SOLID PHASE EXTRACTION PRECONCENTRATION OF TRACES OF INORGANICS

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DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"SOLID PHASE EXTRACTION PRECONCENTRATION OF TRACES OF INORGANICS"** is the result of the investigations carried out by me under the guidance of **Dr. T. Prasada Rao**, Regional Research Laboratory (CSIR), Thiruvananthapuram. I further declare that this thesis or part thereof has not previously been formed the basis for the award of any degree or diploma.

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled **“SOLID PHASE EXTRACTION PRECONCENTRATION OF TRACES OF INORGANICS”** has been carried out by Mrs.C.R.Preetha under my supervision. The content of this thesis or part thereof has not been submitted to any other university or institute for the award of any degree or diploma.

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PREFACE

Today Solid phase extraction (SPE) is the most sought after preconcentration /separation technique in many areas of chemistry including environmental, pharmaceutical, clinical, food and industrial chemistry. Solid phase extraction (SPE) is an attractive alternative in sample preparation as it overcomes most of the drawbacks associated with other conventional techniques. Better enrichment and selectivity can be achieved by modifying the extractant materials in different ways. Of late, ion imprinted polymers are the most innovative solid phase extractants for selective separation of inorganics from complex matrices.

In the present study, different solid phase extractants were prepared by modifying solid sorbents with different chelating agents and by synthesizing new imprinted polymer particles. These sorbent materials were used for the preconcentration and /or separation of different inorganics present at trace levels.

Chapter 1 deals with the general introduction to solid phase extraction. The mechanisms involved in SPE, various sorbents used and techniques of SPE are discussed in the introduction chapter.

Chapter 2 describes the SPE preconcentration of thorium with 5,7-dichloroquinoline-8-ol (DCQ) embedded benzophenone. Various parameters that influence the preconcentration of thorium by solid phase extraction were systematically optimized and the results obtained are discussed in this chapter.

The solid phase extractive precocentration of uranium(VI) with dicyclohexano-18-crown-6 embedded benzophenone and 1-(2-pyridylazo)-2-naphthol (PAN) embedded benzophenone/naphthalene is described in chapters 3&4. The effect of various cations and anions on the preconcentration of uranium(VI) in conjunction with the Arsenazo III determination procedure has been studied. The accuracy of the developed preconcentration procedure in conjunction with spectrophotometry was tested by analyzing marine sediment reference material (MESS-3). Furthermore, the uranium(VI) content of sediment and soils was also estimated using the above method.

The preparation and application of 1-(2-thiazolylazo)-2-naphthol (TAN) sorbed activated carbon for the selective enrichment of uranium(VI) from dilute solutions and complex real samples using column dynamic method have been described in chapter 5.

Chapter 6 gives a detailed account of the synthesis of uranyl ion imprinted polymer particles(IIP) by employing U(VI), salicylaldoxime and 4-vinyl pyridine ternary complex and polymerizing thermally in the presence of styrene, divinylbenzene and 2,2'-azobisisobutyronitrile as functional, cross linking monomer and initiator respectively . These polymer particles were used as SPE material to separate/ enrich uranium(VI) species selectively from synthetic nuclear spent fuel.

Chapter 7 concerns with the development of on-line Flow Injection-Flame Atomic Absorption Spectrometry (FI-FAAS) technique for the determination of zinc at μg l^{-1} level, using commercially available C_{18} bonded silica gel micro column. The application of the method for the speciation studies of zinc in soil samples has been described.

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INTRODUCTION

Accurate analysis of various complex samples (natural and waste waters, geological, industrial and high purity materials) especially at trace levels is one of the most difficult and complicated analytical tasks. The rapid development in instrumentation has created powerful analytical tools for trace element determination. At the same time, due to pronounced matrix effects and the role of separation chemistry in instrumental methods have assumed importance. During the last few years, the importance of preconcentration and separation techniques in the trace analysis has increased considerably [1]. Pretreatment of an aqueous sample by a sorption technique not only increases the ion concentration but also eliminates matrix effects. Such a pretreatment technique should provide an enrichment factor up to several hundred folds, better separation from interferent ions and the possibility of combining with different determination methods [2-5].

1.1 PRECONCENTRATION

Despite the selectivity and sensitivity of analytical techniques, there is a crucial need for the preconcentration of trace elements before analysis. An enrichment technique is essential in those cases,

(1) where the concentration of the desired trace element is below the relative detection limit of the determination technique,

(2) where substances which interfere with the determination exist in the sample,

(3) where the sample is highly toxic/ radioactive / expensive to be wasted,

(4) where the desired trace elements are not homogenously distributed in the sample,

(5) where suitable standard samples required for the calibration are not available, and

(6) where the chemical or physical states of the sample are not suitable for the direct determination [6].

Enrichment (preconcentration) of the desired trace elements prior to the determination can overcome these difficulties, extend the absolute and relative detection limits, improve the precision and accuracy of analytical results, and widen the scope of the determination techniques. Actually enrichment is a process in which the ratio of the amount of a desired trace element to that of the original matrix is increased Thus the original matrix is converted into a new matrix which is more suitable for determination.

There are several methods frequently employed for the preconcentration of inorganics.

1.1.1 Liquid-liquid extraction

Liquid-liquid extraction is a technique in which a solution (usually aqueous) is brought into contact with a second solvent (usually organic), essentially immiscible with the first, in order to bring about a transfer of one or more solutes into the second solvent [7].

