as they are responsible for the binding interactions in the imprinted sites. Use of di-block copolymer self-assembly was reported earlier by Li *et al*. [2006] for the preparation of molecularly imprinted polymer nanospheres. In effect, factors such as polarity and hydrogen bonding strength of the solvent and polymerization reaction temperature also contribute to template-monomer interactions during imprinting.

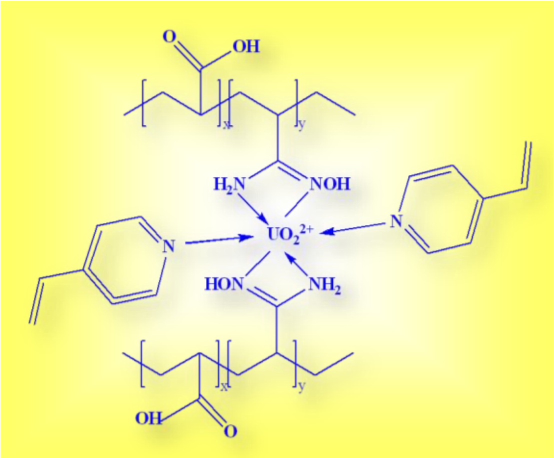


Figure 3.3 *Self-assembly of uranyl ion template with amidoxime functionalities in the copolymer chain and vinylated ligand forming ternary complex*

3.4 Removal of Uranyl Ion Template from Imprinted Polymers by Mineral Acid Leaching

Imprinted uranyl ions were completely leached out from the polymer matrix using 6 molL^{-1} of HCl. The complete flushing out of uranium from the polymer network without disturbing the amidoxime functionalities and crosslinked network was achieved within a time period of 6 h and thereby creating selective binding sites whose size, shape, and chemical functionality complement that of the template. The resultant polymer material was dried in an oven at 55 °C. NIPs were also leached similar to IIP to ensure uniform morphological characteristics of both polymers so as to make comparison of imprinting effect uncomplicated. The whole process is schematically represented in Figure 3.4.

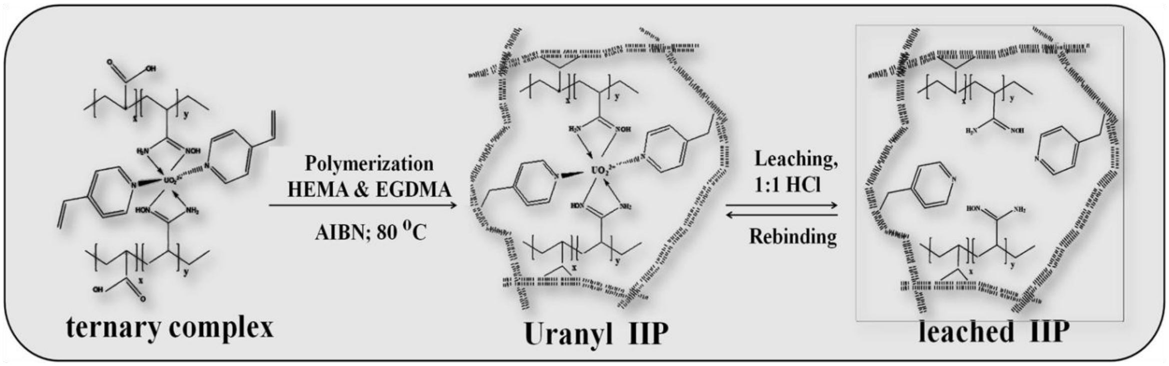


Figure 3.4 *Process of imprinting polymerization and template leaching*

3.5 Characterization of Imprinted and Non-Imprinted Polymers

Imprinted polymers are difficult to characterize completely because of their insoluble nature. A degree of characterization is possible including its chemical and morphological characterization and also the determination of ionic recognition behavior.

3.5.1 Evidence for the Existence of Amidoxime Functionality inside the Polymer Matrix after Leaching Process

3.5.1.1 FT-IR Spectroscopy

FT-IR spectra of unleached and leached IIP material show peaks at wavelengths 3200-3500 cm^{-1} (broad), 1640 cm^{-1}, and 940 cm^{-1} corresponding to O-H stretching and NH_2, C=N, and N-O respectively. This clearly indicates that the amidoxime functionality is held intact inside the polymeric matrix even after the removal of uranyl template ions by HCl leaching. The disappearance of (O=U=O) stretching vibration peak at 834 cm^{-1} in leached IIP material indicate the removal of uranyl template.

3.5.1.2 XPS Analysis

The leaching of uranyl ions from Set I-IIP materials on treatment with HCl was proved by disappearance of the peak at 381.7 eV for uranium in (+6) oxidation state (See Figure 3.5a). From the XPS spectra it is shown that unleached IIP of Set II- show a clear peak at 381.4eV of uranium (VI) and which is not seen in leached material (Figure 3.5b).

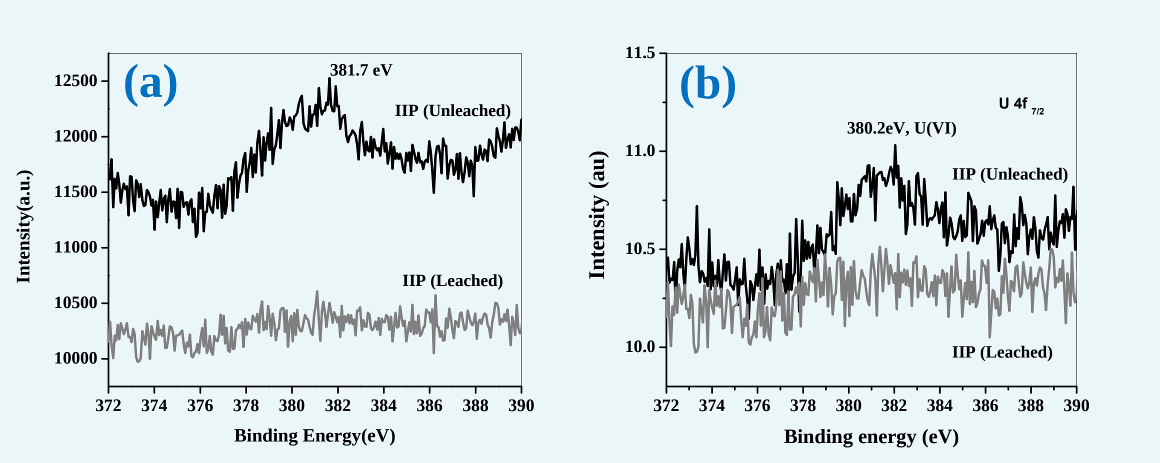


Figure 3.5 *XPS Spectra of unleached and leached uranyl IIPs of Set I (a) and Set II (b)*

3.5.1.3 EDS Analysis

The complete leaching of uranyl ions from both sets of unleached IIP materials with 50% (v/v) HCl was evidenced on comparison of EDS spectra of unleached and leached IIP materials as seen from Figure 3.6 a & b.

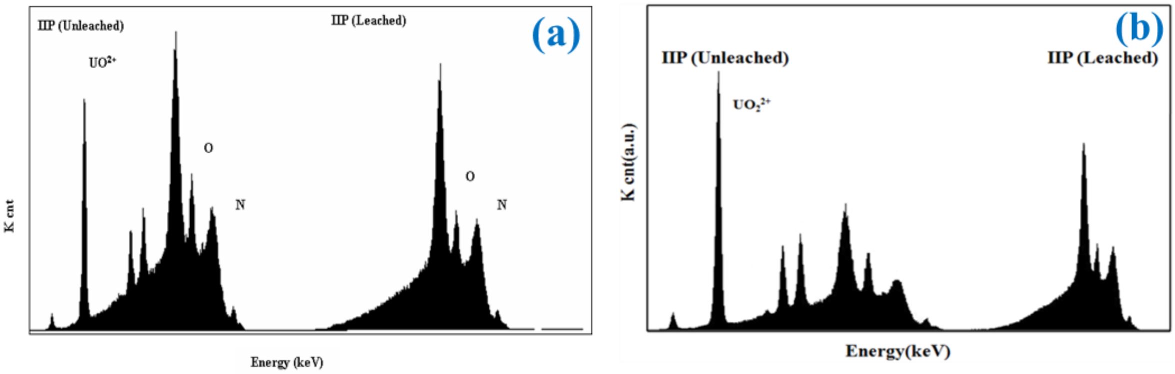


Figure 3.6 *EDS profiles of unleached and leached uranyl IIP materials of Set I (a) & II (b)*

3.5.2. Surface Characteristics

3.5.2.1 Scanning Electron Microscopy

The scanning electron micrograph of leached Set I- IIP material prepared by bulk polymerization is shown in Figure 3.7a which shows irregularly shaped materials with porous nature. This may be due to the bulky amidoxime groups which resulted in highly porous surface having selective binding sites for uranyl ion.

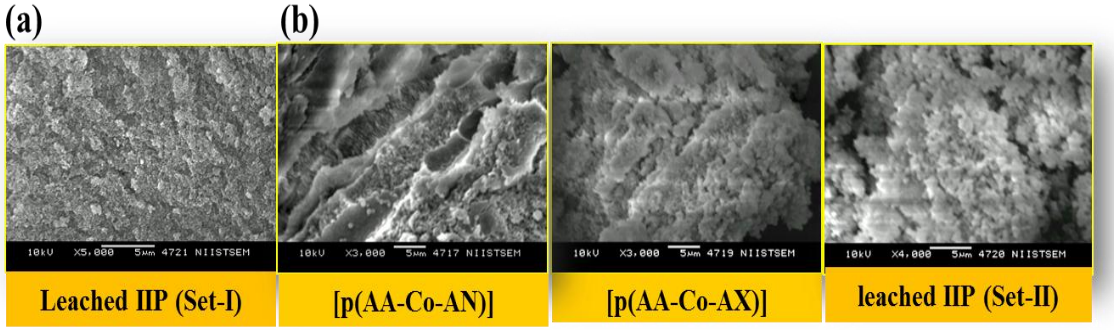


Figure 3.7*a)* *SEM photographs of IIP of Set I and* ***b)*** *SEM photographs of [p(AA-Co-AN)], [p(AA-Co-AX)] and leached uranyl IIP of Set II*

The SEM micrograph of [p(AA-co-AN)] showed a layered surface morphology which was significantly altered on chemical modification. This may be because of the formation of bulky amidoxime groups in the copolymer chain. SEM photographs of leached IIP material of Set II also taken, which showed a highly uniform surface morphology having specific and selective binding sites for uranyl ion (Figure 3.7b).

3.5.2.2 Surface Area and Pore Size Analysis

Porosity is an important factor as it can change the surface area of the material and thus increases the selective rebinding of uranyl ion from complex matrices. The BJH analysis shows that Set I IIP material is having an average pore diameter of 8.8 nm and it establishes the prominent mesoporous nature of the newly prepared IIP material. Surface area measurement done by N_2 gas adsorption experiments reveals high surface area of 138.9 m^2g^{-1} for leached IIP (Set I) material. But leached IIP of Set II showed a still more high surface area of 369.24 m^2g^{-1} and its NIP has 237.28 m^2g^{-1} which may contribute to the high retention/sorption capacity of IIP for uranyl ion. The probable reason for high surface area of Set II over Set I imprinted material is due to the development of some nanostructures by copolymer micelle formation (Lazzari *et al.*, 2003; Fo¨ster *et al.*, 1998] during the complexation of uranyl ions in the porogenic solvent.

From the above characterization methods it is evident that amidoxime chelating functionality was kept intact inside the crosslinked matrix of IIP & NIP after template leaching. Imprinted uranyl ions complexed by the amidoxime functionality were completely removed from the IIP material prior to rebinding as evidenced by FT-IR, XPS and EDS. Thus the complete removal of template was ensured to avoid possible template bleeding into environment during subsequent detoxification studies. Such leaching of uranyl ion template leaves behind cavities with complementary size and shape i.e., creation of geometrically well defined vacant sites. The cavity is also lined with complementary functionality, which is provided by the chelating ligands formamidoxime and VP. So, the vacant sites are completely available in the polymeric network and can act as the shape memory points for the same template during detoxification studies.

3.6 Rebinding Experiments for Uranium(VI) by Batch Static Method

Rebinding studies were conducted with 100 ml of aqueous phase containing 100 µg of uranium after adjusting the pH with a suitable buffer solution. For both sets of polymers pH was adjusted by adding 10 ml of 0.1M hexamine buffer. Sorbent materials of required amounts were added to aqueous phase of 100 µg U(VI) and preconcentration was carried out by stirring for a definite time so that the uranium can rebind at the vacant imprinted sites of the leached polymers. Rebound uranyl ions were eluted using 1M HCl for 30 min. Eluent solution was subjected to spectrophotometric determination of uranium, employing Arsenazo III procedure. All these experiments were performed for NIPs along with their corresponding IIPs to study the imprinting effect. The same procedure was applied for uranium rebinding studies by both copolymers and two sets of imprinted polymers.

3.7 Optimization of Experimental Parameters

Different sets of experiments were carried out for optimizing the experimental parameters employed in uranium rebinding experiments like weight of the polymer materials, pH of the preconcentration or rebinding medium, time required for preconcentration and elution steps, volume of the eluent etc.

3.7.1 Effect of pH on Rebinding of Uranium

The pH of the sample is an essential factor for the rebinding of uranium as the complexation of U(VI) with amidoxime functionality is significantly dependent on the pH of the preconcentration medium. Zhang *et al.* [2005] have studied the mechanism and kinetics of U(VI) sorption in details using amidoxime functionalized fibrous polymer and showed that the U(VI) binding with amidoxime is highly dependent on the pH of the equilibration solution. The pH of the sorption medium for our studies was scanned over different pH ranges for quantitative rebinding of uranium. An increase in percent rebinding of uranium is observed for IIP compared to NIP at all pH values including the optimum pH in both sets of polymers (see Figure 3.8a & b) which clearly explains the imprinting effect at all pH conditions. The quantitative rebinding of uranium was possible only in the pH range of 8.0 to 9.0 for Set I polymers and at a pH of 8.0 for Set II polymers. In acidic pH, protonation of the amidoxime groups may decrease its reactivity and thus the complexation of uranium (VI) may get blocked. As the pH value increases, uranyl ions became hydrolyzed to give $UO_2(OH)^+$ and a large amount of H^+ ions dissociated from formamidoxime was neutralized by $(OH)^-$ ions in the aqueous phase which support the strong complexation of uranium (VI) with amidoxime moiety. But further increase in pH may result in the hydrolysis of uranyl ions to form non-complexable species like $UO_2(OH)_2$, $UO_2(OH)_3^-$ etc.

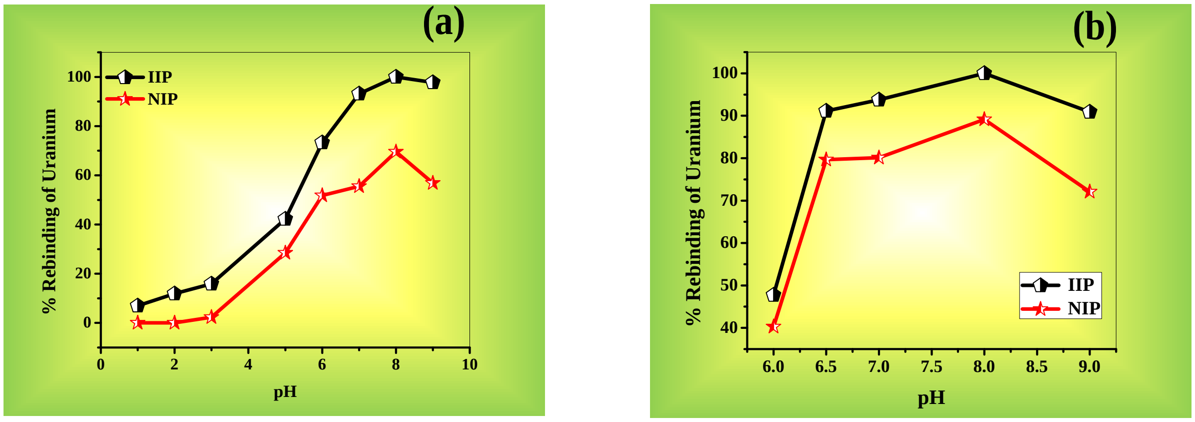


Figure 3.8 *Effect of pH on percent rebinding of uranium using ion imprinted (IIP) and non-imprinted (NIP) polymers of Set I (a) and Set II (b)*

3.7.2 Effect of Weight of the Polymers

Different weights of polymers ranging between 0.02-0.10 g were used for the rebinding experiments. It was found that a minimum of 0.075 g of IIP material was required for the quantitative rebinding of 100 µg uranium from 100 ml of aqueous phase in the case of Set I polymers (See Figure 3.9a) but 0.05 g of material was enough for Set II polymer material (Figure 1.9b). The percent uranium rebinding for IIP & NIP for each sets are given as: IIP-I (>99.9%), NIP-I (81.1%), using 0.075 g polymer and for IIP-II (>99.9%), NIP-II (87.12%) using 0.075 g polymer material. The increase in percent rebinding for IIP compared to NIP can be attributed to imprinting effect. Increased surface area and the availability of a large number of vacant binding sites in the imprinted material permit the complete rebinding possible even with lower amount of IIP material for Set II.

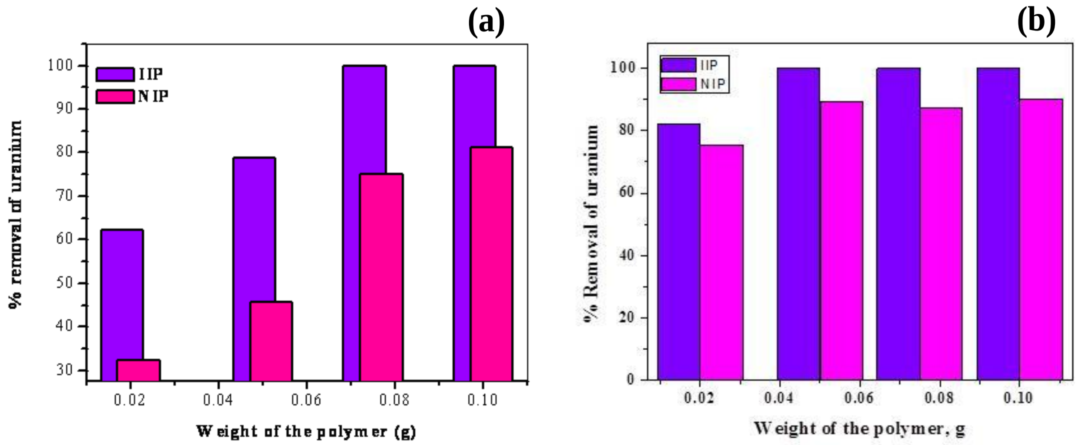


Figure 3.9 *Effect of weight of polymer material on percent rebinding of uranium using ion imprinted (IIP) and non-imprinted (NIP) polymers of Set I (a) and Set II (b)*

3.7.3 Effect of Other Experimental Parameters

Other experimental parameters viz. preconcentration time, nature and concentration of eluent, volume of eluent and time of elution were optimized sequentially for both IIP & NIP materials. For the quantitative rebinding of uranium(VI) at an optimal pH of 8.0 with 0.075g leached Set I-IIP material, the optimum time required for the rebinding was optimized as 30 min. The IIP material can be regenerated by eluting with 10 ml of 1M HCl within 20 min. Imprinting effect was noticed in all instances. Preconcentration times of 5, 10, 20, 30 and 60 min. were allowed for two sets of polymers and it was found that 25 min.

was essential for quantitative rebinding for Set II polymers. But complete elution was possible within 10 min. Eluent selected for the present study was hydrochloric acid and 1.0 M concentration of HCl (in 10 mL) was found to be enough for the complete elution of preconcentrated U(VI). All the experiments were done by checking the percent rebinding of 100µg of uranyl ion present in 100 mL of aqueous solution by stirring with 50 mg of IIP or NIP resins.

3.8 Retention Capacity Studies

The maximum amount of the template ions that can be sorbed per gram of the leached imprinted polymer material is termed as the retention/sorption capacity of IIP. It was calculated by saturating 0.02 g of both IIP materials with 2.5 mg of uranium (VI) in 25 ml. of preconcentration medium, under optimal conditions. Imprinted polymers prepared from both binary and ternary complexes of uranium were taken for sorption capacity experiments. The amount of uranium present was determined by using Arsenazo III procedure. Imprinted polymers of both binary and ternary complexes were studied for the comparison of their binding efficiencies.

Ternary complex based Set I-IIP showed high retention capacity of 80.0µmol/g, than those based on uranium - amidoxime binary complex (25.9µmolg^{-1}). Ternary complex based IIP of Set II also offered higher retention capacity of 88.5 µmolg^{-1} than the corresponding binary complex based IIP (35.4 µmolg^{-1}). This higher value of retention capacity for IIP formed from ternary complex may be due to the stable ternary complex formation which in turn resulted in IIP having a large number of selective binding sites with selective amidoxime functionalities after leaching. Retention capacity of amidoxime - VP based IIP material is higher or comparable with various SPE sorbents reported so far for uranium which is compiled by Rao *et al.* [2006] elsewhere.

3.9 Selectivity Studies

The adsorbents used for the removal of uranium from complex real samples should be highly selective as it contains a number of metal ions which may coexist with uranyl ions. So, it is essential to check how selective the newly prepared IIP towards uranyl ions. Selectivity studies for both di-block copolymers, [p(AA-Co-AN)] and [p(AA-Co-AX)], NIP and IIP materials of Sets I & II were carried out. Under optimal conditions, 100µg of individual inorganic species which are likely to coexist with uranium like Cu(II), Co(II), Mn(II), Zn(II), Cr(VI), Fe(III), N(II) etc. were equilibrated individually with IIP materials and the enriched elements were eluted using 1N HCl. The quantification of uranium is done by employing Arsenazo III (spectrophotometry) method as described. Flame atomic absorption spectrometry (FAAS) was used for quantification of these species present in eluent. The percent extraction, distribution ratios and selectivity coefficients were calculated for each metal ion. The percent removal of uranium and other selected inorganic ions are given by percent rebinding equal to $C_A\text{-}C_B/C_C \times 100$ where C_A and C_B are the concentrations of metal ion (µg L^{-1}) before and after rebinding. The distribution ratio (D) was given by $D = C_A\text{-}C_B/C_A \times V/m$ where V is the volume of the solution and m is the mass of the polymer. Selectivity coefficient is defined as $S_{UO2^{2+}/Mn+} = D_{UO2^{2+}}/D_{Mn+}$.

Selectivity coefficients of uranyl ion with respect to other metal ions using NIP and IIP materials are summarized in Table 3.1 for Set I polymers. The selectivity coefficients of

IIP were greater by 100 fold than that of NIP clearly indicating imprinting effect due to the multiple interaction or contact between the uranyl template ion and the polymer.

Table 3.1 *Selectivity coefficients of NIP and uranyl IIP for Set I polymers: (Uranium(VI) or* M^{n+} *= 100µg, pH = 8, weight of the polymer material = 0.075 g, sample volume = 100 ml, equilibration time = 25 min.)*

Metal ion M^{n+}	**Selectivity Coefficient** $(S_{UO_2^{2+}/M^{n+}})$	
	Non-Imprinted Polymer (NIP)	**Ion Imprinted Polymer (IIP)**
U(VI)	-	-
Cu(II)	0.3	100
Ni(II)	1.3	270
Mn(II)	9.1	340
Fe(III)	19.6	110
Co(II)	3.1	50
Cr(VI)	0.1	40
Zn(II)	1.9	160

The selectivity of different polymers are in the order IIP (ternary) > [p(AA-Co-AX)] > NIP > [p(AA-Co-AN)] for Set II polymers and the data is given in Table 3.2. Imprinting effect in percent rebinding of uranium using IIP is well explicated from the data rather using simple copolymeric functionalities. The selectivity coefficients of IIP materials were greater by 10-60 folds than that of NIP clearly indicating the imprinting effect.