In the case of inorganic solutes, it is concerned largely with samples in aqueous solution so that it is necessary to produce entities, such as neutral metal chelates and ion-association complexes, which are capable of extraction into organic solvents. For organic solutes, however, the extraction system may sometimes involve two immiscible organic solvents rather than the aqueous-organic type of extraction.

The technique of liquid-liquid extraction has, of course, been used to separate the components of organic system, in particular, solvent extraction may be employed to effect a ‘clean up’ and to achieve preconcentration of solutes of interest prior to analysis.

1.1.2 Ion-exchange

Ion-exchange means the exchange of ions of like sign between a solution and a solid of highly insoluble body in contact with it. Ion exchangers consist of a framework carrying a positive or negative surplus charge which is compensated by mobile counter ions of opposite sign. To concentrate analytes of interest, it is passed through a column of appropriate ion-exchange resin, the exchangeable ions will be exchanged. Then it is eluted as a small volume of more concentrated ions. The ion exchange resin bed can also be regenerated with a proper electrolyte solution. The capacity of ion exchangers is defined in terms of the number of exchangeable counter ions in the material [8].

1.1.3 Flotation

Flotation is defined as the process by which suspended matter and solutes in aqueous solutions are selectively floated to the solution surface with the aid of a rising stream of a gas bubbles. Hydrophobic substances are easily attached to the bubbles and floated. Therefore, when hydrophilic substances are to be floated, they are generally rendered hydrophobic in combination with suitable surfactants before hand. A well known industrial application of this technique is the concentration of valuable minerals and ores.

1.1.4 Sorption or Immobilization

Sorption is the common term used for both absorption and adsorption. These terms are often confused. Absorption is the incorporation of a substance in one state into another different state. Adsorption is the physical adherence or bonding of ions and molecules onto the surface of a sorbent.

The enrichment techniques are based on the distribution of substances between a solution and a solid sorbent by mechanisms such as physical sorption, complex formation and other chemical reactions on or in the sorbents. Many materials can be used as sorbents for the preconcentration of trace metals from an aqueous solution such as activated carbon, porous organic polymers, chelating resins and ligand modified resins.

1.1.5 Co-precipitation

It is a phenomenon in which soluble substances are picked up from solution by the precipitate during its formation. Co-precipitation implies removal of soluble substances from the solution by the precipitate through some other phenomena, such as surface adsorption, mixed-crystal formation, occlusion and mechanical entrapment. To minimize the loss of the desired element, the following means are usually adopted: (1) masking of the desired trace elements with a suitable complexing agent, (2) precipitation from homogenous solution, (3) prolonged digestion, (4) reprecipitation, (5) washing the precipitate with an appropriate solution. Coprecipitation is used mainly to preconcentrate trace constituents of analytes in solution to the levels that can be quantitated by a particular analytical technique [9].

1.1.6 Electrodeposition

The term electrodeposition has been used for the electrochemical reaction in which the product is insoluble in the solution phase and deposits on or in 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. In this cell, reduction takes place at one electrode which is called the cathode, and an oxidation at the other, which is called the anode. The electrodeposition may occur at either electrode. Three processes may be considered for the transfer of ions to the electrode surface: (1) diffusion, (2) convection and (3) electrolytic migration

1.1.7 Solid phase extraction (SPE)

The use of an appropriate separation technique is must in any analysis where the desired component is present in traces in presence of a host of other matrix species. Liquid-liquid extraction (LLE) is a classical method for separating the desired species/ or matrix removal. Solid phase extraction was initially developed as complementary or alternative approach to liquid-liquid extraction, but in recent times, solid phase extraction has emerged as the most powerful technique for sample handling in many areas of chemistry. Apart from its main goal of separation at trace levels, solid phase extraction finds application in preconcentration, matrix simplification (sample clean up) and medium exchange (transfer from the sample matrix to a different solvent or to the gas phase) [10].

Solid phase extraction finds its origin in 1950’s when carbon filters were used for the concentration of organic compounds from surface waters. From 1960’s to 1980’s, a large number of solid phase extraction procedures were developed for finding out the best solid phase extraction material and even now new solid phase extraction materials are being developed. However, the efforts are on to find the optimum material for a particular problem [11]. Simultaneously, the major attention of the analysts was being gradually shifted to technological issues. It was in 1970’s that the idea of substituting the off-line sequence (of analyte elution, eluate processing and the transport of the eluate to analytical system) with direct on-line elution from the sorbent worked out. Coupling of solid phase extraction precolumn to HPLC or GC was proved to be a promising approach. In recent years, different types of copolymers, chemically modified resins, membrane extraction disks were also introduced in solid phase extraction research.

1.1.7.1 Solid phase micro-extraction (SPME)

The ability to scale down solid phase extraction has become critical in an era in which increased efficiencies are a top priority. In fact, solid phase micro-extraction has become a much discussed spin-off of traditional solid phase extraction for dealing with high value, low value samples. SPME has only become commercially available since mid 1990’s [12]. Rather than relying on loose particles or membranes, the technique uses a small solid rod of fused silica (typically 1.0 cm long with a 0.11 cm outer diameter). The silica is precoated with an absorbent polymer chosen for a particular application required. For example, polar coatings such as polyacrylate and polyethylene glycol are used to bind polar compounds, non-polar coatings (such as polydimethylsiloxane) are used for nonpolar compounds. Key benefits of using such a fiber include its ability to be inserted into a sample for drawing up material and its structural strength, which allows it to be moved throughout a sample to prevent the formation of a depletion zone around the fiber.