Table 3.2 *Selectivity coefficients of [p(AA-Co-AN)], [p(AA-Co-AX)], NIP and IIP (pH = 8.0, sample volume = 100 mL, weight of polymeric resin = 50 mg, mixed metal ion solution = U(VI) (10 µg) + 100 µg* M^{n+} *)*

Metal ion	Selectivity coefficient ($S_{UO_2^{2+}/M^{n+}}$)			
	[p(AA-Co-AN)]	[p(AA-Co-AX)]	NIP	IIP
U(VI)	-	-	-	-
Cu(II)	1.16	18.56	0.324	16.31
Ni(II)	1.25	4.44	1.27	36.67
Mn(II)	1.46	6.56	1.01	61.11
Fe(III)	9.41	67.26	0.26	5.01
Co(II)	1.58	9.06	2.53	117.86
Cr(VI)	43.37	372.71	31.17	1000
Zn(II)	0.831	5.015	0.37	24.57

3.10 Applications

3.10.1 Removal of Uranium from Mining Industry Feed Simulants Using Set I Imprinted Polymers

The prepared IIP material was applied for the possible removal of toxic uranium from mining industry feed simulant solutions. Simulant solution of the sulphuric acid leach liquor from Jadaguda mine (Jharkhand, India) which is processed for chemical winning of uranium at Uranium Corporation of India, Ltd. (UCIL), India was prepared. It contains 5.9 g/L of Fe^{3+}, 2 g/L of SiO_2, 49 g/L of SO_4^{2-}, 0.8 g/L of P_2O_3, 4 g/L of Mn^{2+} and 0.4 g/L of rare earths along with 1 g/L of uranium. The acid leach liquor contains uranium and other impurities which have been solubilized. Uranium exists as anionic complexes of sulphates along with other impurities listed above. Imprinted polymer having amidoxime functional group are recognized to remove this uranyl ions without sulphate ions by ligand displacement reaction. Detoxification studies were carried out as described in Section 3.6. Even though the simulant matrix composition with respect to uranium was increased up to 25 folds of the original composition, the IIP material quantitatively removes 25µg uranium from 500 ml of the simulant solution. The developed material is capable of removing as low concentrations of uranium as 7 ppb which is well below the maximum permissible limit of 30 ppb for uranium in drinking water as per USEPA regulations. Thus, the use of IIP material having amidoxime chelating functionality for the selective detoxification of uranium from uranium mining industry feed simulant was successfully demonstrated by spiking known amounts of uranium as seen from Table 3.3.

Table 3.3 *Detoxification of uranium from mining industry feed simulants*

Sl. No.	Composition of the sample (uranium to feed simulant matrix* ratio)	% Uranium Removal*
1	1:1	104.4 ± 3.05
2	1:10	102.3 ± 2.30
3	1:25	99.6 ± 1.78
4	1:50	69.6 ± 2.05

*Average of triplicate measurements

3.10.2 Removal of Uranium from Simulated High-Level Nuclear Waste Solution Using Set II Imprinted Polymers

Highly caustic simulated HLW solution containing 1.33 M NaOH, 2.6 M $NaNO_3$, 0.43 M $NaAl(OH)_4$, 0.34 M $NaNO_2$, 0.52 M Na_2SO_4 and 0.026 M Na_2CO_3 was prepared [Duff *et al.*, 2004] and spiked with known amounts of U(VI). High concentrations of various salts in HLW make it more alkaline and the concentration of uranium remains very low, typically 10-15 μgmL^{-1}. Since the typical uranium levels in HLW are in the order 10-15 μgmL^{-1}, HLW simulant solutions (after adjusting the pH to 8) are spiked with 5-25 μgmL^{-1} of uranium and detoxification studies were conducted. 50 mg of IIP material could completely remove such lower amounts of uranium selectively as seen in Table 3.4.

Table 3.4 *Detoxification of uranium from simulated high-level nuclear waste solution (uranium spiked = 5-25 μgmL^{-1}, Volume of HLW=100 mL, pH=8, Equilibration time=30 min.)*

Composition of simulated HLW Solution	**Uranium spiked (μg mL^{-1})**	**Uranium found (μg mL^{-1})**	**% Removal***
1.33M NaOH, 2.6M $NaNO_3$, 0.43M $NaAl(OH)_4$, 0.34M $NaNO_2$, 0.52MNa_2SO_4, 0.026M Na_2CO_3	5	4.83	96.59 ± 2.57
	10	10.02	99.99 ± 1.60
	25	24.43	97.72 ± 1.88

* Average of triplicate measurements

3.11 Experimental

3.11.1 Materials

All reagents used in this work are of Analytical Reagent grade. Uranyl nitrate hexahydrate ($UO_2(NO_3)_2.6H_2O$) used for the synthesis and preparation of standard solutions were purchased from Spectrochem Pvt. Ltd. (Bangalore, India) and a stock solution of uranium (VI) was prepared using above uranyl salt in deionized water. All other uranium solutions were obtained by diluting the stock solution. Acrylonitrile and acrylic acid were obtained from Aldrich (Milwaukee, WI, USA). Hydroxylamine hydrochloride, Sodium Carbonate and various solvents used in synthesis steps were obtained from Merck, India. Formamidoxime, 4-Vinyl Pyridine (VP), 2-hydroxy ethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA), 2, 2'-azobisisobutyronitrile (AIBN), Arsenazo-III, 2-methoxy ethanol were purchased from Aldrich (Milwake, WI, USA).

3.11.2 Instrumentation

FT-IR spectra were recorded by using a Perkin-Elmer, Spectrum One FT-IR spectrometer. A Perkin-Elmer series two elemental analyzer 2400 was used for elemental analysis studies. Absorbance measurements were taken on a Shimadzu UV-2401 PC controlled spectrophotometer and pH measurements of samples were done using ELICO LI-120 digital pH meter. A Perkin-Elmer AAnalyst-100 atomic absorption spectrometer was used for the quanttative analysis of different metal ions. Scanning electron micrographs and Energy dispersive X-ray spectroscopic analysis (EDS) profiles were also taken by using a JEOL JSM-5600 LV instrument. XPS spectra were recorded in a VG Scientific ESCA-LAB Mark-II XPS unit by irradiating the samples with Al K_α radiation with a mean binding energy of 1486.6 eV at a vacuum of 10^{-10} mbar. BET- surface area was determined from N_2 adsorption experiments using micrometrics ASAP 2020 surface area analyzer. LI-120 digital pH meter was used for the pH measurements.

3.12 Conclusions

Uranyl ion imprinted polymers prepared from ternary complexes of uranyl ions were found to show high recognition and selectivity towards uranyl ions and has a higher retention capacity compared to binary complex based uranyl IIPs. Again the copolymer based IIP (Set II) has shown better uranium rebinding than Set I polymer. Set II-IIP containing copolymer uranophile show efficient uptake for uranyl ions (quantitative rebinding with 50 mg of IIP) compared to Set I-IIP (75 mg) containing amidoxime unit alone. This may be due to the hydrophilic nature of the acrylic acid groups in the copolymer chain of Set II-IIP which made them more aqua compatible leading to more template-uranophile interactions. In addition to that, high surface area of Set II-IIP also helps in providing high retention capacity than Set I-IIPs. Set I-IIP was applied for uranium removal from mining industry feed simulant and natural waters (down to 7 ppb) so that the pollution of nearby areas with deadly toxic uranium can be avoided. The selective uranium removal from simulated non-radioactive high-level nuclear waste was demonstrated by using Set II polymers at ~ pH 8.

Chapter 4

OPTICAL & ELECTROCHEMICAL SENSORS: AN OVERVIEW

4.1 Role of Chemical Sensors in Environmental Monitoring

In recent years, increased concern about toxic effects of chemicals in the environment has awakened the researchers to think about the necessity of monitoring pollutant levels in natural environment and industrial, agricultural, and urban sites. The conventional analytical procedures are sensitive, but, are based on laboratory instruments, require skilled technicians, demands tedious sampling, transportation and storage protocols, and often need time consuming separation or pre-concentration and clean up methodologies such as liquid-liquid extraction, liquid-solid extraction, solid phase extraction or solid phase micro extraction. But continuous field monitoring is crucial in the present scenario of increasing environmental pollution and can make it feasible only by the help of ‘portable, reversible, fast-responsive and continuous monitoring’ probes namely “sensors”. In addition, these sensors have to be highly stable and selective with sufficient sensitivity and long lifetime. Chemical sensors are grown into a full-fledged technology today for providing exact and reliable information about the chemical composition of the surrounding environment. They can respond continuously and reversibly to various concentrations of chemical pollutants and so became much popular for on-site monitoring of pollutants, as well as for addressing other environmental needs. A chemical sensor show high selectivity and sensitivity towards specific analyte and thus satisfies many of the requirements for on-site environmental analysis like fastness, accuracy, compactness, and portability. They can be developed and used at lower costs than the conventional sampling and analysis techniques.

4.2 Classification of Chemical Sensors

A sensor is a device that produces a measurable response to a change in physical or chemical information. As per IUPAC recommendations a chemical sensor is defined as a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal [Hulanicki *et al*., 1991]. Important components of a sensor include a receptor part and a transducer part where the receptor transforms the chemical information received into a suitable form of energy and the transducer converts it into a useful analytical signal. Receptor part contains the sensing platform composed of specific & selective receptor molecules. The mechanism involved in a sensor is schematically represented in Figure 4.1.

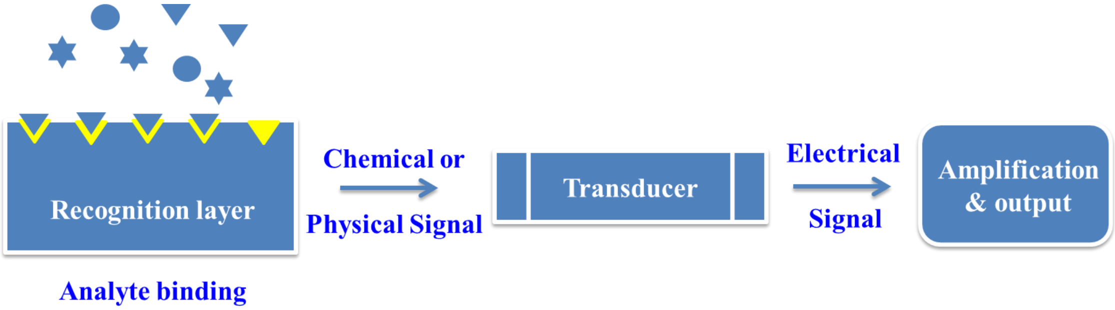


Figure 4.1 *Mechanism involved in a sensor*

Chemical sensors can be classified based on various analytical parameters involved in the sensing mechanism. According to the phase of the analyte exist they can be broadly classified into gas, liquid, and solid state sensors. But the major classification is by the operating principle of the transducers such as optical, electrochemical, thermometric, and gravimetric (mass sensitive) sensors etc. (See Figure 4.2).

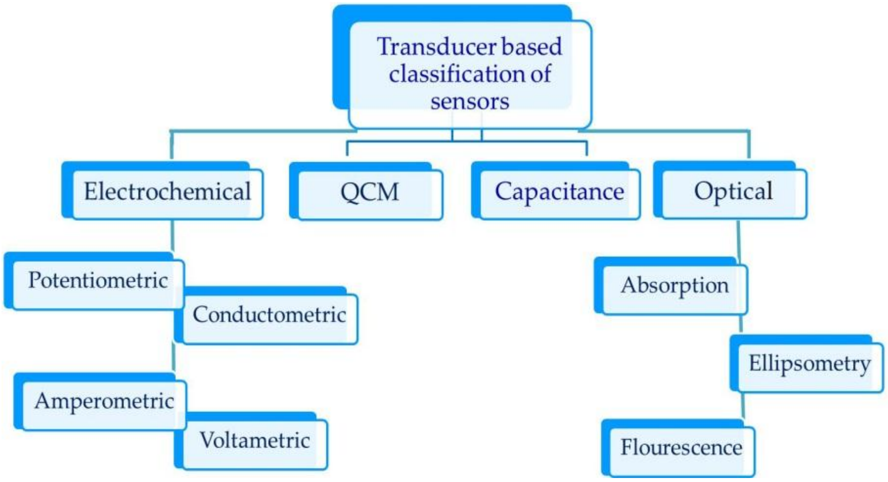


Figure 4.2 *Classification of chemical sensors based on transduction phenomena*

As per the reports of worldwide marketed sensors, it is found that electrochemical sensors constitute 58% of whole sensor devices followed by optical sensors in second position (See Figure 4.3). Both of these chemical sensors offer a good platform for sensing of pollutants in our environment. In spite of the continuing demand for commercial success, major advances in sensor technology are required in terms of i) simple structure, ii) low cost, iii) selectivity, iv) sensitivity (high signal-to-noise ratio), v) quality and stability of various components of sensing device including sensing material, vi) adequate adhesion of sensing material to transducer, vii) affordability and non-toxicity of sensing material and viii) compatibility with transducer components. Special interest is given for optical and electrochemical sensors in the second part of the thesis due to their easier integration and adaptability to different environments especially for environmental monitoring applications. The detailed mechanism behind these sensing devices is explained, followed by their utilities in the analysis of environmental pollutants.

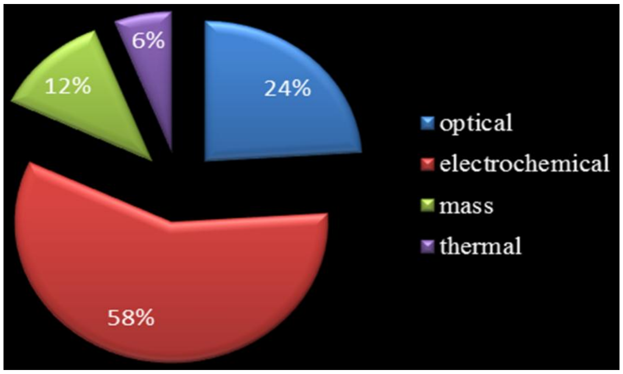


Figure 4.3 *Worldwide distributions of marketed sensors*

4.3 Optical Sensors (Optodes) for Inorganic Pollutants

Optical sensors are devices which transforms a change in the optical phenomenon as a result of the interaction of the analyte with the receptor part containing the recognition element. The optical phenomenon can be absorbance, reflectance, luminescence etc. Among numerous chemical sensors exist; optical sensors are highly advantageous for the analysis of trace amounts of inorganic toxic species where the optical signaling and transduction mechanism merges to give high throughput. They are highly selective towards a specific analyte by the multiple interactions between analyte and recognition element in a complementary fashion.

Solid platforms of optical sensors are generally termed as optodes or optrodes (the word originated from Greek, optrode means “optical path” etymologically more correct, optodes) and optically measures a binding process usually with the aid of a chemical transducer. Lubbers and Opitz [1975] coined the term optode in 1975 to describe a fibre-optic sensor with immobilised indicator to measure carbon dioxide or oxygen. They extended the concept to make an optical biosensor for alcohol by immobilising alcohol oxidase on the end of a fibre-optic oxygen sensor [Voelkl *et al.*, 1980]. Important constituents of an optode include a sensing element that responds to the analyte, a polymer matrix to immobilise the sensing element and the instrumentation. Optical sensing usually occurs through different chemical features of the sensing element upon binding with the analyte, like absorption, reflection, evanescent wave, luminescence (fluorescence and phosphorescence), chemiluminescence, surface plasmon resonance etc., followed by an optical transduction. This transduction can be performed by using optical fibres, light sources, detectors and other electronics. So optodes can be classified either by optical features of the sensing element or by the chemical transducers used/transduction mechanism.

Even though optodes were introduced around four decades back only, their low-cost, high stability and possible applications in variety of fields marked them as the most promising devices in chemical sensing. Miniaturized optodes are able to circumvent electrical noises and could found applications even in remote sensing. Fibre optics [Seitz and Sepaniak, 1988; Wise, 1991; Wolfbeis, 1991] is one of the fastest growing research area in optical sensing. Optic fibre sensors (OFS) facilitate optical spectroscopy to be performed on sites which are inaccessible to conventional spectroscopic techniques. They are very resistant to electromagnetic interference, because of the absence of electrical currents at the sensing point. OFS can survive in difficult environments, *e.g.* high doses of radiation, and so can have potential applications in the nuclear industry [Wingard, 1991]. They are available with transmissions over a wide spectral range. Fibre bundles are used for imaging purposes.

Various formats of optical sensors were developed such as test strips, disposable tests and optical waveguides. Selective optical indicators were used as recognition elements for metal binding, but most of them bind with more than one metal and finally it has to be sensed by pH adjustments. Many of them are not suitable for the purpose because of analytical wavelengths, poor (photo) stability, low molar absorptivity, need for additional reagents and their un-purified forms. More selective indicators including chromophores and flourophores were synthesized by incorporating specific functionalities to improve the sensitivity and selectivity factors of sensors. Specific ionophore can also be designed to enhance their optical properties by attaching chromophores and flourophores to them.

Transparent polymers like polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) etc. are used as solid supports to immobilize the sensing elements in the receptor part. Hydrophilic groups of the polymers and addition of plasticizers help in making aqueous compatible sensing devices which can especially find much applications environmental analysis. Thin membrane or film formats are usually seen for optical sensors as they can offer fast response and stability. Dynamic range and reversibility are also of prime importance in the sensing mechanism.

Even though most of the hurdles in sensing technology were circumvented by the developments in material science and technology, still it is facing issues related to preparation, stability (both operational and storage), and selectivity which have limited the commercialization of many sensors. Selectivity is the prime factor for a chemical sensor and improvements have been achieved by incorporating various chromophores and analyte specific ligands. As we have seen in the first introduction part of the thesis, the novel technology of imprinting had introduced a new platform in material science which facilitated the separation and sensing of toxic analytes very selectively. Ion imprinted polymers (IIP) offer a better platform for optical sensing with high selectivity. Among the several optical detection methods used in IIP sensor development, fluorescence and light absorption (UV-Vis) based optodes are a thriving area with its enormous environmental applications. In this section we will be discussing about MIP based absorptiometric and fluoro-optodes and their environmental applications.

4.4 Ion Imprinted Polymers (IIPS) in Optical Sensing

Efficiency for sensitive signaling of the binding event is important for an imprinted polymer based optical sensors. Stability, low cost and synthetic efficiency of ion imprinted polymers make them suitable for sensing applications in harsh environments. The basic principle behind the IIP based optical sensor is described by the specific interaction of the recognition layer with the target analyte and its transformation into an electrical signal. IIP based optodes also can be classified on the basis of different transducers as in the case of general optodes. Binding event may be expressed in terms of absorption, fluorescence, surface plasmon resonance, surface-enhanced Raman-scattering, chemiluminescence etc. Optodes can be designed in the form of thin films by grafting specific imprinted polymers on different substrates such as glass and quartz that can be easily coupled with optical transducers for sensing purposes. Sellergren and co-workers [Rückert *et al.*, 2002] have done several studies for the preparation of imprinted thin films on the surface of silica beads and polystyrene-based resin beads.

The developments in imprinted polymer based optical sensor technology up to 2000 were reviewed by AI-Kindy *et al.* [2000]where he categorized optodes by the optical properties of analytes. IIPs having analytes with native optical properties can make a surge in the sensitivity by the pre-concentration of the analyte onto the IIP. Sensing of polycyclic aromatic hydrocarbons was done by Dickert *et al*. on quartz substrate [1996; 1998; 1999] and further the technology has developed into a mature sensing platform for different organic and biomolecules. This methodology was applicable for successful and efficient sensing of inorganic metal ions, particularly some toxic species by the development of specific optodes.

Another approach for designing imprinted polymer optodes is by the inclusion of imprinted polymer material in another polymer matrix and casting thin films on a suitable transparent support. Gräfe *et al.* [2006] have prepared thin polymer membranes containing a chromogenic functional dye that shows a significant colour change upon reversible chemical reaction with the analyte. Various fluorescent and UV-labeled ligands can be accommodated properly in the imprinted polymer matrix and used for efficient optical sensing. The main advantage of imprinted thin films is their transparency in the visible region.

Optical fibres were also used professionally for imprinted polymer based sensor fabrications. Polymers were prepared on the distal end of an optical fiber whose surface was designed by binding a polymerizable agent on the surface. Murray's group developed a lead ion imprinted fluoro-optrode for monitoring the presence of toxic lead in water streams to control the contamination. This optode was prepared by binding 3% lead(II)-methyl-3,5-divinyl benzoate complex by in situ copolymerization on 400µm optical fibre surface (See

Figure 4.4). The lead(II) ion was then removed by first swelling it in a mixture of methanol and water and then soaking it in a stirred solution of EDTA. Numerous selectivity studies were conducted to characterize the selectivity of the sensor. The device was studied for stability and interference effects and can be applied to environmental field trials to identify sources of wastewater seepage into streams [Murray *et al.*, 1997]. Novel combination of imprinting and optical fibre technologies is described for the development of a fluorescence sensor for aluminium by Ng *et al.* [2006]. Another fibre optic sensor for copper was developed [Ng and Narayanaswamy, 2010] and has a great potential to be performed as a portable, simple and cheap optical sensor for the monitoring of Cu(II) ion, a metal ion that is crucial to biological system and also a potential toxic environment pollutant [Uriu-Adams and Keen, 2005; Sidhu *et al.*, 1995].

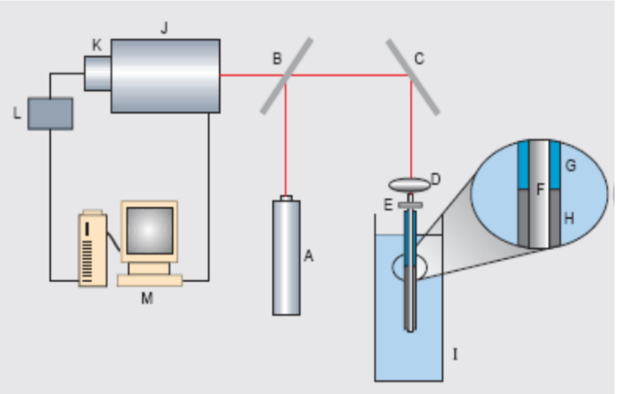


Figure 4.4 *Lead(II) ion measuring fibre optrode developed by Murray's group*

An optical flow through sensor was developed by Al-Kindy *et al*. [2002] using IIP based on Al(III)–morin complex as fluorescent signalling receptor molecule. They have used conventional Hellma flow cell placed in the sample compartment of the spectrofluorimeter filled with polymer and the analytical performance was assessed under optimum conditions. The limit of detection was found to be 0.01 µg mL^{-1} and this approach permits the adequate selection of the signaling receptor molecule for recognition of a given metal ion.

Challenges still existing in the development of imprinted polymer based optical sensors are the specific optical and material properties of the polymer phase and their optimization studies. IIPs are difficult to prepare as optically transparent and uniform thin films as they form in the form of small polymer microspheres so that they may scatter light, and most IIPs are opaque. Because of high cross-linking density they may suffer from acute contraction during polymerization, which leads to extensive cracking and peeling of MIP thin films. One solution for this issue is to monitor fluorescence and not transmittance where opaque IIP particles can be used. Another way is to reduce the crosslinking density. Controlling the kinetics of polymerization and by using low-volatility solvents can yield the desired UV-curable optically transparent MIP thin films. The major limitation towards the application of imprinted polymer based membranes in optical sensor development are the difficulties associated with the preparation of reproducible, thin and stable membranes from highly cross-linked polymers and the mass transfer in and through the membranes which made them very inefficient for real sample applications. Research in this field is in progress to overcome these limitations for an efficient MIP sensor development.

4.5 Electrochemical Sensors for Environmental Monitoring

Electrochemical sensors represent the most rapidly growing class of chemical sensors. Because of their experimental simplicity, low cost and sensitivity they are proved suitable for continuous monitoring environment. As we have seen in section 4.2 they have a leading position among the commercialized sensors. Electrochemical devices transform the effect of the electrochemical interaction of an analyte with electrode surface into a useful signal. Such effects may be stimulated electrically or may result in a spontaneous interaction at the zero-current condition. Significant technological advances have further facilitated their environmental applications more user friendly. Electrochemical sensors are mainly classified as potentiometric, conductometric and amperometric sensors. Among this classification, potentiometry embodies the simplest platform for rapid, inexpensive, and reliable detection of numerous inorganic in the field applications.

4.6 Understanding the Fundamentals of Potentiometry

Potentiometry is one of the simplest instrumental techniques among electrochemical sensors with widespread practical applicability since the early 1930’s. However, basic simplicity does not mean that their applications are limited. Major classification of potentiometric sensors includes ion-selective electrodes (ISE), coated wire electrodes (CWE) and field effect transistors (FET). The ion selective electrode is an indicator electrode which can measure the activity of a particular ionic species with selectivity. They are mainly membrane-based devices, consisting of permselective ion-conducting materials as per the classical configuration. A basic ISE measurement system consists of a selective ISE as the working electrode and a reference electrode of constant potential. The potential difference (cell potential) between the electrodes is related to the concentration of the dissolved ion. Potentiometry makes use of the development of electrical potential at membrane solution interface under zero current conditions when bound with ionic (ion sensing or selective electrodes) or molecule (molecule sensing or selective electrodes) guests. The most widely used potentiometric device is the pH electrode, which has been used for several decades but is limited to measurements in aqueous media. Coated-wire electrodes (CWEs) were first introduced by Freiser [1980; 1986], in which a conductor is directly coated with an ion-selective polymer membrane to form an electrode system that is sensitive to various analyte concentrations. The CWE response [Cunningham and Freiser, 1986] is similar to that of classical ISE, with regard to detectability and range of concentration. A CWE design does not need an internal reference electrode, beneficial during miniaturization. Another class of ion-selective field effect transistors (ISFET) is an extension of CWE incorporating the ion-sensing membrane directly on the gate area of a field effect transistor (FET). Whilst potentiometry has its beginning very long back, the recent advances in ion selective electrodes make it a valuable technique in modern chemistry and widened up the scope of the potentiometry.