Lord and Pawtiszyn [13] described the development of the concepts, techniques and devices associated with SPME, as a response to the evolution of understanding of the fundamental principles behind this technique. Two comprehensive reviews highlighting the application of SPME to the fields of elemental and organometallic analysis with special emphasis on detection techniques was presented by Mester and Sturgeon [14,15].

The newly emerged microextraction methods include stirbar sorptive extraction (SBSE), single droplet microextraction and membrane protected SPME and SDME.

1.2 THEORY OF SOLID PHASE EXTRACTION (SPE)

The principle of SPE is similar to that of liquid-liquid extraction, which involves the distribution of solute molecules between two immiscible phases. Unlike in LLE, SPE involves the partitioning between a liquid phase and a solid phase. The analytes are preconcentrated to a solid phase where they are retained for the duration of sampling process. The solid phase is then isolated from the sample and the analytes recovered by elution using a suitable eluent.

1.3 PRACTICAL PROCESS OF SPE

A solid phase extraction method always consists of three to four major steps (See *Fig.1.1*).

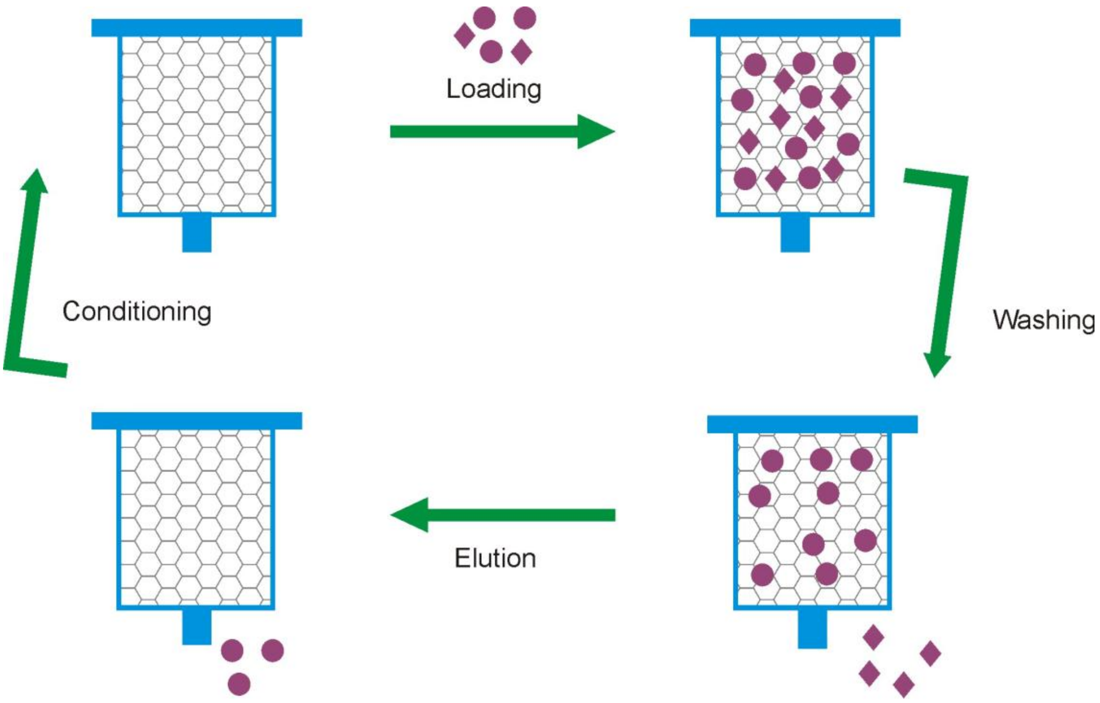

Fig.1.1 The practical process of SPE

1.3.1 Washing and conditioning of the solid sorbent

Here the solid sorbent is first conditioned using an appropriate solvent, i.e, the same solvent as the sample solvent. This step is very crucial in the sense that it enables the wetting of the packing material, the solvation of functional groups, the removal of impurities and the removal of air present in the column [16].

1.3.2 Percolation of the sample

In this step, the sample is applied to the column under gravity or by an automated system. During this step, the analyte is concentrated on the sorbent. This step enables matrix separation to some extent and thereby sample purification.

1.3.3 Washing of solid sorbent

In this optional step, some of the matrix components are eliminated by washing the solid sorbent with a solvent of low elution strength.

1.3.4 Elution of the analyte

The final step consists of the elution of the analytes of interest by an appropriate solvent, without removing the retained matrix components.

1.4 MECHANISMS INVOLVED IN SPE

Solid phase extraction may progress through any of the following mechanisms:

1.4.1 Adsorption

Trace elements are usually adsorbed on the solid support through van der Waal's forces and hydrophobic interaction. In certain systems like styrene-divinyl benzene, it provides additional $\pi - \pi$ interactions when π electrons are present in the analyte.

1.4.2 Chelation

Several functional groups are capable of chelating trace elements. The nature of the functional group will give an idea of the selectivity of the ligand towards the elements. The interactions between the metal cation and the active site of the ligand are governed by Pearson's HSAB theory.

1.4.3 Ion-pairing

When a non-polar sorbent is to be used, an ion-pair reagent (IP) can be added to the sorbent. Such reagents contain a non-polar portion and a polar portion. The non-polar portion interacts with the reversed-phase non-polar sorbent while the polar portion forms an ion-pair with ionic species present in the matrix.

1.4.4 Ion-exchange

Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange with the associated counter-ion. Strong and weak sites are present as ion-exchange sites. An ion-exchanger may be characterized by its capacity, resulting from the effective number of functional active groups per unit mass of the material. Retention on ion-exchangers depends on the distribution ratio of the ion on the resin, the stability constants of the complexes in the solution, the exchange kinetics and presence of other competing ions.

1.5   ADVANTAGES OF SPE

SPE was initially developed as an alternative for liquid-liquid extraction (LLE). Conventional LLE is labor intensive, difficult to automate, and is frequently plagued by practical problems, such as emulsion formation. In addition, it consumes relatively large volumes of high-purity solvents with expensive disposal requirements. By contrast, SPE benefits from low intrinsic costs, shorter processing times, low solvent consumption and hence environmentally friendlier. SPE methods are easier to automate and safe with respect to the analysis of hazardous samples. Moreover, SPE has favorable properties for field sampling, eliminating the need to transport and store bulk samples for processing in the laboratory. Its application for preconcentration of trace metals from different samples is also very convenient due to sorption of target species on the solid surface in a more stable chemical form than in solution [10]. SPE affords precise and quantitative recoveries along with higher enrichment factors therefore a broader range of applications are forth coming than LLE due to the large choice of solid sorbents and low consumption of solvents.

1.6   SPE OF ORGANICS

SPE is an attractive technique as it makes on-line determination by hyphenation with various chromatographic techniques. SPE and SPME has been widely used for capturing organic pollutants, monitoring pesticides from different sources, i.e. SPE has been there in the analysis of environmental pollutants since long [17].

The mechanism of retention of organic molecules on the solid sorbent is based on hydrophobic interactions between the solutes and the stationary phase and on secondary interaction such as hydrogen bonding and dipole-dipole forces. Chemically modified silica, porous polystyrene resins, XAD-2, XAD-4 resins, PRP-1, PLRP-S, Padapack RDX, Isolute ENV and Lichrolut EN are some of the commercially available sorbents widely used for retaining organic pollutants. These kinds of sorbents have greater surface area and are relatively selective for analytes with aromatic ring because of the specific $\pi - \pi$ interaction. *Table 1.1* gives a picture of various organic entities sorbed on different SPE phases.

1.7 SPE OF INORGANICS

Over the last two decades, the need has increased for the determination of extremely low concentrations of metals in various samples. SPE finds itself the best candidate for the preconcentrative separation of the metals prior to determination. Solid phase extraction procedures have been developed for almost all metals during the last half century.

The various enrichment procedures for inorganic trace analysis using oxines as preconcentrating agent had been reviewed by Rao *et al* [34]. Again, the same authors reviewed the role of oxines as preconcentrating agents in on-line enrichment technique – FI-AAS [35]. The theory of SPE and different sorbents used so far in SPE of elements at trace levels has been described by Camel [36]. A critical review on the SPE and preconcentration for the determination of trace amounts of platinum group metals was presented by Vlasankova and Sommer [37]. A review comprising recent advances in SPE of platinum with special emphasis on the different solid sorbents used was given by Pyrzynska in 1998 [38].

Table 1.1

S.No.	Analyte	SPE phase	Ref.
1	Phenols and pesticides	Benzoyl PS-PVB	[18]
2	Triazines	o-carboxybenzoyl-PS-PVB	[19]
3	Triazine herbicides	PRPX-100	[20]
4	Phenols, alcohols, carboxylic acids, aldehydes, ketones, esters, chloroalkanes, amines and nitrosamines	Sulfonated PS-PVB	[21]
5	Phenoxy acid herbicide residues	MEE-polymer containing quaternary ammonium groups	[22]
6	Aliphatic amines	SCX cartridge – disks, C_{18}	[23]
7	Aromatic amines	SDVB	[24]
8	Heterocyclic aromatic amines	C_{18} cartridges, PRS	[25]
9	Aromatic acid	Sep-Pak C_{18}	[26]
10	Naphthalene sulphonates	C_{18}, SCX cartridge	[27]
11	Chlorsufuron, metsulfuron and chlormuron	C_{18} cartridge	[28]
12	Organotin compounds	C_{18}, C_8, phenyl functionalized sorbent, Amberlite XAD-2 and Amberlite XAD-4	[29]
13	Metallo-cyanide complexes	Sep-Pak C_{18} cartridges	[30]
14	EDTA	SAX disks	[31]
15	Alkyl phosphonic acids	Barium, silver and catridges	[32]
16	Chloro-nitrophenols	Crosslinked polystyrene cartridge	[33]

A brief overview of the application of naphthols as reagents for solid phase preconcentration/separation of inorganics based on published data was presented by Rao *et al* [39]. The use of ion imprinted polymers for the solid phase extraction of metals including lanthanides, actinides, and transition metals was listed by Rao *et al* [40] recently. A very comprehensive review devoting separate sections to each of the preconcentration techniques employed for the enrichment of individual or mixtures of lanthanides since 1980 was presented by Kala *et al* [41]. Recently, Praveen *et al [42]* discussed the role of styrene-divinyl benzene copolymers as solid-phase extractants in the trace analysis of various mono- and multielement analysis of inorganics.