The theories advocated to explain the potentiometric response include classical total equilibrium, local (diffusion) equilibrium models and advanced (Nernst-Planck-Poisson) approach. In classical models the electrical potential developed is considered as the sum of boundary potential and diffusion potential inside the membrane and is idealised in such a way to avoid mathematical, numerical and computational difficulties.

Potentiometric measurements are based on monitoring potential values under a zero current flow regime and are calculated using the Nernst equation. The potential difference across a semi-permeable membrane of an ISE depends on the ion activity in the sample. The Nernst equation explains the potential difference at the interface according to the activities of ionic species in the sample solution (s) and in the electrode (β):

$$\mathbf{E = E^0 + \frac{RT}{Z_iF} \ln \frac{a_i^{\,s}}{a_i^{\,\beta}}}$$

where E^0 is the standard electrode potential of the sensor electrode; a_i is the activity of the ion, R is the universal gas constant; T is the absolute temperature; F is the Faraday constant; Z_i is the valency of the ion. Glass electrodes and solid-state membranes are well established for sensing a number of cations and anions, but the detection limits were poor. Later so many researches were carried out for improving LOD by using highly selective ionophore incorporated inside the polymer membranes. Figure 4.5 explains a typical ion selective electrode where the transduction between the ion and electron takes place at the internal reference electrode (Ag/AgCl) immersed in the inner filling solution (KCl), as:

$\mathbf{AgCl + e^- \leftrightarrow Ag + Cl^-}$

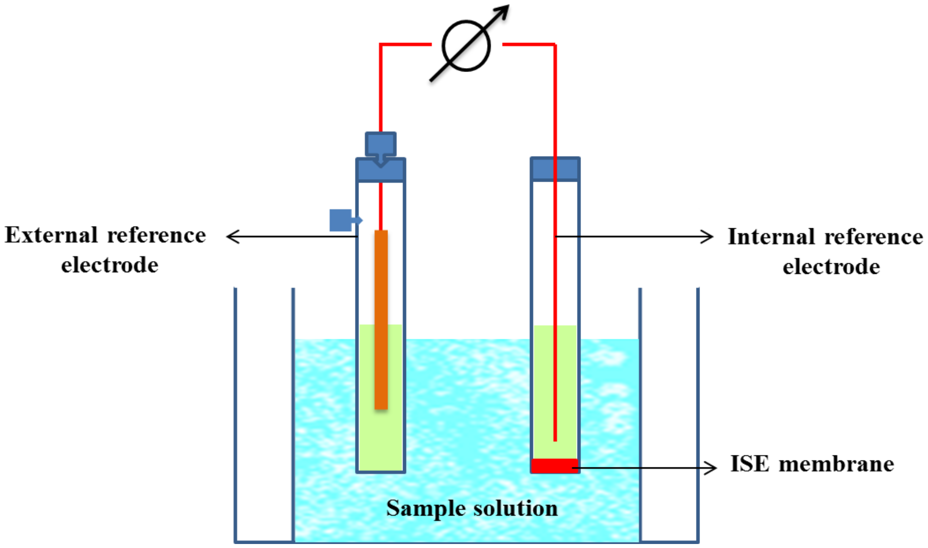


Figure 4.5 *A classical ion-selective electrode ISE*

In the context of practical applications, it is important to remember that ISEs are quite unique in their capability to assess free ion activities. ISEs are very attractive for various on-line monitoring systems5, especially due to their small-size and portability, and low cost. They have lower detection limits towards the sub-nanomolar concentration levels [Sokalski *et al.*, 1997], making them suitable for trace analysis of inorganic toxins [Bakker and Pretsch, 2005].

4.7 Non-Conducting Polymer Based ISEs

Almost all the ISEs are based on non-conducting polymers which used as a matrix for the incorporation of the sensing element. The basic components of such an ISE membrane are a polymeric matrix, sensing element (which can be a solid crystal or ionophore), membrane solvent (plasticizer) and ionic additives (if necessary). Nature and the amount of each component have great influence in determining the performance of ISE. The polymeric membrane separates the test solution inside the ISE from the outer target ion solution [Ganjali *et al.*, 2007]. Most commonly used polymer for ISE membrane preparation is poly vinyl chloride (PVC) because of its semi permeable nature. A typical composition for ISE membrane is: 33% (w/w) PVC as the polymeric matrix, 66% plasticizer for the matrix homogenization and 1% ionophore and the polymer could provide the required physical properties (e.g. elasticity and mechanical stability). Aside from PVC, other polymers can be also employed in membrane fabrication.

The ionophore or the ion carrier is the selectivity and sensitivity determining factors of the polymeric membrane sensor. The ionophore or the membrane active recognition can be an ion exchanger or a neutral macrocyclic compound [Ganjali *et al.*, 2006]. The binding phenomenon between the ionophore and the target ion is sensed by the ISE. Plasticizers used for ISE membrane preparation increases the plasticity or fluidity of the polymer material and thereby selectivity. Most commonly used plasticizers for ISE fabrication are: benzyl acetate (BA) [Ganjali *et al.*, 2006], bis-(1-butylpentyl)ad ipate (BBPA) [Xu and Katsu, 2001], bis(2-ethylhexyl) adipate (DOA) [Saad *et al.*, 2005], bis(2-ethylhexyl) phthalate, dioctyl phthalate (DOP) [Ganjali *et al.*, 2004], bis(2-ethylhexyl) sebacate (BEHS) [Segui *et al.*, 2007], bis(*n*-octyl)sebacate (DOS) [Segui *et al.*, 2006], bibenzyl ether (DBE) [Siswata *et al.*, 1994], dibutyl phthalates (DBP) [Shamsipur *et al.*, 2003], dibutyl sebacate (DBS) [93], didecylphthalate (DDP) [Akl *et al.*, 2006], 2-nitrophenyl phenyl ether (*o*-NPPE) [Peper *et al.*, 2005], *o*-nitrophenyl octyl ether (*o*-NPOE) [Zamani *et al.*, 2006, Ganjali *et al.*, 2003] and tri-*n*-butyl phosphate (TBP) [Gupta *et al.*, 2007].

4.8 Non-Conducting Polymer Membrane Sensors for Inorganic Anions

A series of ISEs have recently been developed with lower detection limits that are far better than the expectations (Bakker and Pretsch, 2001). These ISEs can now compete with the most sophisticated methods of trace analysis. More importantly and parallel to these developments, a sound theoretical understanding of the basic mechanisms has been achieved, which makes it possible to optimize the electrodes very efficiently (Ion *et al.*, 2001; Ceresa *et al.*, 2001; Morf *et al.*, 1999). The most important practical applications seen today are toxic metal analysis in drinking water, other environmental samples, and biological samples, which demand high selectivity, ruggedness, and short response and calibration times. The anion selective electrodes, just like the cation selective ones, are an important group of the ion selective electrodes. The number of the anion selective electrodes is lower than that of the cationic sensors, due to reasons like the relative larger size of the anions, their various shapes and theiTar high hydration energy. Nevertheless, a relatively large number of sensors for the anionic species have been published during the past decade.

In the early stages of ISE developments, solid-state ISE membranes were fabricated by using a variety of inorganic single crystals, polycrystalline pellets, or mixed crystals that are selective towards anions (e.g.; F^-, Cl^-, Br^-, I^-, SCN^-, S^{2-}) or cations (e.g.; Cd^{2+}, Cu^{2+}, Pb^{2+}) [Wang, 1994]. In 1937 Kolthoff [1937] first proposed fused silver chloride and silver bromide discs for the detection of chloride and bromide. Later in 1961 Pungor's group have [Pungor and Hollós-Rokosinyi, 1961] designed iodide ISE using silver iodide precipitate incorporated in paraffin wax. The precipitate electrodes can be prepared ether from single crystals, pressed crystals, or from crystals embedded in a suitable material. The first two kinds of electrodes form the group of homogeneous electrodes, while the third type gives the heterogeneous electrodes. The ISE response was explained in those cases by ion transport across the membrane but the charge transport through the crystal lattice is important as paper of Durst and Ross [1968] explained in the case of LaF_3-ISE (See Figure 4.6). Table 4.1 gives an idea about solid state electrodes for anionic species by make use of respective inorganic crystalline materials.

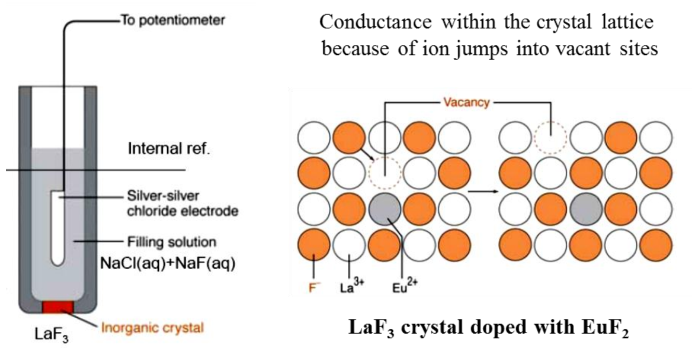


Figure 4.6 *Fluoride-ISE made of LaF_3 crystalline membrane*

Table 4.1 *Properties of solid state ion selective electrodes*

Anion	Concentration Range (M)	Membrane Material	pH Range	Interfering Species
F^-	10^{-6}-1	LaF_3	5-8	OH^- (0.1 M)
Cl^-	10^{-4}-1	AgCl	2-11	CN^-, S^{2-}, I^-, $S_2O_3^{2-}$, Br^-
Br^-	10^{-5}-1	AgBr	2-12	CN^-, S^{2-}, I^-
I^-	10^{-6}-1	AgI	3-12	S^{2-}
SCN^-	10^{-5}-1	AgSCN	2-12	S^{2-}, I^-, CN^-, Br^-, $S_2O_3^{2-}$
CN^-	10^{-6}-10^{-2}	AgI	11-13	S^{2-}, I^-
S^{2-}	10^{-5}-1	Ag_2S	13-14	-

Later ionophore based ISEs were developed where a strong interaction between the ionophore and the anion in a selective fashion is beneficiated in order to form the complex. The potentiometric response of the membranes, doped with these complexes, is believed to be based on the coordination of the analyte anion axial ligand to the metal center of the carrier molecule. All these polymeric membrane electrodes were useful for trace analysis [Sokalski *et al.*, 1997; Mathison and Bakker, 1998]. ISEs have been applied for trace-level measurements of different metal ons in seawater [Zirino *et al.*, 2002]. Electrodes based on chalcogenide glasses as sensing materials have been used for the analysis of Fe^{3+} [De Marco and Mackey, 2000] and Hg^{2+} [De Marco and Shacketon, 1999] in seawater. The performance of ISEs has been steadily improved during recent years in terms of accessibility to ions, selectivities, response time, and ruggedness [Bakker and Pretsch, 2001; 2002]. A lead ion-selective electrode was optimized for measurements in drinking water samples

[Ceresa *et al.*, 2001]. More recently, an ISE has been developed for the determination of copper ions in drinking water [Szigeti *et al.*, 2005]. In another recent application was the monitoring of uptake of cadmium ions by yeast and Arabidopsis-cell cultures with a Cd^{2+}-selective electrode [Plaza *et al.*, 2005]. Its lower detection limit was 10^{-10} in the presence of $Ca(NO_3)_2$. Literature survey reveals that during the past decade more than 70 anion selective membrane sensors have been reported based on non-conducting polymers and Figure 4.7 [Faridbod *et al.*, 2008] explains the impact of research going on the non-conducting polymer based ISE membrane sensors for inorganic anions compared to the conducting polymer based ones.

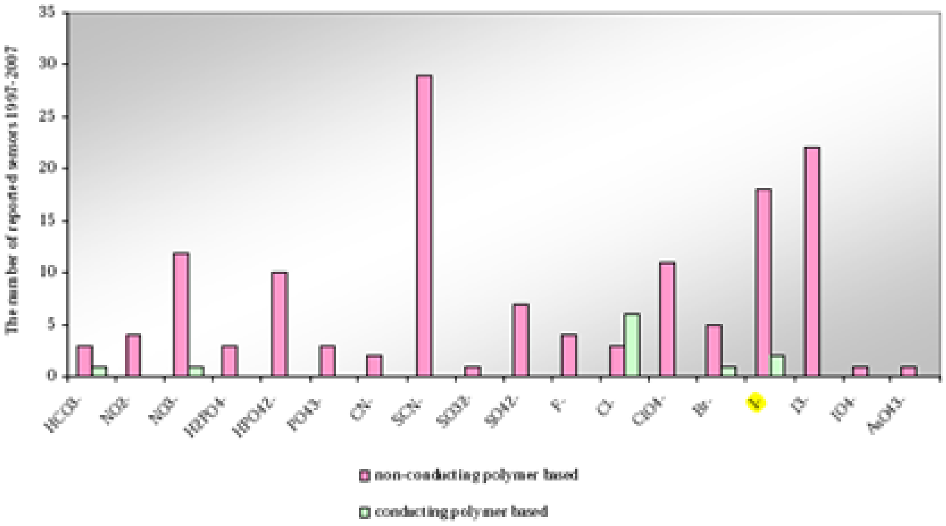
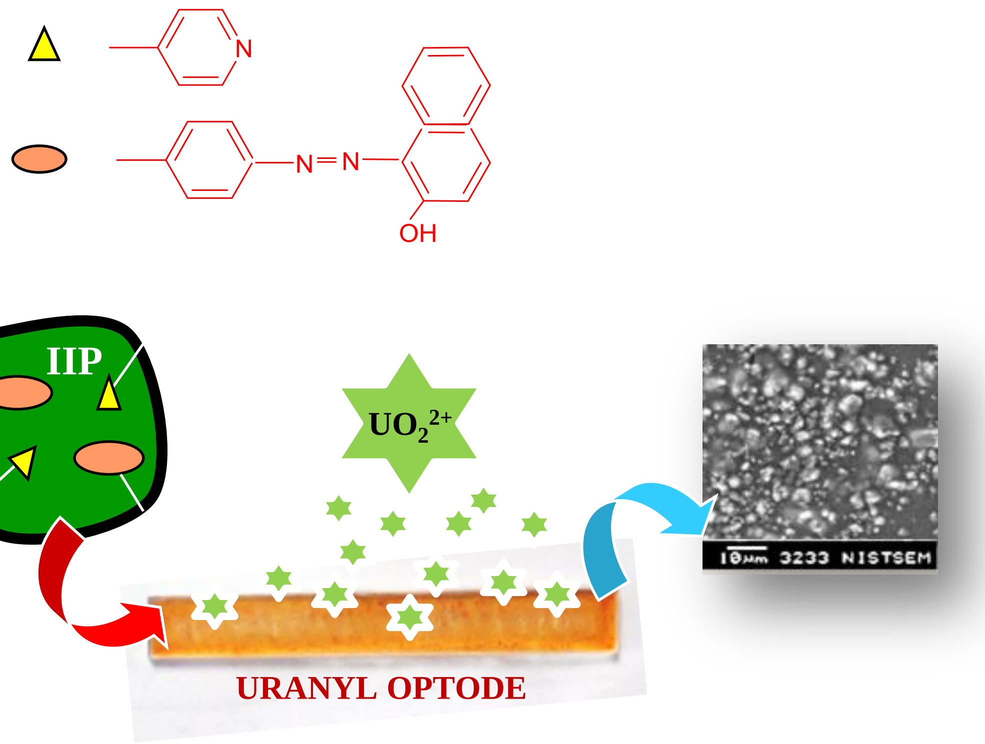


Figure 4.7 *The statistical diagram of the reported potentiometric membrane sensors based on non-conducting and conducting polymer for inorganic anions*

There are so many possibilities still exist to improve the response of ion selective electrodes in terms of lower detection limits and response time, improved selectivity and sensitivity factors and the polymer membrane characteristics. Such an efficient ISE can be used for highly sensitive signaling of inorganic pollutants in highly complexed matrices. So in the coming chapters we will be discussing some of our efforts to improve the sensing parameters of different chemical sensors (optical & potentiometric) especially for some selected inorganic toxins exist in our environment.

Chapter 5

BIOMIMETIC TWO DIMENSIONAL OPTODE FOR URANIUM SENSING



5.1 *Abstract*

Optodes are defined as portable field devices that respond selectively and sensitively to specific analytes, resulting in optical information. In the present chapter an optode which is selective towards uranyl ions with multiple interactions in a complementary fashion was developed using ion imprinted polymer materials as the sensing element. It was designed by the inclusion of uranyl ion imprinted polymer (IIP) material into polymethyl methacrylate followed by casting a thin film on a glass slide without any plasticizer. The IIP material was prepared via covalent immobilization of the newly synthesized ligand 4-vinyl phenylazo-2-naphthol (VPAN) into the crosslinked polymer matrix by thermal polymerization. Operational parameters such as pH, response time and the amount of sensing material for uranium rebinding were optimized. The response characteristics of the imprinted and the corresponding non-imprinted polymer inclusion optodes were compared under optimal conditions. The imprinted polymer inclusion optode responds linearly to uranium concentration in the range 0-1.0μg mL^{-1} with a detection limit of 0.18μg mL^{-1}, which is much better than the solution studies using 4-vinyl phenylazo-2-naphthol (1.5μg mL^{-1}). The developed optode was found to be stable for 3 months and can be used without any loss in sensitivity. The predetermined selectivity and operational stability of the sensing material (IIP) are some of the advantages over conventional optical sensors. The applicability of the designed optode for analyzing ground, lake and tap-water samples collected from the vicinity of uranium deposits was successfully demonstrated in this chapter. Thus, the developed two dimensional optode offers wide possibility for simultaneous preconcentration and detection/quantification of the analyte especially from complex environmental samples.

5.2 Introduction

The development of portable sensors in conjunction with more compact and low cost instruments are highly desirable for facilitating the task of on-site monitoring of environmental pollutants/toxins. Of those, optical sensors or optodes that are selective toward a specific analyte, and allows multiple interactions between host and guest species in a complementary fashion, have to be especially advantageous for field, in situ, and environmental applications [Lieberzeit *et al.,* 2007]. Advances in selective optical sensor technology can be a substitution for conventional analytical procedures especially for aqueous samples. Most of the inorganic toxins originated from industrial and agricultural processes finally seeped into water streams and persist as special ionic species which can cause major health hazards through drinking water. As we have already discussed in the previous chapters, uranium is well known for its chemical toxicity than radioactivity and highly persistent in the environment. The possibility of ground water contamination happens due to their seepage from the areas close to uranium deposits or because of uranium mining operations. The WHO, Health Canada and Australian drinking water guidelines fixed the maximum uranium concentration in drinking waters to be less than 9, 20 and 20μgL^{-1} respectively [WHO Guidelines, 2003]. Hence, there is a need to develop portable sensors that has the capability of analyzing the concentration of toxin, selectively. But, extremely low levels of these toxins in a variety of environmental samples, makes the preconcentration step much tedious and time consuming for the determination and quantification. Here comes the role of two dimensional sensors [Hill *et al.,* 2002]. Two dimensional sensors are based on the preconcentrative separation of target analyte from complex matrices of real samples and the subsequent generation of optical signal proportional to the concentration of the analyte. They offer a unique possibility of simultaneous preconcentration and detection of the analyte and are well suited to this type of application as they can be easily incorporated into low-cost, easy-to-use kits [Oehme *et al.,* 2005].

General method used for the fabrication of optodes was by immobilizing the sensing element in a suitable polymer matrix for generating the sensitive optical layer. Polymer inclusion or encapsulation membranes (PIMs) are widely used in literature for the separation or preconcentration process due to its superior stability compared to other carrier mediated membranes [Nghiem *et al.,* 2006; Scindia *et al.,* 2002]. These membranes can be regarded as a combination of surface and bulk optode types and both adsorption and encapsulation techniques are operative in their fabrication. Chemical interactions between the analyte and the indicator occur at the sensing layer and produce a detectable optical signal. So the selection of polymer platform used for the immobilization of indicators is equally important and critical as that of sensing element. Optodes can be classified as membrane, surface and bulk types according to the indicator immobilization techniques [Seiler and Simon, 1992]. Mass transfer is faster in the surface type optodes than the bulk, but may suffer from bleeding of indicators leading to loss of reagent. PIMs are simple in preparation and are highly reproducible, more compatible for the fabrication of optical fibre sensors and reagent is strongly immobilized either by hydrogen bonding or by physical entrapment force of the covered polymer matrix [Kuswandi and Narayanaswamy, 1999].

Optical sensors for uranium were developed using Alizarin Red S-tetraoctyl ammonium bromide ion pair on a triacetyl cellulose membrane [Safavi *et al.,* 2005] and mesoporous thin films functionalized with silylated *β*-diketone compounds [Nicole *et al.,* 2004]. Even though optical sensors designed by immobilization techniques [Malcik *et al.,* 1998; Sands *et al.,* 2002; Safavi *et al.,* 2004] are better in some of the aspects such as non-leaching of indicators and quick response but, lacks in antibody-like selectivity. The selectivity, which is the bottle neck in most of the sensing devices with different transducers, can be achieved by employing the plastic antibodies, i.e. molecularly/ion imprinted polymers [Haupt *et al.,* 2000; Murray *et al.,* 2001; Hillberg *et al.,* 2005].

MIPs have been proved for their capability as best recognition elements for the design of optical sensor devices. Analytes having native optical properties can make a surge in the sensitivity of optodes by pre-concentrating the analyte onto MIP. Since IIPs have specific binding sites for specific target metal ions, they can be effectively incorporated in optode designs for alarming toxic inorganic contaminations. Simple preparation, low cost and long term storage durability of IIPs make them suitable candidates for opical sensing [Prasada Rao *et al.,* 2006; 2007]. Murray's design of fluoro-optode for toxic lead ion explored the inclusive possibilities of fibre optics in environmental field trials to identify sources of contamination [Murray *et al.,* 1997]. Later many metal ion optodes were fabricated by various groups for relevant applications in various environmental issues. [Al-Kindy *et al.,* 2002; Uriu-Adams *et al.,* 2005; Sidhu *et al.,* 1995; Ng *et al.,* 2006; 2010].

By amalgamating the twin concepts of ion imprinted polymers (IIP) and polymer inclusion membranes (PIM), novel ion imprinted polymer inclusion membranes (IPIM) were prepared effectively for potentiometric sensor developments [Prasada Rao *et al.,* 2007; Metilda *et al.,* 2007]. In the present study, IIPs were used as a the sensing material for the development of IPI optode due to the high selectivity and retention capacity compared to corresponding NIP material arising out of the “imprinting effect”. Compared to thick film formats, thin films are better to interact with the environment in a measurable way. Polymethyl methacrylate (PMMA) is a commercially available polymer and is used to cast thin films by using IIPs as the sensing material. PMMA is a promising candidate for polymeric sensors due to its processability and mechanical stability, special optical properties, environmental durability, in comparison with other polymer supports [Cywinski *et al.*, 2007]. The extensive literature survey revealed that there is no optode developed for sensing or quantification of uranium based on imprinted polymer technology.

In this chapter, we describe the synthesis of uranyl IIP material by chemical immobilization of mixed ligand complex, (uranium - (4-vinylphenylazo-2-naphthol) - 4-vinyl pyridine) and the polymerization with matrix forming monomers. Furthermore the use of IIP for the design of imprinted polymer inclusion (IPI) optode by the inclusion of uranyl ion imprinted material in polymethyl methacrylate (PMMA) matrix is described and its possible application to natural waters is demonstrated.

5.3 Synthesis of Polymerizable Ligand

18 mmol (2.1mL) of 4-vinyl aniline was dissolved in a mixture of 1:1 HCl (15mL) to form 4-vinyl aniline hydrochloride and the solution was cooled until the temperature falls below 5 °C. The diazotization of 4-vinyl aniline hydrochloride was carried out by adding 27 mmol (1.9g) of $NaNO_2$ solution in small volumes with stirring. Care has been taken in such a way that the reaction temperature should not rise above 10 °C in order to prevent the decomposition of diazonium compound. 18 mmol of 2-naphthol (2g) was dissolved in

NaOH solution and cooled. The diazotized compound was coupled with this 2-naphthol solution. The cold mixture was acidified with conc. HCl. The resulting product was filtered and washed with water until it is free from acid. The residue obtained was purified by column chromatography (see Figure 5.1 for scheme).