1.8 EXTRACTANTS IN SPE

The functional group atoms capable of acting as extractants of metals include oxygen, nitrogen and sulphur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether and some other groups. Sulphur is in the form of thiol, thio ether, thiocarbamate, disulphide groups etc [43]. Chelating extractants are made use of to a large extent in analytical chemistry as they can form comparatively more stable complexes with metal ions. Various oxines, oximes, β-diketones and naphthols come under this category [44,45].

1.9 SORBENTS IN SPE

Sorbents play a key role in SPE. History of sorbents passed over a long way from the first use of silica, carbon filter, alumina, Florosil and Kieselguhr in 1930's as solid sorbent, to the introduction of the Sep-Pak in 1978, to the introduction of polymeric resins and highly selective molecularly imprinted polymers in 1990's [46].

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology. The essential requirements of a sorbent are (1) the possibility to extract a large number of trace elements over a wide pH range, (2) fast and quantitative sorption and elution, (3) a high capacity, (4) regenerability, (5) accessibility and (6) mechanical and chemical strength. Sorbents can be mainly categorized as organic based ones, inorganic based ones and inorganic-organic hybrid materials (like C_{18} bonded silica gel, aminopropyl silica gel and ion imprinted polymers). The selective extraction of a single trace element from other interfering ions represents a direct challenge for finding a suitable phase capable of exhibiting a sufficient affinity to selectively bind that metal ion. For particular application, the combination of two sorbents may thus be advisable.

Inorganic based sorbents are mainly made of silica gel even though some other inorganic oxides are also used like TiO_2, Al_2O_3, ZrO_2 and MgO. Silica gel based sorbents are quite stable in terms of mechanical, thermal and chemical grounds. The limited pH range and residual surface silanol groups are the two main limitations usually encountered with silica supports.

In addition to this, chelating agents can be easily loaded on silica gel with high stability. As there is free silanol group, silica gel as such is capable of extracting many metal ions including Cu, Ni, Co, Zn and Fe [47]. To increase the selectivity of silica gel, the surface is loaded with specific organic compounds through chemical immobilization or physical adsorption. Application to the determination of trace elements has been reported for more than twenty years with several functional groups such as amines, dithiodicarbamate, iminodithiodicarbamates or dithioacetals [48-50]. Macrocycles like 18-crown-6 and calixarenes can be bound to silica [51].

1.9.1 Other inorganic oxides

SiO_2, due to its acidic properties, is expected to absorb only cations, basic oxides (such as MgO) should absorb only anion. Amphoteric oxides (such as Al_2O_3, TiO_2 and ZnO_2) adsorb cations under basic conditions and anions under acidic conditions. So the last category of sorbents can be used in speciation studies [52].

1.9.2 Organic based sorbents

Organic based sorbents are generally divided into two classes – natural and polymeric materials.

A. Natural materials

(1) Carbon based sorbents

Activated carbon (AC) owing to large surface areas (300-1000 m^2/g) are well known for their extraction capacities towards organics and inorganics. Two types of adsorption sites are identified in activated carbon (a) the graphite like basal plane which enable adsorption through π electron interactions and van der Waals forces (b) presence of polar groups like carbonyls, hydroxyls and carboxyls [36]. AC can be used as such for trace element enrichment or the metal chelate can be loaded on to it.

The main drawback regarding activated carbon is its heterogenous surface area and its catalytic capabilities. During the last decade, graphitized carbon blacks (GCB) were introduced which could offer a more homogenous structure and reproducible properties. More recently, carbon nanotubes are used for the enrichment of certain metals, Liang *et al* [53] reported single walled carbon nanotubes as column sorbent material for the on-line column preconcentration of lanthanides.

(ii) Cellulose based sorbents

Unsubstituted cellulose has very low ion exchange capacity. But, cellulose sorbents with chemically bound chelating groups offer new possibilities for trace metal preconcentration. An activation step is carried out before the attachment of ligands [54]. Carboxy cellulose, carboxymethylcellulose, diethylaminoethyl cellulose and phosphorylated and sulphonated cellulose have been synthesized and studied as supports for trace ion preconcentration. Huang and Jiang [55] have utilized carboxymethylcelluloseoxine 7-quinolyl ester for preconcentrating several transition metals. Selenium speciation has been reported on cellulose functionalized with quaternary amine due to the selective elution of the retained Se(IV) and Se(VI) species [56]. Metilda *et al* used quinoline-8-ol modified cellulose as solid phase extractant (SPE) for preconcentrative separation and determination of thorium(IV) [57].