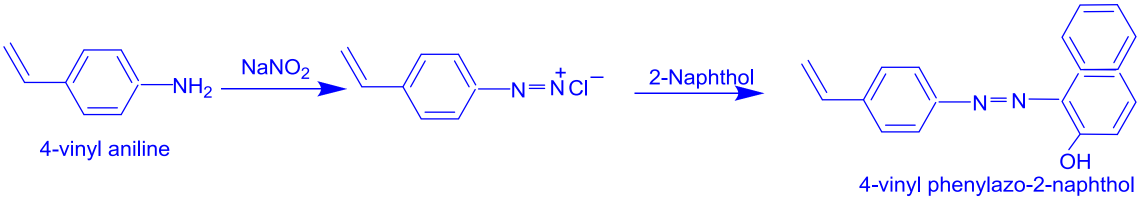


Figure 5.1 *Schematic representation of the synthesis of 4-vinyl phenylazo-2-naphthol*

5.3.1 Characterization of the ligand

The above synthesized ligand, 4-vinyl phenylazo-2-naphthol was characterized by IR, NMR, Mass Spectroscopy and elemental analysis techniques. Melting point of the compound was checked in a melting point apparatus and was 110-115 °C. Elemental analysis of the synthesized ligand shows a compositon of 78.66 % (C), 5.93 % (H) and 9.8 % (N) and was in good agreement with the expected data of 78.81 % (C), 5.14 % (H) and 10.21 % (N). Mass spectrum showed a peak corresponding to the protonated VPAN at m/z-274.

IR (KBr pellets, cm^{-1}): 3377 (O-H), 1615 (C = C, vinyl), 1600 (C=C, ring), 1552 (Ar-H), 1507 (N=N), 1451 (C=CH) 1257 (C-OH).

^{1}H-NMR (DMSO-d6, TMS, ppm): 5.34 (1H, d, CHH=CH), 5.85 (1H, d, CHH=CH), 6.81 (1H, dd, CHH=CH), 7.42 (2H, d, ArH), 7.59 (3 H, d, ArH), 7.79 (5H, d, ArH), 8.59 (1H, OH).

5.4 Preparation and Characterization of Uranyl Ion Imprinted (IIP) Polymer Material

5.4.1 Synthesis Procedure

Uranyl ion imprinted polymer was prepared by thermal polymerization method. Uranium VI (1 mmol) was complexed with VPAN (2 mmol) and 4-vinyl pyridine (2mmol) to form mixed ligand complex, which was then mixed with 10 mmol of VP (functional monomer) and 32 mmol of EGDMA (crosslinking monomer) to form the imprinted polymer. The above prepared prepolymer mixture was polymerized using AIBN (0.05g) as initiator at 80 °C under inert atmosphere. The IIP materials obtained were crushed and sieved to get uniform sized particles.

Selective enrichment is an inherent property for imprinted polymers. Hence, the polymerizable ligand 4-vinyl phenylazo-2 naphthol (VPAN) synthesized was used for the preparation of optode sensing material, i.e. uranyl IIP. 4-vinyl pyridine was not only used for uranyl complex formation but also has a role in the formation of polymer matrix along with the crosslinking monomer (EGDMA). The formation of ternary mixed ligand complex was confirmed by UV-visible spectral studies. Figure 5.2 shows the absorption spectra of individual monomers and complexes; (a) U(VI), (b) 4-vinylpyridine (VP), (c) 4-vinyl phenylazo-2 naphthol (VPAN), (d) U(VI) - VP, (e) U(VI) - VPAN, (f) U(VI) - VPAN - VP in 2-methoxy ethanol. The absorption spectra of ternary mixed ligand complex shows hyperchromic shift compared to the corresponding binary complexes (U(VI) - VP, U(VI) - VPAN) and individual ligands. This stands as confirmation for the formation of ternary complex in prepolymer solution. Complex formation prior to imprinted polymer synthesis is advantageous because of the control on the structure and the amount of species incorporated into the polymer and thereby regulating their microenvironment leading to predetermined selectivity.

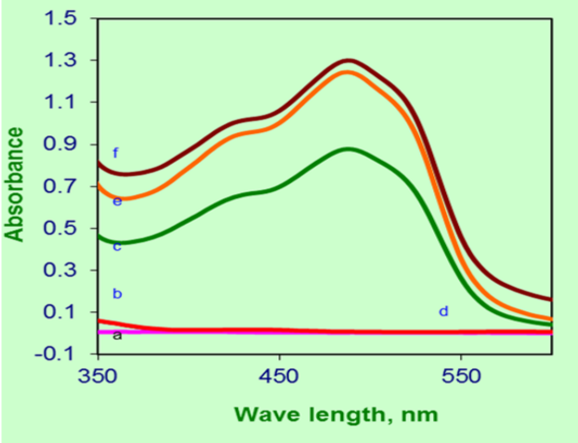


Figure 5.2 *UV-Vis absorption spectra : (a)* UO_2^{2+}*, (b) VP, (c) VPAN, (d)* UO_2^{2+}*-VP, (e)* UO_2^{2+}*-VPAN, (f)* UO_2^{2+}*-VPAN –VP in 2-methoxy ethanol*

The imprinted uranyl ion was leached by using 5.0 molL^{-1} HCl for 6h. The resultant material can rebind uranium selectively from aqueous solutions. The synthesis of corresponding non-imprinted polymer was carried out by omitting uranyl ion under the same conditions as that of IIPs.

5.4.2 Characterization Studies

5.4.2.1 Scanning Electron Microscopy

The scanning electron micrograph of leached uranyl ion imprinted polymer materials prepared by bulk polymerization (Figure 5.3) showed irregular shaped particles with porous surface morphology.

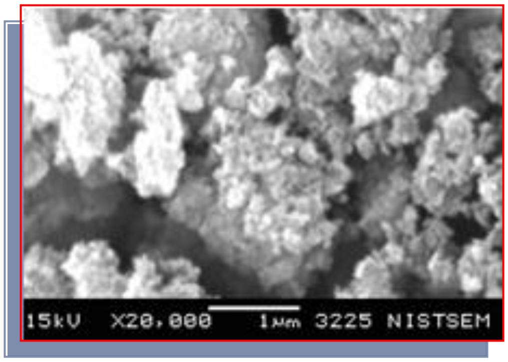


Figure 5.3 *SEM micrograph of IIP material*

5.4.2.2 Surface Area and Pore Size Analysis

The surface area and pore size analysis of leached uranyl IIP materials has been carried out from the nitrogen gas adsorbed at the temperature of liquid nitrogen by BET method. The BET surface area of the IIP material was found to be 172.16 m^2g^{-1} and the BJH average pore diameter during adsorption is 8-9 nm which confirms that the IIP material is mesoporous in nature.

5.5 Solid Phase Extraction (SPE) Studies Using IIP and NIP Materials

The preconcentration of U(VI) ion in 1L of aqueous solution was carried out with both ion-imprinted and non-imprinted polymer materials to ascertain the imprinting effect. A solution containing 100μg of uranium(VI) in 1L of solution was preconcentrated using 0.05g of leached IIP and NIP materials at pH 7.0. The pH was adjusted after adding 10 mL of 1M ammonia-ammonium chloride buffer and stirred for 30 minutes. The preconcentrated uranyl ions were eluted from the polymer material using 15 mL of 1.0 M HCl by stirring for 30 min. The polymer materials were removed by filtration. The U(VI) ion content was determined spectrophotometrically using Arsenazo III method [Snell, Wiley, 1978].

The percent enrichment of uranyl ion is quantitative in the case of IIP (>99%) and is only 57.4% for the corresponding NIP material. The imprinting effect is more pronounced compared to other uranyl IIP materials (except chloroacrylic acid (CAA)-EGDMA based IIP) reported by several researchers [Dai *et al.,* 1997; Saunders *et al.,* 2000; Bae *et al.,* 1999; Say *et al.,* 2003; Metilda *et al.,* 2004; 2007]. Even though (CAA-EGDMA) based IIP possess better imprinting efficiency, the amount of IIP required for enrichment study was about 2.6g which is very high compared to other sets of IIPs [Saunders *et al.,* 2000].

5.5.1 Retention Capacity Studies

The maximum amount of uranyl ion preconcentrated per gram of the material viz. retention capacity was determined by saturating 0.02 g of material in 25 ml of solution with 2.5mg of uranyl ion under optimal conditions described in the case of IIP solid phase extraction (SPE) procedure. The maximum amount of uranium preconcentrated onto the polymer was eluted using 15 mL of 1.0 M HCl and determined by Arsenazo III method. The retention capacity of IIP and NIP materials are 126.0 and 60.0 µmol g^{-1} respectively. The higher retention capacity for IIP than the corresponding NIP can be attributed to the imprinting effect which is similar to the imprinting effect noticed during SPE studies carried out elsewhere using 5,7-dichloro-8-hydroxy quinoline and 4-VP as the ligands to from the mixed ligand complex with U(VI) [Metilda *et al.,* 2004; 2007]. The retention capacity of the IIP material in the present investigation is comparable to various uranyl IIP materials prepared via trapping and better compared to other extractants reported in the literature so far. Again, the retention capacity of this IIP material (VPAN-VP) is of the same order as that of commercial ion exchangers namely Dowex 50wx-8 and Chelex 100.

5.5.2 Selectivity Factors for IIP and NIP

Selectivity is a basic criterion for a successful optical sensor which comes from the selectivity feature of the corresponding sensing material. Hence, the selectivity study for IIP and NIP was carried out. 100µg of each of individual inorganic species which are likely to coexist with U(VI) were equilibrated with 0.05 g of IIP and the enriched elements were determined by either spectrophotometry or flame atomic absorption spectrometry (FAAS). The percent extraction and the selectivity coefficients of uranyl ion using NIP & IIP materials with respect to other metal ions are listed in Table 5.1.

Table 5.1 *Percent rebinding and selectivity coefficients of IIP and NIP polymer materials*

M^{n+}	Percent Extraction*		Selectivity Coefficient $S_{UO_2^{2+}/M^{n+}}$	
	NIP	IIP	NIP	IIP
U(VI)	57.40 ± 0.92	99.00	-	-
Th(IV)	82.40 ± 0.85	90.60 ± 0.78	0.28	10.3
Co(II)	19.30 ± 2.26	6.57 ± 0.22	5.54	$1.40\text{x}10^3$
Ni(II)	28.26 ± 3.07	7.27 ± 0.01	3.41	$1.27\text{x}10^3$
Mn(II)	14.46 ± 0.74	2.57 ± 0.06	7.82	$3.80\text{x}10^3$
Fe(III)	77.23 ± 0.78	64.50 ± 1.46	0.39	54.5
Cu(II)	14.07 ± 1.74	59.60 ± 0.75	8.31	66.9
Cr(VI)	12.14 ± 0.01	11.11 ± 0.23	9.50	790
Zn(II)	18.19 ± 1.46	11.55 ± 0.24	6.05	760

* Average of triplicate experiments of preconcentration and determination

It is clear from the table that the magnitudes of selectivity coefficients obtained with IIP in comparison with NIP are higher, indicating once again the significant imprinting effect. Moreover, selective enrichment was possible in the presence Co(II), Ni(II) and Mn(II) ions. The selectivity coefficients of uranium with respect to Th(IV), Fe(III), Cu(II) and Zn(II) are also fairly good. From the above studies, the IIP material can selectively rebind the uranyl ion in the presence of other inorganic interferents. Hence, this material is used to design the optode for the selective sensing of uranium.

5.6 Spectrophotometric Solution Measurements

It was observed that VPAN is insoluble in water and soluble in DMSO. Hence 0.05% of VPAN in 25 mL of DMSO was prepared for solution measurements. To a series of U(VI) solutions containing 0-250 µg in 250 mL, add 5 mL of 1M NH_3-NH_4Cl buffer solution and 2 mL of 0.05% VPAN. The pH was adjusted to 7.0 ±1.5 using dil. HCl. The spectrum was recorded between 400-700 nm.

5.7 Fabrication of Uranyl Optode

PMMA (20 mg) was dissolved in 0.5 mL of $CHCl_3$ and 5 mg of leached IIP/NIP materials were included into the polymeric matrix. The polymer was dispersed into the PMMA matrix using a cyclomixer to get homogeneous mixture. The mixed solution was uniformly coated onto a pre-cleaned glass plate (5x1cm). Cleaning of the glass plates were done by washing in Conc. HNO_3 followed by ethanol, finally with distilled water and dried at 100 °C. Fabricated optodes were kept for drying at room temperature. NIPI films were also casted in a similar manner but using the NIP material. Various steps involved in IPI optode fabrication and optode surface features are explained in Figure 5.4. Thickness of the films were measured using a Leica optical microscope for all the films prepared in different batches and was found to be in the range ~ 68 - 70 µm.

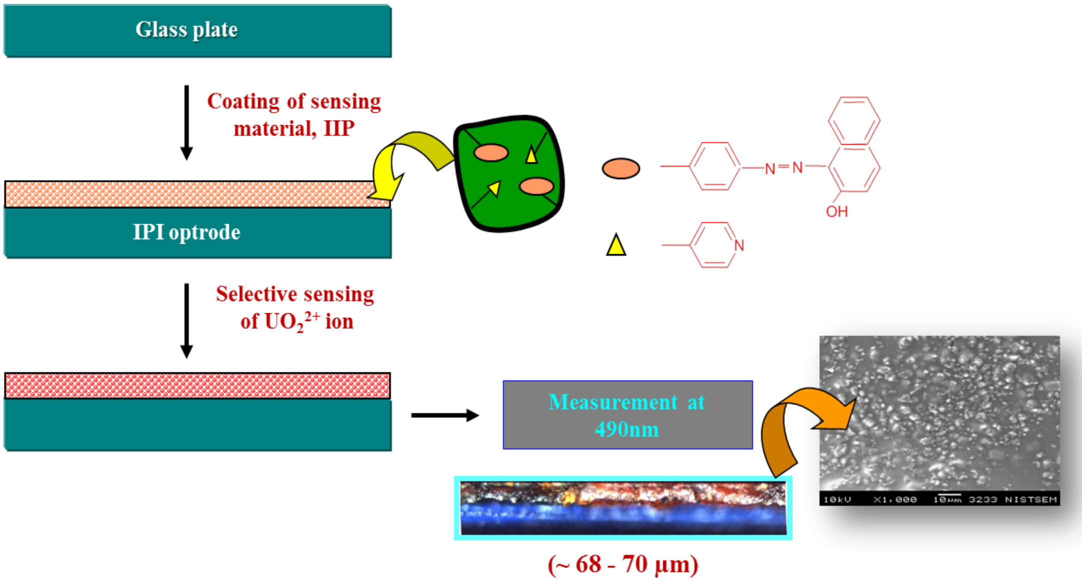


Figure 5.4 *Fabrication of IPI optode for the selective sensing of uranium*

Surface morphology of the optode film was studied using SEM and observed that the IIP material is almost uniformly dispersed in PMMA matrix which is responsible for the reproducible sensing of uranium as shown in Figure 5.5. IIP materials are seen encapsulated by PMMA on the surface of IPI optode film. Covalent immobilization of IIP containing the uranophile to the polymer matrix helps to avoid bleeding, crystallization or evaporation of components and thereby leading to high operational stability of the sensor. Photograph of fabricated IPI optodes after proper drying are displayed in Figure 5.5.

Figure 5.5 *Fabricated IPI optodes after proper drying*

5.8 Determination of Uranium Using IPI Optode

The test solution (250 mL) containing uranium (VI) was adjusted to a pH of 7.0 ± 1.5 after adding 5 mL of 1.0 M NH_3-NH_4Cl buffer. The IPI optode was exposed to the solution for 30 minutes with stirring. The response of the sensor was measured at a λ_{max} of 490 nm. The measurement was taken as the difference in absorbance between the optodes exposed to U(VI) sample solution and deionized water. NIPI films casted in a similar manner were also tested for uranium response. PMMA films incorporated with VPAN alone were checked for sensing of uranium. The values obtained were with less sensitivity compared to IPI optode and no selectivity was observed. Uranium concentration was varied in the range 0-1.0 µg mL^{-1}. The change in the absorbance of optode depends on the concentration of analyte and a hyperchromic shift was noted with increase in analyte concentration as shown in the Figure 5.6.

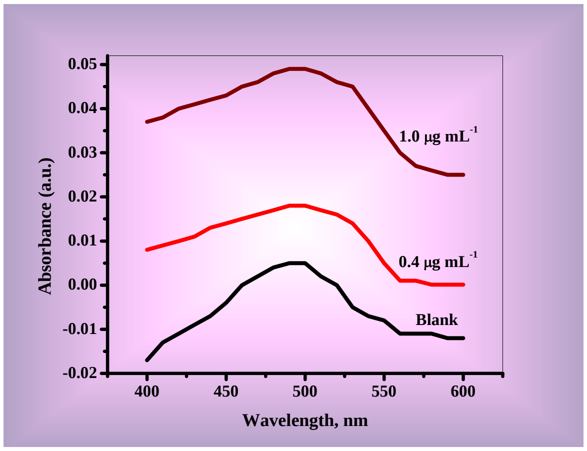


Figure 5.6 *Differential absorbance of two dimensional IPI optode after exposing to U(VI)*

Sensing performance of the optode was tuned by proper selection of pH. The effects of pH on the sensor response was investigated in the pH range 4-9 using 0.4 µgL^{-1} uranyl ion concentration in 250 mL of aqueous solution. The optimal pH range was found to be 5-8.5 as shown in Figure 5.7. The pH 7.0 was selected for further studies so that the absorbance can be maximum for uranium complexation or rebinding. The ability of the imprinted polymer to bind uranyl ion at this elevated pH levels reflects the stability of the uranyl complex and the affinity of the interaction points in the imprinted cavity. The observed drift in absorbance at higher pH values (>8.5) could be due to the formation of hydroxyl complexes of uranyl ion in solution. Moreover, no uranyl IIP material was reported which can be used to analyze the U(VI) in this pH range.

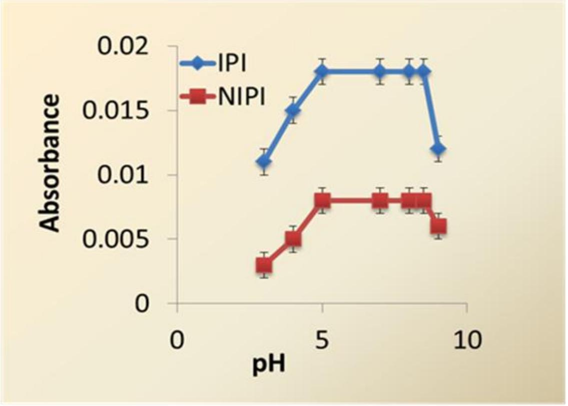


Figure 5.7 *Effect of pH on response of two dimensional NIPI and IPI optodes*

5.9 Evaluation of Sensing Parameters

Composition and nature of the film is important to improve the sensing characteristics of the optode. Hence the amount of IIP materials included into PMMA matrix was varied in the range 2.5-20 mg. The film became brittle as the concentration of IIP increased. The amount of IIP required for better sensing was optimized as 5 mg and was included into each film along with 20 mg of PMMA in 0.5 ml of $CHCl_3$. On comparison with other membrane based optical sensors, the concentration of sensing element in the current optode was very low [Safavi *et al.,* 2005; Sands *et al.*, 2004]. The reproducibility in film casting was tested by measuring the thickness and magnitude of absorbance of films against plane glass plate at 490 nm (Table 5.2). The thickness of the films were in a range 68-70 µm and negligible change in their absorbance values proves the uniform coating of sensing material on glass plates. The response time of a two dimensional sensor mainly depends on the time required for the analyte to preconcentrate onto the optode. This was varied from 5 to 45 min. A minimum equilibration/enrichment time of 30 min was required to get an optimal absorbance of 0.018 for 100µg U(VI) in 250 mL of aqueous solution.

Table 5.2 *Reproducibility in optode preparation*

Sl. No.	**Absorbance* (nm)**	**Thickness* (µm)**
1	1.453	68
2	1.461	70
3	1.469	69
4	1.453	68
5	1.413	68

* Average of triplicate measurements

5.10 Mechanism of Sensing

Direct analysis of traces of uranium in environmental samples is difficult because of the complex nature of their matrices. Therefore pretreatment steps in analytical procedures such as preconcentration of the analyte before its determination will enhance the specificity of response and reduce false positive or negative responses [Mizuike, Springer, 1983]. The developed IPI optode is based on preconcentration of target analyte by the sensing material and subsequent change in the microenvironment with predetermined selectivity leading to the generation of optical response signal, which is proportional to the amount of analyte. The IPI optode responds linearly to uranium solutions of increasing concentrations by the formation of ternary mixed ligand complex with VPAN and VP on measuring the absorbance at 490 nm.

5.11 Calibration Plot and Reproducibility of Uranyl Optode

Under optimum conditions described above, the calibration plot (See Figure 5.8) shows linearity over the concentration range 0-250 µg of U(VI) in 250 mL of aqueous solution.

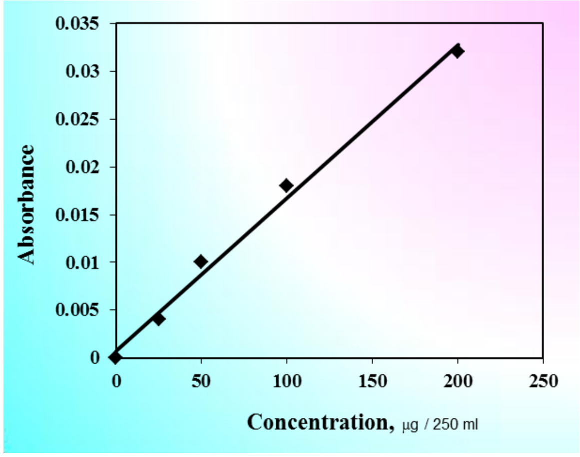


Figure 5.8 *Calibration plot for uranium sensing*

The linear equation with regression is as follows:

$$A = 1.4 \times 10^{-3} + 7.5 \times 10^{-5}\, C \text{ (for NIPI optode)}$$

$$A = 8.0 \times 10^{-4} + 1.6 \times 10^{-4}\, C \text{ (for IPI optode)}$$

where correlation coefficients are 0.9966 and 0.9962, A is the absorbance and C is the concentration in microgram of U(VI) ion per 250 mL. The lowest concentration which can be analyzed using the developed optode was 0.18 µg mL^{-1}, calculated as the concentration of

U(VI) which provided a signal equal to the three times the standard deviation of the blank which is much better compared to the corresponding NIPI optode (2 µg mL^{-1}) and U-VPAN solution studies (1.5 µg mL^{-1}). Thus lowering of detection limit with IPI compared to NIPI optode is due to the chemical immobilization of ligands via polymerization and the concept of imprinting.

The reproducibility of the sensor was evaluated by analyzing 0.4 µg mL^{-1} of U(VI) (three determinations each) using three films prepared at different timings. The relative standard deviation was found to be 8.33%.

5.12 Stability of the Optode

The stability of the optode film was established by measuring the signal at various intervals of time, after exposing the film to test solution. There is no change in absorbance for more than 3 days. No loss in material was observed when the film is exposed to aqueous solution (24 h). Also, no leakage of the ligand from the coated surface of the film was observed on continuous stirring and this may be due to the chemical immobilization of the ligand inside the imprinted polymer during the process of polymerization. The IPI-optode was found to be stable for 3 months without loss in memory as confirmed by reproducibility of calibration data, detection limit and slope of the calibration curve.

5.13 Analysis of Real Samples

The developed sensor was applied for the analysis of uranium in the natural water samples collected from locations in the vicinity of uranium [Cuddappa (1&2), India] and monazite sand deposits [Chavara (3) and Manavalakurichy (4), India]. The uranyl content of these samples was determined using uranyl IPI optode by standard addition method. Sample solution (250 mL) was adjusted to pH 7.0 using 5 mL of 1.0 M NH_3-NH_4Cl buffer (pH 7.0) and the U(VI) content was determined by adding 50 and 100 µg of uranium. The response of the sensor was measured as described above and the results obtained are shown in Table 5.3. It is clear from the data that the uranium recoveries obtained by spiking known amounts of uranium are quantitative, indicating the suitability of developed method for the routine monitoring or screening of natural waters for uranium.