(iii) Naphthalene based sorbents

Naphthalene based sorbents otherwise called low melting extractants include naphthalene, diphenyl, benzophenone and p-dichlorobenzene. Molten naphthalene is used for the preconcentration of trace metals. Here the extraction is performed when the extractant is in melt form, after which the system is cooled, as a result the extract solidifies and separates from the solution phase. But this method can not be used for thermally unstable complexes. Fujinaga and Kuwamoto [58] adopted a method involving “solid-liquid separation after liquid-liquid extraction with microcrystalline naphthalene” which is simple and rapid method for trace analysis of metal ion. Solid phase extraction using molten naphthalene [59] or adsorption of metal chelate complex onto microcrystalline naphthalene [60] or column chromatographic preconcentration onto chelate modified naphthalene [61] procedures were developed for inorganics. Burns *et al* [62,63] and Sharma [64] used p-dichlorobenzene and benzophenone as solid sorbents. Gladis *et al* [65] reported a method in which naphthalene was first modified with the chelating agent through co-precipitation and then used for enriching uranium(VI).

B. Polymeric sorbents

Chemically modified resins have been developed and used in the SPE of polar compounds mainly from aqueous samples. These resins have excellent hydrophilicity and also give higher recoveries than their unmodified analogues [66,67]. This can be attributed to the increase in surface polarity which enables the aqueous sample to make better contact with the resin surface. New polymeric sorbents have been synthesized either by direct polycondensation or polymerization of monomers containing chelating groups or chemically bonding chelating groups to polymeric cross linked chains.

The most widely used polymeric sorbents are the polystyrene-divinyl benzene copolymers. The chemical modification of the PS-DVB resins and the application of these polymeric supports for the sample preparation was described by Leon-Gonzalez *et al* [68]. The main limitation of the polymer is its hydrophobic nature, which can be overcome by attaching polar groups like acetyl, benzoyl, hydroxymethyl or sulphonate [68].

The non-aromatic ethylene-dimethaacrylate resins (Amberlite XAD-7 and XAD-8) fall in the category of polyacrylate polymers. Polyurethane foams are well known for their sorption capacity towards metal ions. Polyethylene resins and polytetrafluoroethylene polymers are also used for preconcentrating several metal complexes. Polyamide resin, polyacrylonitrile based sorbents and crown ether polymers are also used for metal preconcentration.

Recently, new extraction sorbents involving reversible and selective antigen-antibody interactions, called immunosorbents (ISs) have been synthesized in order to trap structurally related pollutants. Immunosorbents are obtained by covalently binding antibodies onto appropriate sorbents. The high degree of molecular selectivity is because of the specificity of the antibody-antigen spatial fitting and interactions. Antibodies to the analyte in question are bound to the silica or polymeric matrix used for extraction. The analyte behaving like a typical antigen, then binds in a lock-and-key fashion to the specific antibody sites. An appropriate buffer wash can release the concentrated molecules from the matrix.

According to Masque *et al* [69], the recent popularity of using immunosorbents for SPE of analytes from complex matrices such as blood, urine and environmental water samples has led to a demand for less difficult to develop and more cost-effective alternatives to antibodies. Synthetic antibody mimics, known as molecular imprinted polymers, or MIPs seem to provide the answer. MIPs are cross-linked molecules bearing tailor-made binding sites for target nucleus [69]. They are formed by an ingenious method of complexing monomers containing functional groups with the target compound. The monomers bind to appropriate locations on the target. A large excess of crosslinker is subsequently added to form a highly crosslinked polymer network from which the target molecule (which has now served as a template) is then washed off. The process is equivalent to forming a mold that fits specific portions of the target molecules in the same sort of lock-and-key fashion. The new molecularly imprinted polymer materials can then be used to selectively rebind new target molecules.

1.10 MOLECULAR IMPRINTING POLYMERS FOR SPE

Solid phase extraction finds a promising and innovative reliance in molecularly imprinting polymer technology. MIPs are crosslinked polymers with specific binding sites which are tailor made *in situ*. When the template is removed, it leaves recognition sites which can re-bind the specific template in preference to other closely related structures. These polymers are used to enrich analytes, as separation materials, sensors, antibody and receptor mimics.

Wulff and Sarhan introduced the concept of MIPs in early 1970's [70,71]. Mosbach and co-workers [72] developed the so-called non-covalent approach. Mosbach's approach of preassembling a non-covalently associated monomer-template complex in solution prior to polymer formation was the breakthrough that enabled molecular imprinting to be used in a variety of applications. Sellergreen [73] has identified importance of polymer and template related factors in the development of MIPs for use in SPE and summarized the results obtained to date in the area of biological, pharmaceutical and environmental analysis.

Ion imprinting polymers (IIPs) are similar to MIPs, but they recognize metal ions after imprinting and retaining all virtues of MIPs [74,75]. IIPs have outstanding advantages such as predetermined selectivity in addition to being simple and convenient to prepare. SPE preconcentration of metal ions (when present in low concentration or in presence of other coexisting ions) is a particularly promising application of IIP. Here, metal ions serve as templates for forming crosslinked polymers via imprinting. One of the first ionic template effects in the synthesis of chelating polymers was reported by Nishide *et al* [75] in the mid 1970's. Takagi and coworkers [76] prepared surface imprinting polymers using functional host monomer, an emulsion stabilizer, a crosslinking agent and a metal cation template, which was selectively complexed by the metal binding groups at the aqueous-organic interface to form recognition sites. Rao *et al* [40] recently reviewed the studies done so far in the area of IIP-SPE of metal ions and outlined the future scenario in this area.

IIPs have the advantage that they are more stable in harsher environments, such as pH, organic solvents, pressure and temperature. The main problems associated with IIPs are the slow rate of mass transfer in binding and release of template from the sites and bleeding of the unleached template. However, IIP-SPE procedures have immense potential to find applications in the preconcentrative separation, speciation of various metal ions, and in the preparation of catalysts, sensors and column materials.

1.11 TECHNIQUES OF SPE

From the methodological stand point, two basic approaches can be recognized in SPE - online and offline. In the offline configuration, the elution and separation of analytes are two separate steps. In the online column configuration, the SPE column output is connected directly to the analytical transducer; preconcentrative separation and determination are effected by computer controlled programme. The chemistry and general principles are the same for both these variants, but the differences in their methodologies are sometimes the reason for certain advantages or drawbacks of either of these approaches in a particular application.

Advantages of the offline approach

1. Operational flexibility
2. Simplicity of the equipment required
3. Handling of higher sample volume
4. Chance of analyzing the same extract using different determination techniques.

Limitations of the offline approach

1. Require a lot of manual work

2. The loss of several microlitres of the eluate solvent can lead to a considerable error in the final result.
3. Poor reproducibility
4. Drying of the wet cartridge affect the recovery of polar compounds.

Advantages of the online approach

1. Minimum operator labour
2. Minimum loss of analyte during handling of the eluate and drying of the SPE column.
3. Better sensitivity and reproducibility
4. Low time consumption
5. High sample throughput.

Limitations

1. Delivery of a large number of other matrix components
2. Need of a trained technical personnel
3. Low flexibility in setting the desorption conditions
4. Hydrophobic, non-polar analytes causes strong adsorption within the preconcentration system [77].

So, it can be concluded that in the case of complex samples, offline SPE should be preferred due to its simplicity and flexibility. As online procedures avoid sample manipulation between preconcentration and analysis steps and thereby offering better precision and accuracy on-line approach is often advantageous.

1.12 SCOPE OF THE WORK

The development of new preconcentration techniques and selective separation of closely related metals are the two important frontier areas of research in analytical chemistry. The accurate determination of analytes in different sample matrices is frequently problematic due to the presence of overwhelming matrix effects. Moreover, in some circumstances, the analyte concentration might be too low to be analyzed directly. In trace analysis, liquid–liquid extractive preconcentration and ion-exchange separation techniques are most widely used methods. Efficient extraction of trace elements by a small volume of an organic solvent from a large volume of aqueous solution, as in traditional solvent extraction, is hampered by the mutual solubility of both phases leading to difficulties in their separation and its large volume of solvent consumption. Ion-exchange materials are used for separation and preconcentration of metal ions, prior to the analysis of the analyte, exchanged ions require to be eluted with large volumes resulting in low enrichment factors. Moreover, the main drawback of ion exchange procedure is the need for the frequent replacement of resin material. These facts led to development of methods like solid phase extraction by modified solid sorbent for preconcentration and separation of metal ions at trace level in complex materials. Hence, in view of the virtues of SPE (in both off-line and on-line modes), the scope of the proposed work is

I. To prepare new solid phase extractant materials for the selective preconcentration/separation of metal
II. Development of suitable preconcentrative separation procedures in conjunction with UV- visible spectrometry/flame atomic absorption spectrometry.
III. Validation of the developed preconcentration procedure by analyzing certified reference materials and
IV. Application of the developed procedures to complex real samples.

The work carried out on these lines and the results thus obtained are discussed in following chapters.

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CHAPTER 2

OFFLINE SOLID PHASE EXTRACTION PRECONCENTRATION OF THORIUM WITH 5,7-DICHLOROQUINOLINE-8-OL EMBEDDED BENZOPHENONE

The separation and preconcentration of thorium is very much significant in the context of increasing energy demands. There is probably more energy available for use from thorium than from both uranium and other fossil fuels. Thorium is important in terms of its non-nuclear uses also. It is used chiefly in gas mantles, in electron tubes, in incandescent lamps. Thorium as such and its oxide find applications in high quality lenses for cameras and scientific instruments. Thorium oxide is used as a catalyst in the conversion of ammonia to nitric acid, in petroleum cracking and in producing sulphuric acid.

Thorium (10 - 20 ppm) is now thought to be about four times as abundant as uranium (4 ppm). The three most significant minerals of thorium are monazite, thorianite and thorite. At present the most important source of thorium is monazite, the phosphate of the cerium rare earths, containing varying amounts of thorium (3 to 9% ThO_2) [1]. Monazite sand from India and Sri Lanka are richest in thorium content.

Indian Rare Earths limited (IRE), Alwaye, Kerala processes monazite sand by treatment with sodium hydroxide followed by acidification with hydrochloric acid. Various radioactive species including radium were then removed by co-precipitation with barium sulphate. Subsequently, thorium was selectively removed from rare earth chloride concentrate by raising the pH and stored in underground tanks for future usage. However, thorium is found to be present in trace levels in the rare earth fraction which is processed for the production of pure and ultra pure rare earth oxides. The presence of thorium impurity in rare earth chloride fraction affects the quality of rare earth products. Hence, a rapid and reliable analysis of traces of thorium in mixed rare earth chloride concentrate is desirable.