Table 5.3 *Analysis of real samples*

Sl. No.	Description of the sample	Uranium µg mL^{-1}		% Recovery
		added	found*	
1.	**Bore well water, Cuddapa**	-	< 0.18	-
		0.2	0.201 ± 0.12	100.5
		0.4	0.402 ± 0.11	100.5
2.	**Lake water, Cuddapa**	-	< 0.18	-
		0.2	0.202 ± 0.13	101
		0.4	0.404 ± 0.11	101
3.	**Pond water, Chavara**	-	< 0.18	-
		0.2	0.203 ± 0.09	101.5
		0.4	0.405 ± 0.14	101.3
4.	**Pond water, Manavalakurichy**	-	< 0.18	-
		0.2	0.204 ± 0.14	102.0
		0.4	0.401± 0.13	100.3

* Average of three successive determinations

5.14 Comparison with other Uranyl Optodes

The developed IPI optode with its selective binding sites in the polymer matrix offer lower detection limit (0.18 µg mL^{-1}) compared to the uranyl optodes using

Alizarin Red S (ARS)-tetraoctyl ammonium bromide ion pair on a triacetyl cellulose membrane (physical immobilization) [1.2 μg mL^{-1}] and mesoporous thin films functionalized (chemical) with silylated β-diketone compounds (1.0 μg mL^{-1}) reported by Safavi *et al.* [Safavi *et al.*, 2005; Nicole *et al.*, 2004] respectively. The IPI optode preparation is highly reproducible analogous to silica meso structured optical sensors [Nicole *et al.*, 2004]. More significantly, this optode can be used over a wider pH range (5.0-8.5) unlike the above mentioned sensors such as optode film with ARS (>5.5). Again, the previous reports were applied to spiked river water samples and the present work addresses the analysis of real samples collected from the vicinity of uranium deposits which throw light in the environmental scenario of the localities.

5.15 Experimental

5.15.1 Instrumentation

A Shimadzu computer controlled UV-VIS spectrophotometer UV-2401 PC (Shimadzu, Kyoto, Japan) was used during preconcentration studies. An AAnalyst Perkin-Elmer atomic absorption spectrometer (Perkin Elmer, Shelton, CT, USA) was used for selectivity studies. pH measurements were carried out using LT-120 digital pH meter (Elico, Hyderabad, India). FT-IR spectra were recorded by KBr pellet method using Perkin-Elmer, Spectrum One FT-IR spectrometer. A 300-MHz Brucker NMR spectrophotometer was used for recording the NMR spectrum (Bruker Avance, Switzerland). Scanning Electron Microscopic (SEM) images were obtained using a JEOL JSM-5600 LV (SEM, Japan). Surface area and pore size analyser (ASAP 2020, Micromeritics, USA) was used to obtain the BET surface area and average pore diameter by N_2 adsorption.

Mass spectrum was recorded using a JEOL JSM 600 fast atom bombardment (FAB) high -resolution mass spectrometer (HRMS), (JEOL, Tokyo, Japan). CHN Analysis was carried out with a Perkin Elmer series 2 elemental analyser 2400. Thickness of the film was measured by the use of Leica, DMRX optical microscope in Qwin software (Leica, Hurbrugg, Switzerland).

5.15.2 Materials

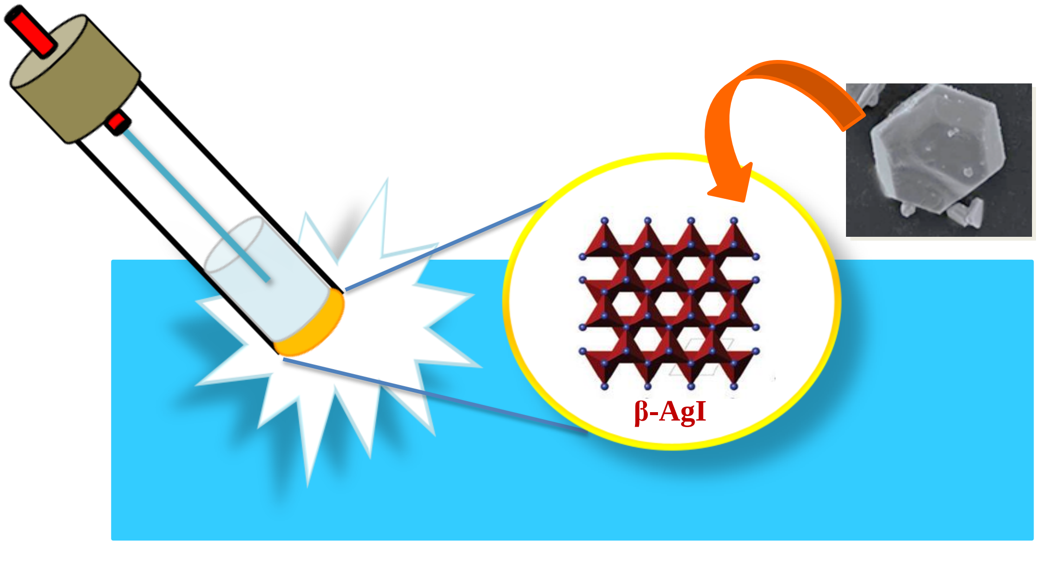
A stock solution of (1000µg mL^{-1}) of uranium (VI) was prepared by dissolving uranyl nitrate, purchased from Aldrich (Milwaukee, WI, USA). Arsenazo III (Aldrich, USA) solution (0.01%) was prepared in 100 mL of deionised water. Polymethyl methacrylate (PMMA), 4-vinyl pyridine (VP), Ethylene glycol dimethacrylate (EGDMA), and 2, 2'-azobisisobutyronitrile (AIBN) were purchased from Aldrich. All other chemicals were of AR grade purchased from Merck, India.

5.16 Conclusions

This chapter explains the fabrication of an IPI optode which is selective for uranyl ions with multiple interactions towards the ligands in a complementary fashion. The predetermined selectivity, operational stability of the sensing material (IIP) is more advantageous compared to conventional optical sensors. The optode developed was simple with its easy preparation and reproducibility and has flexibility in analytical variables such as pH. It can be used for the routine analysis of uranium down to 0.18 µg mL^{-1} in natural waters which is one order lower than other optodes reported previously. Thus the developed optode offer a possibility of simultaneous preconcentration and detection of the analyte especially from the complex environmental samples.

Chapter 6

DESIGN AND DEVELOPMENT OF IODIDE SENSING POTENTIOSELECTRODE



6.1 *Abstract*

Conductive AgI crystals were prepared and stabilized in its β-phase by post microwave irradiation under pressurized condition. Conventionally precipitated AgI crystals which contain more γ-phase than β were also studied for comparison. Permanent defect enhancement in AgI crystal lattice under microwave heating stabilizes the β-phase and increases the ionic conductivity which remains stable even at room temperatures for several months after irradiation. The prepared β-AgI crystals were used for the preparation of a simple and low cost heterogeneous iodide ion selective electrode (ISE) by dispersing in polyvinyl chloride in presence of dioctyl phthalate as plasticizer. The developed ISE could respond to lower and wider range of iodide concentrations ($1x10^{-8}$ *to 1M) within 2 min. without any preconditioning requirements. The ISE has a Nernstian range over* 10^{-8}*M to 1M iodide with a detection limit of 10 nM and has high selectivity towards iodide in presence of interfering ions. Performance of this laboratory made ISE in the analysis of natural and sea water samples are quite encouraging on comparison with other ionophore based iodide ISEs and commercially available iodide ISEs.*

6.2 Introduction

Iodide is an essential component to human health as it helps to ensure proper thyroid gland functioning, used as an antiseptic for skin wounds, and also for the emergency disinfection of drinking water and swimming pool water. Even though its role is vital, excess dosage can cause several health hazards like gastrointestinal irritation and ulceration, chemical pneumonitis, hypothyroidism, hemolytic anemia and acute renal failure due to tubular necrosis congenital goiter [Jakmunee *et al.*, 2001]. In aqueous environment, iodide is the dominant species of iodine especially at low to neutral pH values and positive redox potentials. Exposure to high doses of iodide may occur through drinking water, pharmaceuticals, and food; hence, monitoring the levels of iodide in our environment is very crucial and needs special attention.

Various methods reported for the determination of iodide reveals that most of these techniques either involve several manipulation steps or are very expensive to be used for routine analysis. Electrochemical detection methods have been reported but have not been used as widely as the spectroscopic methods. But among these methods, potentiometric detection is fundamentally the simplest of all, as the response is directly in the electronic domain and no excitation signal has to be applied as in the case of fluorescence studies [Schnierle *et al.*, 1998]. Ion-selective electrodes (ISEs) form a group of simple and inexpensive electroanalytical tools because of its unique characteristics such as fast response, wide dynamic range, ease of preparation and simple experimental procedures [Bakker *et al.*, 1997; Vesely *et al.*, 1978]. ISEs have been enormously used in the determination of ions in various fields like environmental science, life science, clinical, diagnostic, pharmaceutical, and water chemistry and so on.

The mechanism behind all potentiometric measurements can be attributed to the free-energy change associated with mass transfer (by ion-exchange, adsorption, solvent extraction or some other mechanism) across a phase boundary [Irving, 1976]. But specifically ionic conduction is the real mechanism behind the response in solid ion conductor based ISEs. Durst and Ross [1968] explained the mechanism for the response of LaF_3 ISE by crystal defects and the enhanced ion jumps into vacancies due to subsequent Eu doping, thereby increasing the conductance within the crystal. On comparing with liquid phases, solid electrolytes offer the possibilities of easy integration and miniaturization for sensors. In the context of room temperature electrochemical devices, the choice of suitable electrolytes is extremely restricted.

Highly conductive silver iodide plays an exceptional role in sensing not only because of the high mobility of silver ions but also in view of a very high ion exchange rate which made it as the most superconductive material. Silver iodide exists in three polymorphs: γ-AgI (face centered cubic, at room temperature) β-AgI (hexagonal, exists up to 147 ^{0}C) and α-AgI (body-centered cubic, exist above 147 °C) [Prager *et al.*, 1974; Hull *et al.*, 2004] as shown in Figure 6.1.

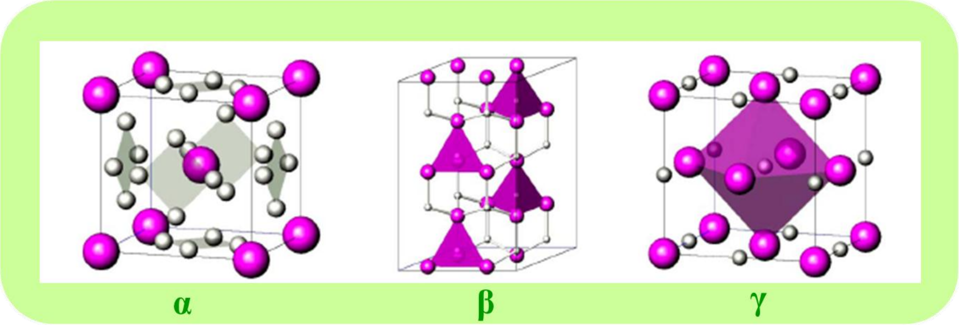


Figure 6.1 *Crystalline forms of Silver Iodide*

The origin of the ionic conductivity in AgI is associated with the fast motion of Ag ions over a number of partially occupied sub lattice sites which is aroused due to the Frenkel defects in the crystal lattice where the Ag atom is displaced to the interstitial positions [Perrino *et al.*, 1972].

Pungor *et al.* have opened up a great era for the development of ion-selective electrodes by fabricating the highly selective iodide ISE in 1961, for direct measurement of iodide ion using silver iodide precipitate incorporated in paraffin wax. Similar electrodes were fabricated further, based on a pressed pellet of AgI alone or with Ag_2S. Later only, carrier-based iodide ISEs were reported based on iodide ionophores comprising complexes of transition metals including Ag(I), Hg(II), Co(II), Fe(III), Mn(II) etc. (See Table 6.1) [Daunert *et al.*, 1991; 1993; Yuan *et al.*, 1993; 1997; 1999; Ganjali *et al.*, 2002; Poursaberi *et al.*, 2002; Shamsipur *et al.*, 2001]. The AgI precipitate based crystalline ISEs are generally classified into homogeneous & heterogeneous as per the IUPAC recommendations [Irving, 1976]. In homogeneous membrane electrodes the membrane is a crystalline material, like AgI prepared from either a single compound or a homogeneous mixture of compounds whereas heterogeneous electrodes consist of an active substance AgI mixed with an inert matrix, such as silicone rubber or PVC, or placed on hydrophobized graphite.

Research in iodide sensing via ISEs are in an advanced stage by making use of ionophore incorporated PVC membranes, but, we are still interested in using Pungor's strategy on simple AgI precipitate but definitely knowing the special features of its crystal lattice and the conductivity enhancement through microwave and pressure treatments.

Table 6.1 *Comparison of the characteristics of current ISE with other reported iodide ISEs including commercial ones.*

Sensing element	Linear range (M)	pH	LOD (μM)	Response Time (s)	Interference	References
Precipitate based ISEs						
AgI in paraffin	-	-	-	-	KCl does not interfere	[Pungor *et al.*, 1973]
AgI in silicon rubber	-	-	-	-	10^{-1}M KCl does not interfere	[Pungor & Tóth, 1973]
Ionophore based iodide ISEs						
Ag (I), Hg (II)	1x10^{-5}-10^{-3}	-	4-6	30-720	-	[Daunert *et al.*,1991; 1993]
Co (II)	4.8x10^{-7}-2.3x10^{-2}	4-8	0.48	40	NO^{2-},SCN^{-}, ClO^{4-}, Br^{-}	[Yuan *et al.*, 1993; 1997]
Fe (III)	1x10^{-6}-0.5	3.5-10	0.45	Average	-	[Ganjali *et al.*, 2002]
Thiopyrilium ion derivative	8x10^{-7}-0.1	5.5-8.0	0.2	15	-	[Poursaberi *et al.*, 2002]
Co (II)	8.4x10^{-7}-2.3x10^{-2}	4-8	0.47	40	OH^{-}	[Yuan *et al.*, 1999]
Mn (II)	3.4x10^{-5}-0.1	3.5-8.5	5	-	-	[Shamsipur *et al.*, 2001]

A set of experiments were reported in literature to obtain the super ionic phase under microwave (MW) heating by making a hysteresis in β-α phase transition temperature. Now it is well explicated that microwaves can cause a hysteresis in the β-α phase transition in silver iodide. Robb *et al.* [2002] observed AgI phase transition under microwave radiation and investigated by time-resolved, in situ X-ray diffraction patterns. Binner *et al*. [2006] also observed the same trend by using conventional & modulated temperature calorimetry and dielectric property measurements. They explained the phenomenon on the basis of multi-phonon coupling between the electromagnetic field and vibrational motions within the AgI crystal, which are speculated to stabilize the high temperature phases. But this effect is too small to account for the stabilization of α-AgI at much lower temperatures once the material is taken away from the influence of microwaves. Beneficial coupling of pressure with microwave heating has been accounted in a very few cases like zeolites using Parr autoclaves since it requires development of nonmetallic pressure vessels that can stand both reasonably high temperatures and pressures [Kosslick *et al.*, 1997]. But the effort can make better enhancement in properties as it can create crystal defects and corresponding ionic conductivity.

Microwave energy has been utilized in many chemical preparations because of its rapid kinetics, high yields, improved reproducibility and selectivity. Microwave energy is found to be more efficient for selective heating in many processes as they offer homogeneous bulk heating with homogeneous heat exchange compared to conventional heating. These processes are more environmentally friendly, requiring less energy than conventional processes. The most recent American Chemical Society monograph on Green Chemistry recommends that we “Use methods that minimize the energy required for a reaction to take place. For example, catalysts or microwave radiation.” [Ryan and Tinnesand, 2002].

In the present chapter we focus on the judicious utilization of microwave power for the stabilization of silver iodide β-crystals by understanding their strong coupling to microwaves via reorientation of the electric dipoles under microwaves. Interestingly, we could make the β-phase of AgI stable for more than 3 months by post microwave irradiation followed by controlled cooling. Effect of MW coupled with pressure at high temperature causes β-phase stability due to the strain or extra defects produced in the crystal lattice. Continuity and high power of microwaves interacts via multiphonon process and the subsequent energy redistribution through all phonons make the phase transition easier, faster and certainly stable. Further, a very simple and low cost heterogeneous polymer membrane ISE was fabricated using solid-state β-AgI crystal incorporated in PVC in presence of dioctyl phthalate as plasticizer. The developed ISE exhibit wide dynamic range, lower detection limit compared to most of the hitherto reported iodide ISEs and has been successfully demonstrated for the routine monitoring of iodide in natural and sea water samples.

6.3 Preparation of AgI by Conventional Precipitation

Silver iodide was precipitated by drop by drop addition of potassium iodide solution into silver nitrate solution taken in a teflon vessel in 1:5 molar ratio. Conventional precipitation of AgI was done at room temperature and at atmospheric pressure using the same molar ratio and allowed for complete preciptation by keeping it for 2 h. with constant stirring. All preparations were performed in darkness to avoid photodegradation of AgI precipitated and the precursors used.

Different molar ratios of KI and $AgNO_3$ were used to prepare AgI. But it was observed that, in the presensce of excess iodide ions, hexagonal phase of AgI was formed [Brauer, 1954] and so a 1:5 molar concentration ratio of $AgNO_3$ to KI was optimized for AgI preparation to avoid the presence of γ-phase along with β. Addition rate of chemicals and drying of AgI samples can also contribute to the phase formation in addition to the concentration ratio. But the hexagonal phase of AgI formed under specific concentration and temperature will not last for long time rather it change to the cubic phase on aging or cooling with a very poor amount of the other. This may be because the phase transition temperature was insufficient to create any permanent or stable change in the crystal lattice by defect enrichment.

6.4 Stabilization of β Phase of AgI Crystals by Microwave Heating

Conventionally precipitated AgI along with mother liquor was subjected to MW irradiation at high temperatures in tightly closed teflon vessels and placed in the microwave cavity of Milestone microwave labstation which is shown in Figure 6.2. Time, temperature, pressure, and MW power conditions of each experiment were monitored and controlled with the “easyWAVE” software package. Temperature was monitored with the aid of a shielded thermocouple inserted directly into the reaction vessel and the pressure inside the vessels was chocked by a pressure sensor (APC-55E). Microwave irradiation was given at various temperatures for different time periods. At first, lower temperatures were tried at 75 °C, 120 °C and 147 °C and finally at 190 °C for 5 min. with maximum MW power of 900W. Initially 10 min. were given for the system to attain the target temperature under full MW power followed by a constant and continuous MW power for 5 min. AgI formed under MW at 147 °C temperature shows crystalline nature and consists of β-AgI. But here also the β-phase was not stable and changed to γ-form. But AgI prepared at 190 °C under maximum MW power contain β form of AgI and was stable for several months on cooling. Different irradiation times were checked with 10, 20 and 30 min. at 190 °C but, 5 min. was found enough to stabilize the β form. So a continuous MW power of 900W for 5 min. was optimized at a temperature of 190 °C to obtain stable β-AgI crystals. The pressure developed inside the closed vessels during irradiation was 0.5 MPa. Thus pressure factor also helps in stabilizing the β-AgI along with microwaves. AgI containing vessels were allowed for controlled cooling after the irradiation (5^0C/min.). AgI formed by both conventional and MW methods were filtered and washed thoroughly with water and dried in vaccum to get fine light yellow powder of AgI. Further grinding of this powder was not performed as it causes a phase change to low conductive γ-form if the pressure exceeds 100 bar [Burley,1963; Takahashi *et al.*, 1969]. In the present study, we have achieved the stable β-phase of AgI through rapid heating under MW for 5 min. inside a pressurized vessel.

Figure 6.2 *Milestone microwave labstation used for MW irradiation*

Booske *et al.* [1992] observed anomalous reductions in activation energy and fast kinetics for microwave sintering processes which can be explained by non-thermal phonon distributions resulting in ion mobilities. Robb & Binner's [2002; 2006] studies have shown lowering of the transition temperature via interaction of microwaves with low-lying transverse optic modes of AgI. But the stabilization of α-AgI was not observed in those experiments after MW irradiation. Another report revealed the increase in AgI conductivity discontinuously by two orders of magnitude at 1.0 GPa, accompanying the transition from wurtzite/zinc-blende structure to NaCl structure [Hao *et al.*, 2007]. The conductivity was shown to be decreased with increase in pressure from 1.0 to 11 GPa indicating that high pressures may have an effect of decreasing the conductivity. These previous studies on AgI demonstrate the effect of microwaves and appropriate pressures on the ionic conductivity of AgI and stand as a support for the present observation of β-AgI stabilization.

Continuity and high power of microwaves interacts via multiphonon process and energy redistribution occurs through all phonons inside the crystal via anharmonicity and phonon-phonon coupling. When AgI is heated, local changes occur in Ag-I bonding and these changes play a leading role in the phase transition. This happens due to the increased anharmonicities in atomic vibrations leading to small changes in the apical Ag-I bond length as shown in Figure 6.3. Local fluctuations of bonding create field of forces that cause ion movement. Lattice vibrations induce overlap of 4d-electron wave functions of (Ag^+) with the 5p-wavefunctions of (I^-) from time to time. Difference in the extent of participation of d-electrons in Ag-I bond leads to fluctuations [Sunandana and Senthil Kumar, 2004]. This may create more interstitial spacing favouring Frenkel defects and the Ag^+ ion transport becomes more feasible to stabilize β-AgI even at room temperature.

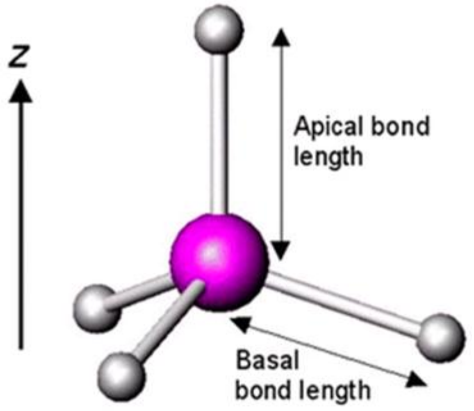


Figure 6.3 *Fluctuations of Ag-I bonding in* Ag_4I *tetrahedron of β-AgI*

For stabilizing the conductive form of AgI, some independent experiments were also attempted under MW by preparing capped AgI using specific stabilizers as reported elsewhere [Makiura *et al.*, 2009]. But, we could not beneficiate the effect of microwave heating during these preparations, since the polymer capping agents used, like PVP (mp.~120 °C), chitosan (mp.~130 °C) etc. get decomposed at high phase transition temperature of AgI. Further preparations were carried out by focussing on the effect of MW on pure AgI crystal lattice.

6.5 Characterization

AgI crystals were charecterized by X-ray diffraction and scanning electron microscopic techniques. From the XRD data, different planes (hkl values) and lattice parameters of the formed crystal lattice can be assigned which will be useful for determining the crystal phase of the AgI formed by conventional method or under microwaves. It can give information about the crystalline nature of the material also. The shape, average size and surface morphology of AgI crystals can be confirmed from the SEM micrographs.

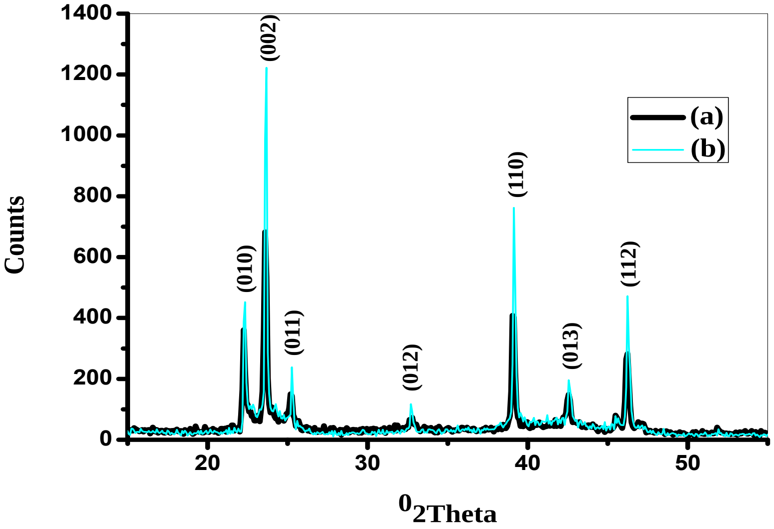


Figure 6.4 *XRD patterns of AgI formed by conventional precipitation (a) and by MW irradiation (b)*

XRD patterns of AgI prepared below 190^{0}C showed less crystalline AgI with γ-phase in predominance but those at 190^{0}C gave high intense peaks for different crystal planes of β-phase (see Figure 6.4). Scanning electron micrographs also shown that the AgI formed was not in any crystalline shape with fine boundaries rather it exists in irregular shapes. But AgI stabilized under MW at 190 °C gave precise hkl values for each crystal planes of β-AgI.

SEM pictures showed definite hexagonal crystals with fine boundaries and further growing nature of crystals were also observed as shown in Figure 6.5 (B & C).

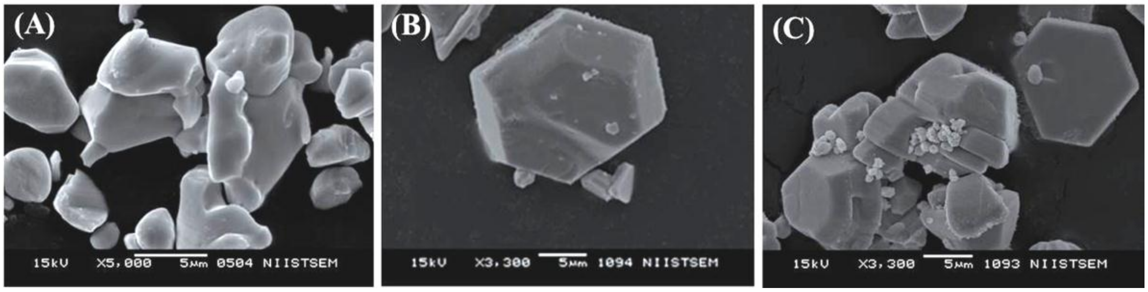


Figure 6.5 *SEM images of AgI formed by conventional precipitation (A) and by MW irradiation (B&C)*

6.6 Fabrication of Ion Selective Electrodes (ISE)

Proposed AgI ISE is a heterogeneous membrane type consisting of an inert polymer matrix, polyvinyl chloride (PVC) and DOP as the plasticizer along with the sensing element. 90 mg of PVC was dissolved in 2 mL of tetrahydrofuran and 0.2 ml of DOP was added to this clear solution. 90 mg of AgI was then dispersed in the above mixture and homogenized using a sonicator. The homogeneous mixture was poured into a teflon mould of 21mm i.d. and the ISE membrane of 0.58 mm dia. was formed after the evaporation of the solvent at room temperature. ISEs were fabricated using both conventionally preciptated and β-phase stabilized AgI for comparitive studies under similar experimental conditions. Casted polymer membranes were fixed onto a glass tube of 10 cm length with adhesives. Membranes were fixed at one end of the tube in such a way that the outer surface of the membrane can interact with the sample solution and internal electrolyte solution can be filled inside the tube as described in Figure 6.6.

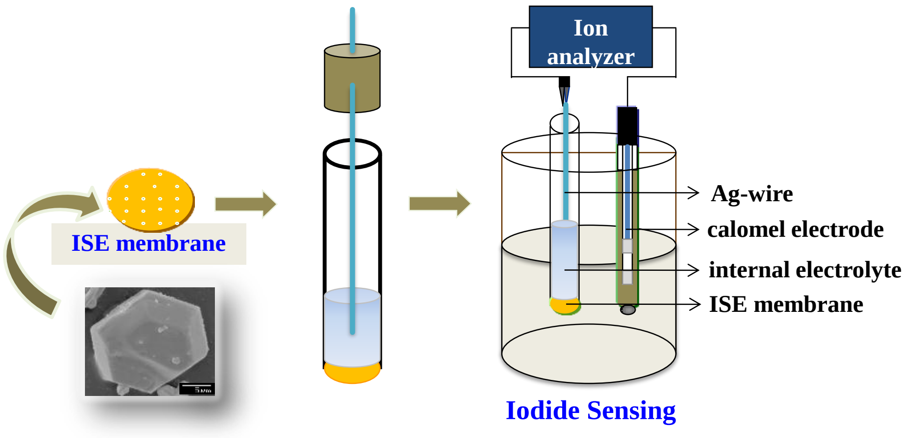


Figure 6.6 *Fabrication of β-AgI based ISE and the potential measuring set up*

6.6.1 Composition of ISE Membrane and the Role of Various Factors in ISE Response

The performance of ion selective electrodes are explained by Nernstian behavior, response time and detection limit which in turn depends on the surface characteristics of electrode membrane and the method of ISE fabrication. The present electrode is of a heterogeneous membrane type, made up of the active substance-crystalline AgI, mixed with an inert matrix- PVC to form the sensing platform and characteristics of the ISE are highly influenced by the nature and the amount of each component. For the preparation of ISE, we have used a typical composition of 24% (w/w) PVC, 52% plasticizer for the matrix homogenization and 24% AgI. PVC can form very good semi-permeable membranes with AgI and have enough elasticity and mechanical stability. Other compositions were also checked in an attempt to decrease the concentration of AgI in the membrane but did not improve the response of the ISE in a better way. Plasticizers are expected to have a key role in determining performance of ISEs. Polar plasticizers led to the lowering of the membrane resistance, compared with nonpolar plasticizers that contain other functional groups with potential coordination sites that might compete with the sensing element [Eugster *et al.*, 1994]. Plasticizer variation has been done using o-nitrophenyloctylether (o-NPOE) and DOP. ISE containing DOP as the plasticizer was selected as the best with low response time, stable response and wide linear range.

6.6.2 Conventionally Precipitated AgI based ISE

AgI formed via normal precipitation without any MW treatment was found to consist mostly of γ-phase. From the XRD pattern, it is clear that the material is not that much crystalline compared to the MW treated one and SEM pictures also, did not show any fine crystalline shaped particles (see Figure 6.4 (a) and 6.5 (A)). ISEs prepared using this AgI material did not show any response at lower iodide concentrations (10^{-6}- 10^{-9}M) and gave Nernstian response only from 10^{-5} M onwards, making the linear range very narrow. Reproducibility and reusability of ISE was lacking in conventionally precipitated AgI based ISE.

6.6.3 Performance of β-AgI based ISE

ISE based on β-AgI performed in a better way compared to normally precipitated AgI based ISE. The response of the membrane was very stable and linear from $1x10^{-8}$ to 1M of iodide concentrations. Presence of β-AgI crystals at the outer surface of the ISE membrane can make an Ag^+ ion concentration at the membrane interface in iodide samples leading to a potential change equal to Nernstian. When compared to conventional AgI-ISE, MW treated AgI-ISE offered better performance and was selected for further studies and applications.

6.7 Preservation of ISE Membrane

Ionic Strength Adjustment Buffers (ISAB) are recommended to use for conditioning ISEs and also in potential measurements to overcome the effect of variable ionic strengths of testing solutions. 5M $NaNO_3$ was used as ISAB in this potentiometric study and ISAB was used in all the testing solutions thereby giving a uniform ionic strength throughout the experiments. Freshly casted ISEs were soaked initially for 30 min. in 2% ISAB and then kept in dark boxes to avoid direct contact with light. It should not be kept in aqueous solutions for long hours as it can slow down performance of the membrane and shorten its life time.

ISE membranes were regenerated by gently polishing the outer electrode surface using soft tissue paper wet with ISAB followed by thorough washing with double distilled water. It is again stored in darkness to avoid photo degradation of the ISE membrane. The current ISE has an advantage that it does not require any preconditioning in standard iodide solution or ISAB before potential measurements even after several days of preparation.

6.8 Potential Measurements

The ISE was immersed in 50 mL of sample solution equilibriated with ISAB and connected to the ion analyzer through a silver wire as the internal reference. Saturated calomel electrode was used as the reference electrode and 10^{-3}M iodide solution was used as the internal electrolyte solution. The experimental set up for potential measurements using ISE is shown in Fiure 6.6. The potentials were measured for each concentration of iodide in a given response time of 2 min. at room temperature. A wide concentration range of 1.0 to 1.0×10^{-9} M iodide was used for studies. The cell assembly is represented as,

Hg/Hg_2Cl_2|KCl (satd.)|test solution (ISAB)||ISE membrane||Ag|10^{-3}M (I-)

6.9 Standard Calibration Procedure

Calibration is carried out by immersing the electrodes in a series of solutions containing known iodide concentrations and plotting a graph of potential (mV) versus the log of the activity of iodide ions. The total ionic strength of various iodide solutions were maintained at a total 1M concentration. The slope of the calibration graph gives the response of ISE per decade of iodide concentration which is equal to -58.5 mV for the current ISE (See Figure. 6.7).

6.10 Linear Range, Total Measuring Range and Detection Limit

The linear range of the ISE is defined as the part of the calibration curve through which a linear regression occurs and demonstrates the data points which do not deviate from linearity by more than 2 mV. The current ISE has a linear range extended from 1 M to 10^{-8} M. The practical limit of detection was calculated from the calibration graph by taking the intersections of two straight lines at the lower end of the linear concentration range and below it and was found to be 10 nM.

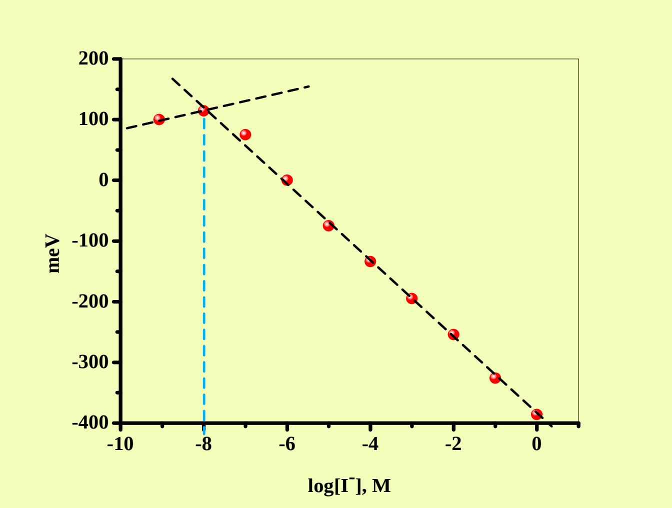


Figure 6.7 *Calibration plot of β-AgI based ISE*

6.11 Response Characteristics

Freshly casted ISE membranes were subjected to an initial soaking in ISAB for 30 min. and after that no conditioning was given over a period of 3 months when stored in dark. ISE was able to give stable response within 2 min. for each additions of iodide concentration. The potentiometric response of the electrode was examined in the concentration range 1.0 x10^{-9} to 1M.

The long-term stability of the electrode was studied periodically by re-calibrating and calculating the slope of the response profile. The calibration plot (see Figure 6.7) shows linearity over the concentration range of 1.0 x10^{-8} to 1M with a detection limit of ca. 10 nM and sensitivity of -58.5 ± 1.0 mV/decade of iodide concentration. The slopes of the electrode responses were reproducible over a period of 3 months. Table 6.2. gives a comparison of response charecteristics of current iodide ISE with commercially available iodide ISEs.

Table 6.2 *Comparison of response characteristics of current iodide ISE with commercially available iodide ISEs*

Sensing element	**Linear range (M)**	**pH**	**LOD (μM)**	**Response Time (s)**
Orion	$5x10^{-8}$-1	-	0.05	20
Omega	$2x10^{-8}$-1	-	-	-
Elit	$9x10^{-8}$-1	-	-	<10
β-AgI in PVC	$1x10^{-8}$-1M	-	0.01	<120

6.12 Response Mechanism

Ross *et al.* [1969] have stated the theory of solid state electrodes based on LaF_3, AgI and Ag_2S ionic conductors that no ions other than those composing the crystal go through the membrane and the potential is a result of ion transport through the membrane. Subsequently, Pungor's group [1987] unequivocally showed that the potential formation is limited to the electrode layers close to the surface. For homogeneous membranes, the reaction resulting in the potential formation proceeds at the outermost layer of the electrode. However, in case of heterogeneous membrane, as in the present case, depth of this layer depends on the distribution of the active component. Surface-exchange theory received impetus from impedence measurements of Brand and Rechnitz [1970] who grouped I^- along with Br^-, S^{2-}, Pb^{2+} and Cd^{2+} unlike LaF_3 or AgCl electrodes, wherein ion transport through the membrane has not been proved and an electric field charge accumulates on the surface. However, Pungor and Toth [1973] has stated unambiguously incase of precipitate based ISEs that electric conductivity is a necessary condition for the electrode response in addition to surface exchange equilibria.

Ross [1969] has applied Nernst-Planck equation for the derivation of an expression for the lower limit of detection of ISEs and reached basically the same conclusion as that of Pungor's group using the theory of Donnan potentials established on the surface [Pungor, 1973]. As stated by Pungor & Toth, experiments carried out with less stable hexagonal (β-AgI) and that of face centered AgI (surface layer found to contain β-AgI) responded to iodide in a similar manner, which is the only report where the presence of β-AgI is mentioned for iodide ISE response [Pungor, 1987]. In the present work we succeeded in stabilizing β-AgI for more than 3 months via post treatment with microwave irradiation under pressure and found to give wider Nernstian response range ($1x10^{-8}$ to1M) and lower limit of detection ($1x10^{-8}$M) compared to conventionally precipitated AgI based ISE. This can be explained by invoking Ross's concept of facile ionic transport through β-AgI crystal lattice upto certain depth of heterogeneous polymer membrane iodide ISE. The interstitial spacing is increased certainly by microwave treatment followed by fast Ag^+ transport. The increased concentration of iodide ions from the test solutions at the ISE membrane surface again enhances the movement of interstitial Ag^+ ions of frenkel pair inside β-AgI crystal lattice of ISE membrane.

6.13 Selectivity of ISE Membranes

The selectivity behavior is the most important characteristic of an ion-selective electrode which determines whether a reliable measurement in the target sample is possible or not. Matched potential method was employed to evaluate the selectivity of the proposed iodide ISE over other ions. According to this method, the specified activity (concentration) of the primary ion ($a=1.0\times10^{-5}$ M) added to a reference solution ($1.0\text{x}10^{-6}$ M of iodide) is measured from the potential change. In a separate experiment, interfering ions are successively added to an identical reference solution, until the measured potential matched with that obtained on the addition of the primary ions. The selectivity coefficient ($\mathrm{Log}K_{\mathrm{I,i}}$) is given by the resulting primary ion to interfering ion activity (concentration) ratio. The ions selected for studies include Cl^-, Br^- ,PO_4^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, CO_3^{2-}, NO_3^{2-}, NO_2^{2-} and SCN^- and the selectivity factors of the ISE are listed in the Table 6.3. As it is evident from table, most of the ions show very low values of selectivity coefficients, indicating no interference in the performance of the membrane electrode assembly.

Table 6.3 Selectivity factors for β-AgI ISE

Interferent ion	**Log$K_{\mathrm{I,i}}$**
	Matched potental method
Chloride	$<1\text{x } 10^{-5}$
Bromide	$<1\text{x } 10^{-5}$
Phosphate	$<1\text{x } 10^{-5}$
Sulphate	$<1\text{x } 10^{-5}$
Oxalate	$<1\text{x } 10^{-5}$
Carbonate	$<1\text{x } 10^{-5}$
Nitrate	$<1\text{x } 10^{-5}$
Nitrite	$<1\text{x } 10^{-5}$
Thiocyanate	$<1\text{x } 10^{-5}$

6.14 Applications

The developed ISE was successfully applied for the determination of iodide content in natural water (well and tap waters) and sea water samples and also in the presence of spiked amounts of iodide concentrations via standard addition method. 50 ml of diluted (ten times) water samples were taken in a 100mL beaker with 1.0×10^{-6} M iodide concentration and equilibrated with ISAB. All water samples were filtered to avoid blocking interference by colloids at ISE surface before measurements. Direct determination of iodide was possible only in tap water as it did not interfere Nernstian response from $1.0\text{x}10^{-7}$ M onwards. Standard additions were done by spiking $2.0\text{x}10^{-6}$ M and $5.0\text{x}10^{-6}$ M iodide subsequently. Regression factors obtained from the calibration plots of standard additions of iodide (average of triplicate measurements) for each water samples are given; deionized water (R^2 =0.9712), tap water (R^2 =0.9682), well water (R^2 =0.9767) and sea water (R^2 =0.9356). Metal ions present in well and sea water form complexes with iodide thereby affecting the Nernstian response of the ISE at lower iodide concentrations. The above account indicates the suitability of the developed ISE for the routine monitoring of iodide at concentrations greater than 10^{-6} M in natural and sea water samples.

6.15 Experimental

6.15.1 Reagents

Sodium Iodide (NaI), high molecular weight polyvinyl chloride (PVC), o-nitrophenyloctylether (o-NPOE) and dioctylphthalate (DOP) were obtained from Aldrich (Milwauke, USA). All metal salts including silver nitrate ($AgNO_3$), potassium Iodide (KI), sodium Nitrate ($NaNO_3$), potassium chloride (KCl), potassium nitrate (KNO_3), disodium oxalate ($Na_2C_2O_4$), sodium carbonate (Na_2CO_3), sodium sulphate (Na_2SO_4), sodium dihydrogen phospahte ($NaH_2PO_4.H_2O$) and tetrahydrofuran (THF) were of analytical grade and used as received from Fluka. Iodide solutions of 1M concentrations were freshly prepared by aqueous dilution of definite volumes of standard stock solution of 10^{-1}M concentration and were kept in amber coloured bottles. Deionized water was used throughout the measurements and also for the preparation of sample solutions.

6.15.2 Instrumentation

Microwave preparations were done in a ‘STRAT D’ microwave labstation with detachable temperature and presssure sensors (MILESTONE, Italy). All potentiometric measurements were done in a digital ion analyzer (Model L1 126, ELICO, India) using the proposed ISE in conjunction with a calomel reference electrode (ELICO, India). X-ray diffraction patterns of AgI samples were taken using a Cu Kα X-ray source and Philips PW 1710 diffractometer (The Netherlands). Scanning electron micrographs were obtained using a JEOL JSM-5600 LV instrument (SEM, Japan).

6.15.2.1 Details of Milestone Microwave Labstation

Microwave irradiation experiments for AgI were carried out in Milestone microwave labstation using a segmented rotor block. Milestone microwave reactor has a single magnetron with rotating diffuser for homogeneous microwave distribution in the cavity (37x34.5x33.5 cm) with a maximum delivered power of 122 W in 1W increments and an output power up to 1200 W. For experiments under high pressures, 100-mL PFA teflon reaction vessels, contained in a rotor block segment, were employed. Teflon vessels were closed tightly after taking the samples with the aid of torque wrench and placed in the rotor. The rotor is then positoned properly in the microwave cavity. Time, temperature, pressure, and MW power conditions of each experiment were monitored and controlled with the “easyWAVE” software package (Vers: 01-M). Temperature was monitored with the aid of a fluoroptic probe (ATC-400 CE) and/or with a shielded thermocouple (ATC-300) inserted directly into the corresponding reaction container. For experiments in sealed vessels a pressure sensor (APC-55E) was additionally employed.

6.16 Conclusions

Current chapter describes the microwave assisted fast preparation and stabilization of β- phase of AgI crystals by combining the effects of microwave heating and pressure. An iodide selective ISE was fabricated by dispersing the stabilized β-AgI crystals in PVC with DOP as plasticizer and was found responding to lower iodide concentrations even without any conditioning in iodide solutions or buffers before measurements. ISE was able to respond from 10^{-9}M onwards and the Nernstian response was obtained in the range of 10^{-8} to 1 M with a response time of 2 min. Limit of detection for this iodide ISE was found to be 10 nM which enables the iodide sensor to monitor the concentration of iodide in natural & sea waters.

Chapter 7

SUMMARY

In view of the growing concern about the environmental pollution, a special attention is given in this thesis for developing various strategies for the separation, removal and sensing of selected inorganic pollutants namely, uranium and iodide which are toxic to human beings. A special focus is given on the solid phase extraction (SPE) of uranium using novel ion imprinted polymers from various environmental samples. Significance of potentiometry for sensing of toxic iodide is also emphasized by the use of highly conductive AgI. Applicability of these novel materials and the developed sensors were tested in a special scenario to address the pollution monitoring of our natural water sources, which get polluted directly or by the seepage of these toxins from their natural or industrial sources.

The first introductory chapter cautions the increasing amounts of inorganic pollutants in our environment and their toxic effects. Urgent requirement of the pre-concentrative separation of these toxins is envisaged followed by a discussion about various preconcentration techniques exist for uranium. The chapter gives a specific introduction to the first part of the thesis including chapters 2 and 3, where the separation and removal of uranium alone is discussed. Special aspects of IIPs as an efficient solid phase extractant is explained by referring to the reports on uranyl ion imprinted polymers.

Chapter 2 introduces the concept of ‘dummy templates’ in ion imprinting as a part of green and economical viewpoints. Synthesis of uranyl IIPs were explained using various bivalent transition metal ions as ‘dummy templates’ instead of highly toxic and costly uranyl ions. Among different dummy templated IIPs, nickel(II) IIP (IIP_d) have shown efficient uptake for uranium. The superior selectivity of IIP_d for uranium over other inorganic ions was influenced by various factors such as formation constants of different dummy template-

DCQ complexes, template size and template-DCQ complex geometry inside the imprinted matrix. IIP_d material was successfully tested for the preconcentrative separation of very low concentrations of uranium from metal ion mixtures and neutral electrolytes which are the constituents of seawater and nuclear power reactor effluents.

Chapter 3 again describes the capability of another set of uranyl IIPs for the removal of uranium from simulants of mining industry feed solution and high-level nuclear waste solution. Amidoxime functionalities were used as uranophiles for the preparation of uranyl IIPs viz., a non-vinylated uranophile, formamidoxime (for set I-IIP) & a copolymer carrying both highly specific uranyl binding amidoxime functionality and substrate anchoring carboxylic group (for set II-IIP). Copolymer based IIP (set-II) has shown better uranium rebinding with lesser amounts of IIP than set-I and is explained by faster rebinding kinetics due to high surface area and retention capacity of set II-IIP.

Chapter 4 discusses about optical and electrochemical sensor platforms used in pollution monitoring including imprinted polymer based optical sensors and conductive electrolyte based potentioselectrodes. This stands as a brief introduction to the next two chapters which are mainly sensor designs for uranium and iodide.

Fabrication of a two dimensional biomimetic optode was dealt in Chapter 5 for the detection and quantification of uranium in natural waters. The receptor part of the optode is designed using uranyl IIP prepared from a newly synthesized uranophile, 4-vinyl phenylazo-2-naphthol (VPAN). High retention capacity of the IIP helps in reducing the amount of sensing element used for optode fabrication. The predetermined selectivity and operational stability of uranyl IIP offer superior sensitivity to the optode and can be used for the routine analysis of uranium down to 0.18 ppm.

Apart from the above chapters which are devoted for uranium toxin using imprinted polymers, we will be looking for another pollutant of concern, i.e., iodide and its potentiometric sensing using conductive AgI. Effect of microwave power on conductive AgI crystals is highlighted for the fast preparation of conductive and stable β-AgI followed by the fabrication of an ion selective electrode (ISE) for iodide. Wide linear range for iodide response, lower response time, high stability and low detection limit enabled the ISE for the analysis of natural and sea water samples.

In summary the thesis describes preconcentrative separation and removal of toxic uranium in the first part (using IIPs employing various uranophiles) and two sensor designs developed for uranium (optical sensor using imprinted polymers) and iodide (ion selective electrode made up of MW treated β-AgI) in the second part. The applicability of the imprinted materials and sensors were tested using various natural and simulant environmental samples and is concluded in Chapter 7.

LIST OF PUBLICATIONS

Research Articles:

“Design of two-dimensional biomimetic uranyl optrode and its application to the analysis of natural waters”
D. James, J. Mary Gladis, A.K. Pandey, G.R.K. Naidu, T. Prasada Rao, *Talanta*, 74, **2008**, 1420–1427.

“Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material”
D. James, G. Venkateswaran, T. Prasada Rao, *Microporous and mesoporous materials*, 119, **2009**, 165-170.

Microwave irradiated β-AgI crystals for potentiometric sensing of iodide, **Dhanya James,** T. Prasada Rao, *Analytica Chimica Acta* (Under review).
Separation of uranium from complex matrices using dummy templated biomimetic resins **Dhanya James,** J. Mary Gladis, G. Venkateswaran T. Prasada Rao, (to be communicated).

Bi-functional copolymer based imprinted material for selective removal of uranium
Dhanya James, G. Venkateswaran, T. Prasada Rao, *Talanta* (under preparation).

Book Chapters:

Optoelectronic sensors for monitoring of inorganic toxins
T. Prasada Rao, **Dhanya James**, Milja T. Elias, Handbook of Molecular Imprinting: Advanced Sensor Applications, Eds: S. Lee & T. Kunitake, *Pan Stanford publishing Pvt. Ltd.* (On invitation, in Press).

Conferences Papers:

Design and development of two dimensional uranyl optrode using ion imprinted polymer materials (**Oral presentation**)
D. James, J. Mary Gladis,T. Prasada Rao, International Conference on "Advanced Materials and Composites" (**ICAMC-2007**) organized by NIIST (CSIR), Trivandrum during October 21-22, 2007.

Ion imprinted polymer material for chemical winning of uranium from high-level nuclear waste simulant (**Poster presentation**)
Dhanya James, G. Venkateswaran, T. Prasada Rao, 4th **CRSI-RSC** joint symposium & 12th CRSI National Symposium in Chemistry held at IICT, Hyderabad during February 4-7, 2010.

β - AgI crystal based ion selective electrode for iodide sensing (**Best poster award**)
Dhanya James, T. Prasada Rao, , International Conference on Recent Trends in Materials Science and Technology (**ICMST 2010**) organized by IIST, Thiruvananthapuram jointly with MRSI, Thiruvananthapuram Chapter during October 29-31, 2010

REFERENCES:

Abbasi, W. A. and Streat, M., "Adsorption of uranium from aqueous solutions using activated carbon", *Sep. Sci. Technol.*, 29, **1994**, 1217-1230.

Adriano, D. C., "Trace elements in the terrestrial environment", Springer-Verlag, New York, **2001**.

AI-Kindy, S.; Badfa, R.; Suarez-Rodrfguez, J. L.; Diez-Gercie, M. E., "Molecularly imprinted polymers and optical sensing applications", *Crit. Rev. Anal. Chem.*, 30, **2000**, 291-309.

Akl, M. A.; Ghoneim, A. K.; Abd El-Aziz, M. H., "Novel plastic chromium (III)-ion selective electrodes based on different ionophoric species and plasticizing solvent mediators", *Electroanalysis*, 18, **2006**, 299-306.

Al-Kindy, S.; Badia, R.; Dfaz-Garcfa, M. E., "Fluorimetric monitoring of molecular imprinted polymer recognition events for aluminium", *Anal. Lett.*, 35, **2002**, 1763-1774.

Andersson, H. S. and Nicholls, I. A., "Spectroscopic evaluation of molecular imprinting polymerization systems", *Bioorg. Chem.*, 25, **1997**, 203-211.

Arshady, R. and Mosbach, K., "Synthesis of substrate-selective polymers by host-guest polymerization", *Macromol. Chem. Phys.*, 182, **1981**, 687-692.

Bae, S. Y.; Southard, G. L.; Murray, G. M., "Molecularly imprinted ion exchange resin for purification, preconcentration and determination of UO_2^{2+} by spectrophotometry and plasma spectrometry", *Anal. Chim. Acta*, 397, **1999**, 173-181.

Bakker, E. and Pretsch, E., "Potentiometric sensors for trace-level analysis", *Trends Anal. Chem.*, 24, **2005**, 199-207.

Bakker, E. and Pretsch, E., "Potentiometry at trace levels", *Trends Anal. Chem.*, 20, **2001**, 11-19.

Bakker, E. and Pretsch, E., "The new wave of ion-selective electrodes", *Anal. Chem.*, 74, **2002**, 420A-426A.

Bakker, E.; Buhlmann, P.; Pretsch, E., "Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics", *Chem. Rev.* 97, **1997**, 3083-3132.

Behrens, E.; Sylvester, P.; Clearfield, A., "Assessment of a sodium nonatitanate and pharmacosiderite-type ion exchangers for strontium and cesium removal from doe waste simulants", *Environ. Sci. Technol.*, 32, **1998**, 101-107.

Bengtsson, L.; Johansson, B.; Hackett, T. J.; McHale, L.; McHale, A. P., "Studies on the biosorption of uranium", *Appl. Microbiol. Biotechnol.*, 45, **1995**, 807-811.

Berg, E.W., "Physical and chemical methods of separation", McGraw-Hill Book Company, New York, **1963**.

Bhaskarapillai, A.; Sevilimedu, N. V.; Sellergren, B., "Synthesis and characterization of imprinted polymers for radioactive waste reduction", *Ind. Eng. Chem. Res.*, 48, **2009**, 3730-3737.

Binner, J. G. P.; Dimitrakis, G.; Price1, D. M.; Reading, M.; Vaidhyanathan, B., "Hysteresis in the β-α phase transition in silver iodide", *J. Therm. Anal. Calorim.*, 84, **2006**, 409-412.

Blantz, R. C.; Pelayo, J. C.; Gushwa, L. C.; Myers, R.; Evan, A. P., "Functional basis for glomerular alterations in uranyl nitrate acute renal failure", *Kidney Int.*, 228, **1985**, 733-743.

Booking, E. C., "Trends in hazardous materials research", Nova Science, New York, **2007**.

Booske, J. H.; Cooper, R. F.; Dobson, I., "Mechanism for nonthermal effects on ionic mobility during microwave processing of crystalline solids", *J. Mater. Res.*, 7, **1992**, 495-501.

Brand, M. J. D. and Rechnitz, G. A., "Mechanistic studies on crystal-membrane ion-selective electrodes', *Anal. Chem.*, 42, **1970**, 478-483.

Brauer, G., "Handbuch der präparativen anorganischen chemie", Verlag, Stuttgart, **1954**.

Burley, G., "Kinetics and mechanism of the low-cubic to hexagonal phase transformation of silver iodide", *J. Phys. Chem.*, 68, **1964**, 1111-1114.

Cannon, H. L. and Hopps, H. C., "Environmental geochemistry in health and disease", Geological Society of America, Boulder, Colorado, **1971**.

Cantaluppi, C.; Deggeto, S., "Civillian and military uses of depleted uranium: environmental and health problems", *Ann. Chim.*, 90, **2000**, 665-676.

Ceresa, A.; Bakker, E.; Günther, D.; Hattendorf, B.; Pretsch, E., "Potentiometric polymeric membrane electrodes for measurement of environmental samples at trace levels: New requirements for selectivities and measuring protocols, and comparison with ICPMS", *Anal. Chem.* 73, **2001**, 343-351.

Chen, H.; Olmstead, M. M.; Albright, R. L.; Devenyi, J.; Fish, R. H., "Metal-ion-templated polymers: synthesis and structure of N(4-Vinylbenzy1)- 1,4,7-

triazacyclononanezinc(11) complexes, their copolymerization with divinylbenzene, and metal-ion selectivity studies of the demetalated resins-evidence for a sandwich complex in the polymer matrix”, *Angew. Chem. Int. Ed. Engl.*, 36, **1997**, 642-645.

Colella, M. B.; Siggia, S.; Barnes, R. M., “Synthesis and characterization of a poly(acrylamidoxime) metal chelating resin”, *Anal. Chem.*, 52, **1980**, 967-972.

Cunningham, L. and Freiser, H., “Coated-wire ion-selective electrodes”, *Anal.Chim. Acta,* 180, **1986**, 271-279.

Cywinski, P.; Sadowska, M.; Danel, A; Buma, W. J.; Brouwer, A. M.; Wandelt, B., “Fluorescent, molecularly imprinted thin-layer films based on a common polymer”, *J. Appl. Poly. Sci.*, 105, **2007**, 229-235.

Dai, S.; Barleigh, M. C.; Shin Y., “Imprint coating synthesis of selective functionalized ordered mesoporous sorbents for separation and sensors”, US Patent 6251280, **2001**.

Dai, S.; Shin, Y. S.; Barnes, C. E.; Toth, I. M., “Enhancement of uranyl adsorption capacity and selectivity on silica sol-gel glasses via molecular imprinting”, *Chem. Mater.*, 9, **1997**, 2521-2525.

Daniel, S.; Prabhakara Rao, P.; Prasada Rao, T., “Investigation of different polymerization methods on the analytical performance of palladium(II) ion imprinted polymer materials”, *Anal. Chim. Acta*, 536, **2005**, 197-206.

Daniel, S.; Praveen, R. S.; Prasada Rao, T., “Ternary ion-association complex based ion imprinted polymers (IIPs) for trace determination of palladium(II) in environmental samples”, *Anal. Chim. Acta*, 570, **2006**, 79-87.

Das, S.; Pandey, A. K.; Athawale, A. A.; Manchanda, V. K., “Exchanges of uranium(VI) species in amidoxime-functionalized sorbents”, *J. Phys. Chem. B*, 113, **2009**, 6328-6335.

Daunert, S.; Florido, A.; Bricker, J.; Dunaway, W.; Bachas, L. G.; Valiente, M., “Iodide-selective electrodes based on a mercury-triisobutylphosphine sulfide complex”, *Electroanalysis*, 5, **1993**, 839-843.

Daunert, S.; Wallace, S.; Florido, A.; Bachas, L. G., “Anion-selective electrodes based on electropolymerized porphyrin films”, *Anal. Chem.*, 63, **1991**, 1676-1679.

De Marco, R. and Mackey, D. J., “Calibration of a chalcogenide glass membrane ion-selective electrode for the determination of Fe(III) in sea water. I. Measurements in UV photo-oxidized seawater”, *Mar. Chem.*, 68, **2000**, 283-294.

De Marco, R. and Shacketon, J., “Calibration of the Hg chalcogenide glass membrane ion-selective electrode in seawater media”, *Talanta*, 49, **1999**, 385-391.

Dickert, F. L. and Thierer, S., “Molecularly imprinted polymers for optochemical sensors”, *Adv. Mater.*, 8, **1996**, 987-990.

Dickert, F. L. and Tortschanoff, M., “Molecularly imprinted sensor layers for the detection of polycyclic aromatic hydrocarbons in water’, *Anal. Chem.*, 71, **1999**, 4559-4563.

Dickert, F. L.; Besenbock, H.; Tortschanoff, M., “Molecular imprinting through van der Waals interactions: Fluorescence detection of PAHS in water”, *Adv. Mater.*, 10, **1998**, 149-151.

Domingo, J. L., “Chemical toxicity of uranium”, *Toxicol. Ecotoxicol. News*, 2, **1995**, 74-78.

Domingo, J. L., “Reproductive and developmental toxicity of natural and depleted uranium: A review”, *Reprod. Toxicol.*, 15, **2001**, 603-609.

Domingo, J. L.; Domingo, A.; Colomina, M. T., “Influence of maternal stress on metal-induced and postnatal effects in mammals: a review”, *Biol. Trace Elem. Res.*, 98, **2004**, 193-207.

Duff, M. C.; Hunter, D. B.; Hobbs, D. T.; Fink, S. D.; Dai, Z.; Bradley, J. P., “Mechanisms of strontium and uranium removal from high-level radioactive waste simulant solutions by the sorbent monosodium titanate”, *Environ. Sci. Technol.*, 38, **2004**, 5201-5207.

Durst, R. A. and Ross Jr., J. W., “Electrochemical generation of fluoride ion by solid-state transference”, *Anal. Chem.*, 40, **1968**, 1343-1344.

Eugster, R.; Rostazin, T.; Rusterholz, B.; Aebersold, B.; Pedrazza, U.; Ruegg, D.; Schmid, A.; Spichiger, U. E.; Simón, W., “Plasticizer for liquid polymeric membranes of ion selective chemical sensors”, *Anal. Chim. Acta*, 289, **1994**, 1-13.

Faridbod, F.; Ganjali, M. R.; Dinarvand, R.; Norouzi, P., “Developments in the field of conducting and non-conducting polymer based potentiometric membrane sensors for ions over the past decade”, *Sensors*, 8, **2008**, 2331-2412.

Fo¨ster, S. and Antonietti, M., “Amphiphilic block copolymers in structure-controlled nanomaterial hybrids”, *Adv. Mater.*, 10, **1998**, 195-217.

Freiser, H., “Coated wire ion-selective electrodes. Principles and practice”, *J. Chem. Soc. Faraday Trans.*, 82, **1986**, 1217-1221.

Freiser, H., “Ion selective electrodes in analytical chemisty”, Plenum Press, New York, **1980**.

Friberg, L. and Vostal, J., “Mercury in the environment; an epidemiological and toxicological appraisal”, Chemical Rubber Co., Cleveland, Ohio, **1972**.

Ganjali, M. R.; Emami, M.; Salavati-Niasari, M.; Yousefi, M., “Determination of trace amounts of Cr(III) in presence of Cr(VI) by a novel potentiometric membrane sensor based on a new tridentate S,N,O Schiff's bas”, *Anal. Lett.*, 36, **2003**, 2735-2747.

Ganjali, M. R.; Kiani-Anbouhi, R.; Shamsipur, M.; Poursaberi, T.; Salavati-Niasari, M.; Talebpour, Z.; Emami, M., “Novel potentiometric PVC-membrane and coated graphite sensors for lanthanum(III)”, *Electroanalysis*, 16, **2004**, 1002-1008.

Ganjali, M. R.; Moghaddamb, M. R.; Norouzi, P.; Shirvani-Arani, S.; Daneshgar, P.; Adib, M.; Sobhi, H. R., “Highly selective and sensitive triiodide PVC-based membrane electrode based on anew charge transfer complex of 2-(((2-(((E)-1-(2-hydroxyphenyl) methylidine) amino) phenyl) imino) methyl) phenol for nano-level monitoring of triiodide”, *Anal. Lett.*, 39, **2006**, 683-695.

Ganjali, M. R.; Norouzi, P.; Faridbod, F.; Rezapour, M.; Pourjavid, M.R., “One decade of research on ion-selective electrodes in iran”, *J. Iran. Chem. Soc.*, 4, **2007**, 1-29.

Ganjali, M. R.; Norouzi, P.; Rezapour, M.; Faridbod, F.; Pourjavid, M. R., “Supramolecular based membrane sensors”, *Sensors*, 6, **2006**, 1018-1086.

Ganjali, M. R.; Poursaberi, T.; Hosseini, M.; Salavati-Niasary, M.; Yousefi, M.; Shamsipur, M., “Highly selective iodide membrane electrode based on a cerium salen”, *Anal. Sci.*, 18, **2002**, 289-292.

Gauglitz, G., “Direct optical sensors: principles and selected applications”, *Anal. Bioanal. Chem.*, 381, **2005**, 141-155.

Gilman, A. P.; Villencuve, D. C.; Seccours, V. E.; Yagminas, A. P.; Tracy, B. L.; Quinn, J. M.; Valli, V. E.; Willies, R. J.; Moss, M. A., “Uranyl nitrate: 28-day and 91-day toxicity studies in the sprague–dawley rat”, *Toxicol. Sci.*, 41, **1998**, 117-128.

Gladis, J. M. and Prasada Rao, T., “Effect of porogen type on the synthesis of uranium ion imprinted polymer materials for the preconcentration/separation of traces of uranium”, *Mikrochim. Acta*, 146, **2004**, 251-258.

Gladis, J. M. and Prasada Rao, T., “Synthesis and analytical applications of uranyl ion imprinted polymer particles”, *Anal. Lett.*, 36, **2003**, 2107-2121.

Gladis, J. M. and Prasada Rao, T., “Synthesis of solid phase extractant materials by polymer imprinting suitable for uptake of uranyl ions and a process thereof”, IPA/516 DEL, **2003**.

Gräfe, A.; Haupt, K.; Mohr, G. J., “Optical sensor materials for the detection of amines in organic solvents”, *Anal. Chim. Acta*, 565, **2006**, 42-47.

Gregg, D. and Folkendt, M., “Uranium from Seawater”, Lawrence Livermore Laboratory, Report No. UCID-19569; DE83000658, **1982**.

Güler, H.; Şahiner, N.; Aycık, G. A.; Güven, O., “Development of novel adsorbent materials for recovery and enrichment of uranium from aqueous media”, *J. Appl. Polym. Sci.*, 66, **1997**, 2475-2480.

Gupta, A. R. and Venkataramani, B., “Sorption of uranyl ions on hydrous oxides. A new surface hydrolysis model”, *Bull. Chem. Soc. Jpn.*, 61, **1988**, 1357-1362.

Gupta, R. D.; Manku, G. S.; Bhat, N.; Jain, B. D.; “Determination and comparison of the stability constants of some bivalent ion complexes of 5,7-dichloro-, 5,7-di bromo-, and 5,7-dinitro-8-hydroxyquinoline and their N-oxides”, *Zeitschrift fur anorganische und allgemeine Chemie. Band*, **1970**, 379.

Gupta, V. K.; Jain, A. K.; Ishtaiwi, Z.; Lang, H.; Maheshwari, G., “Ni^{2+} selective sensors based on meso-tetrakis-{4-[tris-(4-allyl dimethylsilyl-phenyl)-silyl]-phenyl}porphyrin and (sal)(2)trien in poly(vinyl chloride) matrix”, *Talanta*, 73, **2007**, 803-811.

Hao, A.; Gao, C.; Li, M.; He, C.; Huang, X.; G. Zou,; Tian, Y.; Ma, Y., “Conductivity of AgI under high pressure”, *J. Appl. Phys.*, 101, **2007**, 053701-053701-5.

Haupt, K. and Mosbach, K., “molecularly imprinted polymers and their use in biomimetic sensors”, *Chem. Rev.*, 100, **2000**, 2495-2504.

Haupt, K., “Molecularly imprinted polymers in analytical chemistry”, *Analyst*, 126, **2001**, 747-756.

Hellferich, F., “Ion exchange”, McGraw-Hill, New York, **1962**.

Hill, H. H.; Martin Jr., S. J., “Conventional analytical methods for chemical warfare agents”, *Pure Appl. Chem.*, 74, **2002**, 2281-2291.

Hillberg, A. L.; Brain, K. R.; C. J. Allender, “Molecular imprinted polymer sensors: Implications for therapeutics”, *Adv. Drug Delivery Rev.*, 57, **2005**, 1875-1889.

Hobbs, D. T.; Blume, M. S.; Thacker, H. L., “Phase V simulant testing of monosodium titanate adsorption kinetics”, Report-WSRC-TR-2000-00142, Aiken, **2000**.

Hosoya, K.; Watabe, Y.; Ikegami, T.; Tanaka, N.; Kubo, T.; Sano, T.; Kaya, K., "A molecular recognition strategy towards tetra-chlorinated dibenzo-p-dioxins, TCDDs", *Biosens. Bioelectron.,* 20, **2004**, 1185-1189.

Hulanicki, A.; Geab, S.; Ingman, F., "Chemical sensors- definitions and classification", *Pure Appl. Chem.,* 63, **1991**, 1247-1250.

Hull, S., "Superionics crystal structures and conduction processes", *Rep. Prog. Phys.,* 67, **2004**, 1233-1314.

Ion, A. C.; Bakker, E.; Pretsch, E., "A potentiometric Cd^{2+}-selective electrode with a detection limit in the low ppt range", 440, **2001**, 71-79.

Irving, H. M. N. H., "Recommendations for nomenclature of ion-selective electrodes", *Pure Appl. Chem.,* 48, **1976,** 128-132**.**

Jacobs, M. B., "The analytical toxicology of industrial inorganic poisons", Interscience publishers, USA, **1967**.

Jakmunee, J. and Grudpan, K., "Flow injection amperometry for the determination of iodate in iodized table salt", *Anal. Chim. Acta,* 438, **2001**, 299-304.

John, J. M.; Nigel, P. S.; Saunders: G. D.; Walton, P. H., "Detection and extraction of an ion in a solution, particularly uranium ion", EP 1019555 (WO 9915707), **1999**.

Junker-Bucheit, A. and Witzenbacher, M., "Pesticide monitoring of drinking water with the help of solid-phase extraction and high-performance liquid chromatography", *J. Chromatogr. A,* 737, **1996**, 67-74.

Kabanov, V. A.; Efendiev, A. A.; Orujev, D. D., "Complex-forming polymeric sorbents with macromolecular arrangement favorable for ion sorption", *J. Appl. Polym. Sci.*, 24, **1979**, 259-267.

Kabei, N., "Preparation of amidoxime-fiber adsorbents based on poly(methacrylonitrile) for recovery of uranium from seawater", *Sep. Sci. Technol.*, 29, **1994**, 375-384.

Kala, R.; Biju, V. M.; Prasada Rao, T., "Synthesis, characterization, and analytical applications of erbium(III) ion imprinted polymer particles prepared via γ-irradiation with different functional and crosslinking monomers", *Anal. Chim. Acta,* 549, **2005**, 51-58.

Kanno, M., "Present status of study on extraction of uranium from sea water", *J. Nucl. Sci. Technol.,* 21, **1984**, 1-9.

Karadag, E.; Saraydin, D.; Guven, O., "Behaviors of acrylamide/itaconic acid hydrogels in uptake of uranyl ions from aqueous solution", *Sep. Sci. Technol.*, 30, **1995**, 3747-3760.

Kim Y. S. and Zeitlin. H., "Separation of uranium from seawater by adsorbing colloid flotation", *Anal.Chem.*, 43, **1971**, 1390-1393.

Kimaro, A.; Kellya, L. A.; Murray, G. M., "Molecularly imprinted ionically permeable membrane for uranyl ion", *Chem. Commun.*, **2001**, 1282-1283.

Koithoff, M. and H. L. Sanders, "Electric potentials at crystal surfaces, and at silver halide surfaces in particular", *J. Am. Chem. Soc.*, 59, **1937**, 416-420.

Kosslick, H.; Zutowa, H. L.; Lohse, U.; Landmesser, H.; Fricke, R.; Caro, "Microwave processing of zeolites", *J. Ceram. Trans.*, 80, **1997**, 523-537.

Kuchen, W. and Schram, J., "Metal-ion-selective exchange resins by matrix imprint with methacrylates", *Angew. Chem. Int. Ed. Engl.*, 27, **1988**, 1695-1697.

Kuswandi, B. and Narayanaswamy, R., "Polymeric encapsulated membrane for optrodes", *Fresenius J. Anal. Chem.*, 364, **1999**, 605-607.

Lazzari, M. and Lo´pez-Quintela, M. A., "Block copolymers for nanomaterial fabrication", *Adv. Mater.*, 15, **2003**, 1583-1594.

Li, Z. Q.; Yuan, R.; Ying, M.; Song, Y. Q.; Shen, G. L.; Yu, R. Q., "Iodide-selective PVC membrane electrodes based on five transitional metal chelates of bis-furfural-semi-o-tolidine", *Anal. Lett.*, 30, **1997**, 1455-1464.

Li, Z.; Ding, J.; Day, M.; Tao, Y., "Molecularly imprinted polymeric nano-spheres by diblock copolymer self-assembly", *Macromolecules*, 39, **2006**, 2629-2636.

Lieberzeit, P. A.; Dickert, F. L.; "Sensor technology and its application in environmental analysis", *Anal. Bioanal. Chem.*, 387, **2007**, 237-247.

Linares, V.; Sa´nchez, D. J.; Belle´s, M.; Albina, L.; Go´mez, M.; Domingo, J. L., "Pro-oxidant effects in the brain of rats concurrently exposed to uranium and stress", *Toxicology*, 236, **2007**, 82-91.

Lu, Q.; Callahan, J. H.; Collins, G. E., "The selective detection of uranium(VI) on a microchip using a derivatized 4-sulfonic calix[6]arene", *Chem. Commun.*, 19, **2000**, 1913-1914.

Lubbers, D. W.; Opitz, N. Z.; Naturforsch. C., *Biosci.*, 30c, **1975**, 532-533.

Makiura, R.; Yonemura, T.; Yamada, T.; Yamauchi, M.; Ikeda, R.; Kitagawa, H.; Kato, K.; Takata, M., "Size-controlled stabilisation of the superionic phase to room temperature in polymer-coated AgI nanoparticles", *Nature Materials*, 8, **2009**, 476-480.

Malcik, N.; Oktar, O.; Ozser, M. E.; Caglar, P.; Bushby, L.; Vaughan, A.; Kuswandi , B.; Narayanaswamy, R., "Immobilized reagents for optical heavy metal ion sensing", *Sensors and Actuators B*, 53, **1998**, 211-221.

Mandarino, J. A. and Back, M. E., "Fleischer's glossary of mineral species", The Mineralogical Record Inc., Tucson, Arizona, USA, **2004**.

Masque, N.; Marce, F.; Borrull, F., "Molecularly imprinted polymers: New tailor-made materials for selective solid-phase extraction", *Trends Anal. Chem.*, 20, **2001**, 477-486.

Mathison, S. and Bakker, E., "Effect of transmembrane electrolyte diffusion on the detection limit of carrier-based potentiometric ion sensors", *Anal. Chem.* 70, **1998**, 303-309.

Matsui, J.; Fujiwara, K.; Takeuchi, T., "Atrazine-selective polymers prepared by molecular imprinting of trialkylmelamines as dummy template species of atrazine", *Anal. Chem.*, 72, **2000**, 1810-1813.

Metilda, P.; Gladis J. M.; Prasada Rao, T., "Influence of binary/ternary complex of imprint ion on the preconcentration of uranium(VI) using ion imprinted polymer materials", *Anal. Chim. Acta*, 512, **2004**, 63-73.

Metilda, P.; Mary Gladis, J.; Venkateswaran, G.; Prasada Rao, T., "Investigation of the role of chelating ligand in the synthesis of ion-imprinted polymeric resins on the selective enrichment of uranium(VI)", *Anal. Chim. Acta*, 587, **2007**, 263-271.

Metilda, P.; Prasad, K.; Kala, R.; Gladis, J. M.; Prasada Rao, T.; Naidu, G. R. K., "Ion imprinted polymer based sensor for monitoring toxic uranium in environmental samples", *Anal. Chim. Acta,* 582, **2007**, 147-153.

Michard, P.; Guibal, E.; Vincent, T.; Le Cloirec, P., "Sorption and desorption of uranyl ions by silica gel: pH, particle size and porosity effects", *Micro. Mater.*, 5, **1996**, 309-324.

Milja, T. E.; Prathish, K. P.; Rao, T. P., "Synthesis of surface imprinted nanospheres for selective removal of uranium from simulants of Sambhar salt lake and ground water", *J. Hazard. Mater.,* 188, **2011**, 384-390.

Mizuike, A., "Enrichment techniques for inorganic trace analysis", Springer, Berlin, **1983**.

Morf, W. E.; Badertscher, M.; Zwickl, T.; de Rooij, N. F.; Pretsch, E., "Effects of ion transport on the potential response of ionophore-based membrane electrodes: A theoretical approach", *J. Phys. Chem. B*, 103, **1999**, 11346-11356.

Morrison, G. H. and Freiser, H., "Solvent extraction in analytical chemistry", Wiley, New York, **1957**.

Mosbach, K., "Molecular Imprinting", *Trends Biochem. Sci.*, 19, **1994**, 9-14.

Murray, G. M.; Jenkins, A. L.; Bzhelyansky, A.; Uy, O. M., "Molecularly imprinted polymers for the selective sequestering and sensing of ions", *John Hopkins Appl. Tech. Diggest*, 18, **1997**, 464-472.

Ng, S. M. and Narayanaswamy, R., "Demonstration of a simple, economical and practical technique utilising an imprinted polymer for metal ion sensing", *Microchim Acta*, 169, **2010**, 303-311.

Ng, S. M. and Narayanaswamy, R., "Fluorescence sensor using a molecularly imprinted polymer as recognition receptor for the detection of aluminium ions in aqueous media", *Anal. Bioanal. Chem.*, 386, **2006,** 1235-1244.

Nghiem, L. D.; Mornane, P.; Potter, I. D.; Perera, J. M.; Cattrall, R. W.; Kolev, S. D.; "Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs)", *J. Membr. Sci.*, 281, **2006**, 7-41.

Nicole, L.; Boissie`re, C.; Grosso, D.; Hesemann, P.; Moreaub, J.; Sanchez, C., "Advanced selective optical sensors based on periodically organized mesoporous hybrid silica thin films", *Chem. Commun.*, 20, **2004**, 2312-2313.

Nishide, H. and Tsuchida, E., "Selective adsorption of metal ions on poly(4-vinylpyridine) resins in which the ligand chain is immobilized by crosslinking", *Makromol. Chem.* 177, **1976**, 2295-2310.

Nishide, H.; Deguchi, J.; Tsuchida, E., "Selective adsorption of metal ions on crosslinked poly(vinylpyridine) resin prepared with a metal ion as a template", *Chem. Lett.*, 5, **1976**, 169-174.

Nogami, M.; Kim, S. Y.; Asanuma, N.; Ikeda, Y. J., "Adsorption behavior of amidoxime resin for separating actinide elements from aqueous carbonate solutions", *J. Alloys Compd.*, 374, **2004**, 269-271.

Oehme, I.; Wolfbeis, O. S., "Fundamental Review: Optical Sensors for Determination of Heavy Metal Ions", *Mikrochim. Acta*, 126, **1997**, 177-192.

Okamoto, J.; Sugo, T.; Katakakai, A.; Omichi, H., “Amidoxime-group-containing adsorbents for metal ions synthesized by radiation-induced grafting”, *J. Appl. Polym.*, 30, **1985**, 2967-2997.

Omichi, H.; Katahai, A.; Sugo, T.; Okamoto, J., “A new type of amidoxime-group containing adsorbent for the recovery of uranium from seawater. ii. Effect of grafting of hydrophilic monomers”, *Sep. Sci. Technol.*, 21, **1986**, 299-313.

Pekel, N.; Şahiner, N.; Akkaş, P.; Güven, O., “Uranyl ion adsorptivity of N-vinyl 2-pyrrolidone/acrylonitrile copolymeric hydrogels containing amidoxime groups”, *Polym. Bull.*, 44, **2000**, 593-600.

Peper, S.; Gonczy, C.; Runde, W., “Cs^+-selective membrane electrodes based on ethylene glycolfunctionalized polymeric microspheres”, *Talanta*, 67, **2005**, 713-717.

Perez-Moral, N. and Mayes, A. G., “Comparative study of imprinted polymer particles prepared by different polymerisation methods”, *Anal. Chim. Acta*, 504, **2003**, 15-21.

Perrino, C. T. and Wentrcek, P., “An experiment in solid state chemistry-Conduction in silver iodide”, *J. Chem. Educ.*, 49, **1972**, 543-545.

Plaza, S.; Szigeti, Z.; Geisler, M.; Martinoia, E.; Pretsch, E., “Potentiometric sensor for the measurement of Cd2+ transport in yeast and plants”, *Plant J.*, 44, **2005**, 179-194.

Policarpov, G. C., “Radio ecology of aquatic organisms”, North Holland, New York, **1966**.

Poursaberi, T.; Hosseini, M.; Taghizadeh, M.; Pirelahi, H.; Shamsipur, M.; Ganjali, M. R., “A selective membrane electrode for iodide ion based on a thiopyrilium ion derivative as a new ionophore”, *Microchem. J.*, 72, **2002**, 77-83.

Prager, P., “Crystal physics, diffraction, theoretical and general crystallography”, *Acta Cryst.*, A30, **1974**, 369-373.

Prasada Rao, T.; Kala, R.; Daniel, S., “Metal ion-imprinted polymers- novel materials for selective recognition of inorganics”, *Anal. Chim. Acta*, 578, **2006**, 105-116.

Prasada Rao, T.; Prasad, K.; Kala, R.; Mary Gladis, J., *Crit. Rev. Anal. Chem.*, “Biomimetic sensors for toxic pesticides and inorganics based on optoelectronic/electrochemical transducers-An overview”, 37, **2007**, 191-210.

Preetha, C. R.; Gladis, J. M.; Prasada Rao, T., “Removal of toxic uranium from synthetic nuclear power reactor effluents using uranyl ion imprinted polymer particles”, *Environ. Sci. Technol.*, 40, **2006**, 3070-3074.

Pungor, E. and Toth, K., “Ion-selective electrodes-A review”, *Anal. Sci.*, 3, **1987**, 387-393.

Pungor, E. and Tóth, K., “Precipitate-based ion-selective electrodes”, *Pure & Appl. Chem.*, 34, 1**973**, 105-138.

Pungor, E. and Tóth, K., “Precipitate-based selective ion-sensitive electrodes-Recent developments in theory and applications”, *Pure & Appl. Chem.*, 36, **1973**, 441-456.

Rao T. P.; Metilda, P.; Gladis, J. M., “Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination-an overview.”, *Talanta*, 68, **2006**, 1047-1064.

Rao, T. P. and Gladis, J. M., “Oxines as preconcentration agents in inorganic trace analysis”, *Rev. in Anal. Chem.*, 20, **2001**, 145-157.

Rao, T. P.; Daniel, S.; Gladis, J. M., "Tailored materials for preconcentration or separation of metals by ion imprinted polymers for solid-phase extraction (IIP-SPE)", *Trends Anal. Chem.*, 23, **2004**, 28-35.

Ritcey, G.M. and Ashbrook, A.W., "Solvent extraction: Principles and applications to process metallurgy Part 1", Elsevier Science, London, **1984**.

Robb, G. R.; Harrison A.; Whittaker, A. G., "Temperature-resolved, in-situ powder X-ray diffraction of silver iodide under microwave irradiation", *Phys. Chem. Comm.*, 5, **2002**, 135-137.

Ross Jr., J. W. and Durst, R. A., "Ion-selective electrodes", NBS Spec. Publ., Washington DC, **1969**.

Rückert, B.; Hall, A. J.; Sellergren, B., "Molecularly imprinted composite materials via iniferter-modified supports", *J. Mater. Chem.*, 12, **2002**, 2275-2280.

Ryan, M. A. and Tinnesand M., "Introduction to Green Chemistry", American Chemical Society, Washington DC, **2002**.

Saad, B.; Zin, Z. M.; Jab, M. S.; Rahman, I. A.; Saleh, M. I.; Mahsufi, S., "Flow-through chloroquine sensor and its applications in pharmaceutical analysis", *Anal. Sci.*, 21, **2005**, 521-524.

Safavi, A. and Bagheri, M., "A novel optical sensor for uranium determination", *Anal. Chim. Acta*, 530, **2005**, 55-60.

Safavi, A. and Bagheri, M., "Design and characteristics of a mercury (II) optode based on immobilization of dithizone on a triacetylcellulose membrane", *Sensors and Actuators B: Chemical*, 99, **2004**, 608-612.

Sahiner, N.; Pekel, N.; Akkas, P.; Güven, O.; Sci, J. M., "Amidoximation and characterization of new complexing hydrogels prepared from N-vinyl 2-pyrrolidone/acrylonitrile systems", *J. Macro. Sci. Pure Appl. Chem. A,* 37, **2000**, 1159-1172.

Sahiner, N.; Pekel, N.; Güven, O., "Radiation synthesis of N-vinyl 2 pyrrolidone/acrylonitrile interpenetrating polymer networks and their use in uranium recovery from aqueous systems", *Rad. Phys. Chem.*, 52, **1998**, 271-276.

Şahiner, N.; Pekel, N.; Güven, O., "Radiation synthesis, characterization and amidoximation of N-vinyl-2-pyrrolidone/acrylonitrile interpenetrating polymer networks", *React. Funct. Polym.,* 39, **1999**, 139-146.

Saito, K., "Japanese research plant for uranium from sea-water", *Nuclear Engineering International,* 25, **1980**, 32-33.

Sands, T. J.; Cardwell, T. J.; Cattrall, R.W.; Farrell, J. R.; Iles, P. J.; Kolev, S. D., "A Highly Versatile Stable Optode Based on 4-Decyloxy-2-(2-pyridylaxo)-1-naphthol in Nafion for the Determination of Copper", *Sensors and Actuators,* 85, **2002**, 33-41.

Saunders, G. D.; Foxon, S. P.; Walton, P. H.; Joyce, M. J.; Port, S. N., "A selective uranium extraction agent prepared by polymer imprinting", *Chem. Commun.,* **2000**, 273-274.

Say, R.; Ersoz, A.; Denizli, A., "Selective separation of uranium containing glutamic acid molecular-imprinted polymeric microbeads", *Sep. Sci. Technol.*, 38, **2003**, 3431-3447.

Schaefer, A. I.; Fane, A. G.; and Waite, T. D., "Nanofiltration: Principles and applications", Elsevier, London, **2005**.

Schnierle, P.; Kappes, T.; Hauser, P. C., "Capillary electrophoretic determination of different classes of organic ions by potentiometric detection with coated-wire ion-selective electrodes", *Anal. Chem.,* 70, **1998**, 3585-3589.

Schulz, W. W. and Bray, L. A., "Solvent extraction recovery of byproduct ^{137}Cs and ^{90}Sr from HNO_3 solutions-a technology review and assessment", *Sep. Sci. Technol.,* 22, **1987**, 191-214.

Scindia, Y. M.; Pandey, A. K.; Reddy, A. V. R.; Manohar, S. B., "Selective preconcentration and determination of chromium (vi) using a flat sheet polymer inclusion sorbent", *Anal. Chem.,* 74, **2002**, 4204-4212.

Segui, M. J.; Lizondo-Sabater, J.; Benito, A.; Martinez-Manez, R.; Pardo, T.; Sancenon, F.; Soto, J., "A new ion-selective electrode for anionic surfactants", *Talanta,* 71, **2007**, 333-338.

Segui, M. J.; Lizondo-Sabater, J.; Martinez-Manez, R.; Sancenon, F.; Soto, J. ; Garcia-Breijo, E.; Gil, L., "An ion-selective electrode for anion perchlorate in thick-film technology", *Sensors,* 6, **2006**, 480-491.

Seiler, K.; Simon, W., "Principles and mechanisms of ion-selective optodes", *Sensors and Actuators B: Chemical*, 6, **1992**, 295-298.

Seitz, W. R.; Sepaniak, M. J., "Chemical sensors based on immobilized indicators and fiber optics", *Crit. Rev. in Anal. Chem.,* 19, **1988**, 135-173.

Sellergren, B., "Molecularly imprinted polymers, man-made mimics of antibodies and their applications in analytical chemistry", Elsevier, Amsterdam, **2001**.

Sellergren, B., "Polymer and template related factors influencing the efficiency in molecularly imprinted solid phase extractions", *Trends Anal. Chem.*, 18, **1999**, 164-174.

Sellergren. B., "Imprinted polymers with memory for small molecules, proteins, or crystals", *Angew. Chem. Int. Ed.*, 39, **2000**, 1031-1037.

Sessler, J. L.; Seidel, D.; Vivian, A. E.; Lynch, V.; Scott, B. L.; Keogh, D. W., "Hexaphyrin(1.0.1.0.0.0): An expanded porphyrin ligand for the actinide cations uranyl (UO_2^{2+}) and neptunyl (NpO^{2+}), *Angew. Chem. Int. Ed.*, 40, **2001**, 591-594.

Shamsipur, M.; Fasihi, J.; Ashtari, K., "Grafting of ion-imprinted polymers on the surface of silica gel particles through covalently surface-bound initiators: A selective sorbent for uranyl ion", *Anal. Chem.*, 79, **2007**, 7116-7123.

Shamsipur, M.; Hosseini, M.; Alizadeh, K.; Talebpour, Z.; Mousavi, M. F.; Ganjali, M. R.; Arca, M.; Lippolis, V., "PVC membrane and coated graphite potentiometric sensors based on Et(4)todit for selective determination of samarium(III)", *Anal. Chem.*, 75, **2003**, 5680-5986.

Shamsipur, M.; Soleymanpour, A.; Akhond, M.; Sharghi, H.; Naseri, M. A., "Iodide-selective carbon paste electrodes based on recently synthesized schiff base complexes of Fe(III)", *Anal. Chim. Acta*, 450, **2001**, 37-44

Shan, D.; He, Y.; Wang, S.; Xue, H.; Zheng, H., "A porous poly(acrylonitrile-co-acrylic acid) film-based glucose biosensor constructed by electrochemical entrapment.", *Anal. Biochem.*, 356, **2006**, 215-221.

Sharpe, M., "The science of the unclean", *J. Environ. Monit.*, 3, **2001**, 2N-6N.

Shinkai, S.; Koreishi, H.; Ueda, K.; Arimura, T.; Manabe, O., “Molecular design of calixarene-based uranophiles which exhibit remarkably high stability and selectivity”, *J. Am. Chem. Soc.*, 109, **1987**, 6371-6376.

Sidhu, K. S.; Nash, D. F.; Mcbride, D. E. “Need to revise the national drinking water regulation for copper”, *Regul. Toxicol. Pharmacol.*, 22, **1995**, 95-100.

Sillen, L. G. and Martell, A. E., “Stability constants of metal-ligand complexes”, Sp. Publ., The Chemical Society, London, **1964**.

Simpson, N. J. K, “Solid phase extraction: Principles, strategies and applications”, Marcel Dekker, New York, **2000**.

Siswata, D.; Hisamoto, H.; Tohma, H.; Yamamoto, N.; Suzuki, K., “Novel ammonium ionophores based on glycol dibenzy ethers for an Ion-Selective Eelectrode”, *Chem. Lett.*, 5, **1994**, 945-948.

Snell, F. D., “Photometric and fluorimetric methods of analysis-Metals, Part 2”, Wiley, New York, **1978**.

Sokalski, T.; Ceresa, A.; Zwickl, T.; Pretsch, E. J., “Large improvement of the lower detection limit of ion-selective polymer membrane electrodes”, *J. Am. Chem. Soc.*, 119, **1997**, 11347-11348.

Spivak, D., “Optimization, evaluation, and characterization of molecularly imprinted polymers”, *Adv. Drug. Deliv. Rev.*, 57, **2005**, 1779-1794.

Sugo, T.; Katakai, A.; Seko, N., “Collector for adsorptive recovery of dissolved metal from sea water”, U.S. patent 6863812, **2005**.

Sunandana, C. S. and Senthil Kumar, P., “Theoretical approaches to super ionic conductivity”, *Bull. Mater. Sci.*, 27, **2004**, 1-17.

Szigeti, Z.; Bitter, I.; To´thc, K.; Latkoczy, C.; Fliegel, D. J.; Gu¨nther, D.; Pretsch, E., “A novel polymeric membrane electrode for the potentiometric analysis of Cu^{2+} in drinking water”, *Anal. Chim. Acta*, 532, **2005**, 129-136.

Tabushi, I.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E., “Macrocyclic hexacarboxylic acid-A highly selective host for uranyl ion”, *J. Am. Chem. Soc.*, 102, **1980**, 5947-5948.

Tabushi; Kobuke, Y.; Nishiya, T., “Extraction of uranium from seawater by polymer-bound macrocyclic hexaketone”, *Nature*, 280, **1979**, 665-666.

Takahashi, T.; Kuwabara K.; Yamamoto, O., “The electrical conductivity and the crystal structure of silver iodide”, *J. Electrochem. Soc.*, 116, **1969**, 357-360.

Takeuchi, T.; Fukuma, D.; Matsui, J., “Combinatorial molecular imprinting: An approach to synthetic polymer receptors”, *Anal. Chem.*, 71, **1999**, 285-290.

Theodoridis, G.; Kantifes, A.; Manesiotis, P.; Raikos, N.; Tsoukali-Papadopoulou, H., “Preparation of a molecularly imprinted polymer for the solid-phase extraction of scopolamine with hyoscyamine as a dummy template molecule”, *J. Chromatogr. A*, 987, **2003**, 103-109.

Thuman, E. M. and Mills, M. S., “Solid phase extraction-Principles and practices”, Wiley, New York, **1998**.

Tsezos, M. and Volesky, B., “Biosorption of uranium and thorium”, *Biotechnol. Bioeng.*, 23, **1981**, 583-604.

Tsuhiya, K. and Keijo, J., "Causation of Ouch-Ouch Disease (Itai-Itai Byõ)-an introductory review. I. Nature of the disease", *J. Med.*, 18, **1969**, 181-194.

Uezu, K.; Nakamura, H.; Kanno, J.; Sugo, T.; Goto, Nakashio, F., "Metal ion-imprinted polymer prepared by the combination of surface template polymerization with postirradiation by γ-rays", *Macromolecules*, 30, **1997**, 3888-3891.

Uriu-Adams, J. Y. and Keen, C. L., "Copper, oxidative stress, and human health", *Mol. Aspects Med.*, 26, **2005**, 268-298.

Uriu-Adams, J. Y. and Keen, C. L., "Copper, oxidative stress, and human health", *Mol. Aspects Med.*, 26, **2005**, 268-298.

Vesely, J.; Weiss, D.; Stulik, K., "Analysis with ion selective electrodes", Ellis Horwood, Chichester, UK, **1978**.

Vigneau, O.; Pinel, C.; Lemairea, M., "Ionic imprinted resins based on EDTA and DTPA derivatives for Lanthanides(III) separation", *Anal. Chim. Acta*, 435, **2001**, 75-82.

Vigneau, O.; Pinel, C.; Lemairea, M., "Separation of Lanthanides by ion chromatography with imprinted polymers', *Chem. Lett.*, 32, **2003**, 530-531.

Voelkl, K. P.; Opitz, N.; Lubbers, D. W.; Fres. Z., "Continuous measurement of concentrations of alcohol using a fluorescence-photometric enzymatic method", *Anal. Chem.*, 301, **1980**, 162-163.

Vogel, A. I., "Text book of quantitative chemical analysis", Longman group UK Ltd., London, **1989**.

Wagener, K. and Heitkamp, D., "Humic acids as promising adsorbents for recovering uranium from seawater", *Thalassia Jugoslavica*, 16, **1980**, 185-189.

Wang, J.; "Analytical Electrochemistry", Wiley-VCH: New York, **1994**.

Wang, J.; Guo, R.; Chen, J.; Zhang, Q.; Liang, X., "Phenylurea herbicides-selective polymer prepared by molecular imprinting using N-(4-isopropylphenyl)-N′-butyleneurea as dummy template", *Anal. Chim. Acta*, 540, **2005**, 307-315.

Whitcombe, M. J.; Rodriguez, M. E.; Villar, P.; Vulfson, E. N., "A new method for the introduction of recgnition site functionality into polymers prepared by molecular imprinting: Synthesis and characterization of polymeric receptors for cholesterol", *J. Am. Chem. Soc.*, 117, **1995**, 7105-7111.

WHO: Guidelines for Drinking Water Quality, Geneva, **2003**.

Wise, D. L., "Biosensors with fiber optics", Humana Press, New York, **1991**.

Wolfbeis, O. S., "Fiber optic chemical sensors and biosensors", CRC Press, Boca Raton, Florida, **1991.**

Wulff, G. and Sarhan, A. "The use of polymers with enzyme-analogous structures for the resolution of racemates", *Angew. Chem. Int. Ed.*, 11, **1972**, 341-343.

Wulff, G., "Molecular imprinting in cross-linked materials with the aid of molecular templates-a way towards artificial antibodies", *Angew. Chem., Int. Ed. Engl.*, 34, **1995**, 1812-1832.

Xu, D. F. and Katsu, T., "O,O,O-trialkyl phosphorothioates as simple and effective ionophores for silver ion-selective membrane electrodes", *Anal. Chim. Acta.*, 443, **2001**, 235-240.

Yilmaz. E.; Haupt. K., Mosbach. K., "The use of immobilized templates - A new approach in molecular imprinting", *Angew. Chem. Int. Ed. Engl.*, 39, **2000**, 2115-2118.

Yu, K. Y.; Tsukaghoshi, K.; Maeda, M.; Takagi, M., "Metal ion-imprinted microspheres prepared by reorganization of the coordinating groups on the surface", *Anal. Sci.,* 8, **1992**, 701-703.

Yuan, R., Song, Y. Q., Chai, Y. Q., Xia, X. S., Zhang, Q. Y., Yi, B. M., Ying, G., Shen, L., Yu, R. Q., "Design of Schiff base complexes of Co(II) for the preparation of iodide-selective polymeric membrane electrode", *Talanta,* 48, **1999**, 649-657.

Yuan, R.; Chai, Y.Q.; Liu, D.; Gao, D.; Li, J.Z.; Yu, R.Q., "Schiff base complexes of cobalt(II) as neutral carriers for highly selective iodide electrodes", *Anal. Chem.*, 65, **1993**, 2572-2575.

Yun, C. K., "Development of a process for continuous extraction of uranium from seawater", IAEA-R-1759-F, **1982**.

Zamani, H. A.; Abedini-Torghabeh, J.; Ganjali, M. R., "A highly selective and sensitive calcium(II)-selective PVC membrane based on dimethyl 1-(4-nitrobenzoyl)-8-oxo-2,8-dihydro 1H-pyrazolo[5,1-a]isoindole-2,3-dicarboxylate as a novel ionophore", *Bull. Korean Chem. Soc.,* 27, **2006**, 835-840.

Zamora, M. L.; Tracy, B. L.; Zielinski, J. M.; Meyerhof, D. P.; Moss, M. A., "Chronic ingestion of uranium in drinking water: A study of kidney bioeffects in humans", *Toxicol. Sci.,* 43, **1998**, 68-77.

Zhang, A.; Uchiyama, G.; Asakura, T., "pH effect on the uranium adsorption from seawater by a macroporous fibrous polymeric material containing amidoxime chelating functional group", *React. Funct. Polym.*, 63, **2005**, 143-153.

Zirino, A.; De Marco, R.; Rivera, I.; Pejcic, B., "The influence of diffusion fluxes on the detection limit of the jalpaite copper ion-selective electrode", *Electroanalysis*, 14, **2002**, 493-498.