As mentioned in the previous chapter, sorbents play the main role in every SPE procedure. Solid phase extractants such as thiol cotton [2], activated carbon [3], green tea leaves [4], chelating resins [5], cellulose [6], polythioether [7], silica frits [8], glass beads [9] and polymer supports [10,11] were physically sorbed or chemically immobilized with various reagents and were employed by various researchers for preconcentration of inorganics. Although some of these extractants are fairly effective, their methods of preparation are lengthy and also involve rigid conditions for the elution of the preconcentrated metal ion. On the other hand, SPE procedures involving low melting extractants (which includes naphthalene, benzophenone, p-dichlorobenzene etc) are found to be significant in the trace analysis of metal ions as they are simple and rapid. The main advantages of this kind of sorbents are that equilibrium distribution in the two phases is attained within a small interval of time. As only a small amount of water miscible solvents is required for complete extraction, the sensitivity of the method is reasonably enhanced. Molten naphthalene was used as an extractant for the preconcentration of inorganics. However this technique is unsuitable for preconcentration of metals which form thermally unstable complexes. Subsequently, the solid-liquid separation after co-precipitation of the metal chelates onto microcrystalline naphthalene was widely used as it is rapid, economical.

Solid Phase extraction procedures using molten naphthalene [12], adsorption of metal chelate complex onto microcrystalline naphthalene [13] and column chromatographic preconcentration onto chelate modified naphthalene [14] procedures were reported for inorganics. However, very few SPE procedures were reported for preconcentration using benzophenone. Choi *et al* [15] reported the preconcentration of cadmium by extracting its quinoline-8-ol complex into molten benzophenone. Benzophenone was used as the solid sorbent for the preconcentration of vanadium- 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br PADAP) complex from a fairly large volume of its aqueous sample in weakly acidic conditions [16]. Burns *et al* [17] reported the adsorptive preconcentration of bismuth(III) from dilute sulfuric acid solution as hexadecyltributylphosphoniumtetraiodobismuthate(III) onto microcrystalline benzophenone. A sensitive method was developed by Kim *et al* [18] for the determination of traces of copper by preconcentrative adsorption of its 1-nitroso 2-naphthol complex onto microcrystalline benzophenone. Oh and Choi [19] reported the determination of iron, cobalt and copper after preconcentrative separation by adsorption of their ternary complexes with nitroso-R-salt and cetyltrimethylammonium bromide onto benzophenone. However, to our knowledge no preconcentration procedure was developed for actinides using benzophenone. Furthermore, in all the hitherto developed methods, the metal ion was complexed with the chelating agent first and then adsorbed onto benzophenone or for that matter naphthalene collectors. But in the present method chelating agent was embedded in benzophenone first and the resulting material was used as a solid phase extractant for the preconcentration of thorium from dilute aqueous solutions.

2.1 PRELIMINARY STUDIES

Preliminary studies indicated that benzophenone embedded with quinoline-8-ol or its dihalo derivatives could extract traces of thorium from dilute aqueous solutions. Chelating agent embedded benzophenone materials were prepared by dissolving appropriate amounts of quinoline-8-ol or its dihalo derivatives and benzophenone in minimum amount of acetone and precipitating out the mixture from deionized water by stirring for 2 hours. The material was filtered, washed and dried. A solution containing 20 μg of thorium was made up to 1.0 litre and the pH was adjusted to 6.0. Chelating agent (1.0%) embedded benzophenone (0.5 g) was added to the above solution and stirred for 15 minutes. The filtered residue was dissolved in 5.0 ml of acetone and the thorium content was established by Arsenazo III procedure [20]. Thorium was found to be enriched quantitatively with 5,7-dichloroquinoline-8-ol embedded benzophenone only (cf. *Table 2.1*). Various parameters like pH, aqueous phase volume, amount of solid phase extractant etc. were optimized systematically.

Table 2.1 Effect of chelating agents

S.No	Chelating agent (1.0%) in benzophenone	Enrichment of thorium (%)
1	Quinoline-8-ol	91.0 ± 0.2
2	5,7-Dichloroquinoline-8-ol	>99.0
3	5,7-Dibromoquinoline-8-ol	88.5 ± 0.2
4	5,7-Diiodoquinoline-8-ol	84.0 ± 0.2

2.2 OPTIMIZATION OF EXPERIMENTAL PARAMETERS FOR THE SPE OF THORIUM

2.2.1 Effect of pH

The preconcentration of thorium onto 5,7-dichloroquinoline-8-ol (DCQ) embedded benzophenone was studied in the pH range 4.0 - 8.0. In these studies, the pH of the solution of 20 μg of thorium in 1.0 litre of deionized water was adjusted with Dil.HCl or NaOH. DCQ embedded benzophenone (0.5 g) was added to this solution and stirred for 15 minutes. The residue obtained after filtration was dissolved in 5.0 ml of acetone, treated with 5.0 ml of 50% (v/v) hydrochloric acid and 2.5 ml of 0.1% Arsenazo III and diluted to 25 ml with acetone. The absorbance of the thorium-Arsenazo III complex was measured at 660 nm. Blanks were also prepared for each pH value. *Fig.2.1* shows the percent enrichment of thorium onto SPE at different pHs. The preconcentration of thorium onto DCQ embedded benzophenone was quantitative in the pH range 6.0 - 6.5. So, in the subsequent work, the pH was adjusted to 6.2 ± 0.2 after adding 10 ml of 1.0 mol l^{-1}sodium acetate-acetic acid buffer.

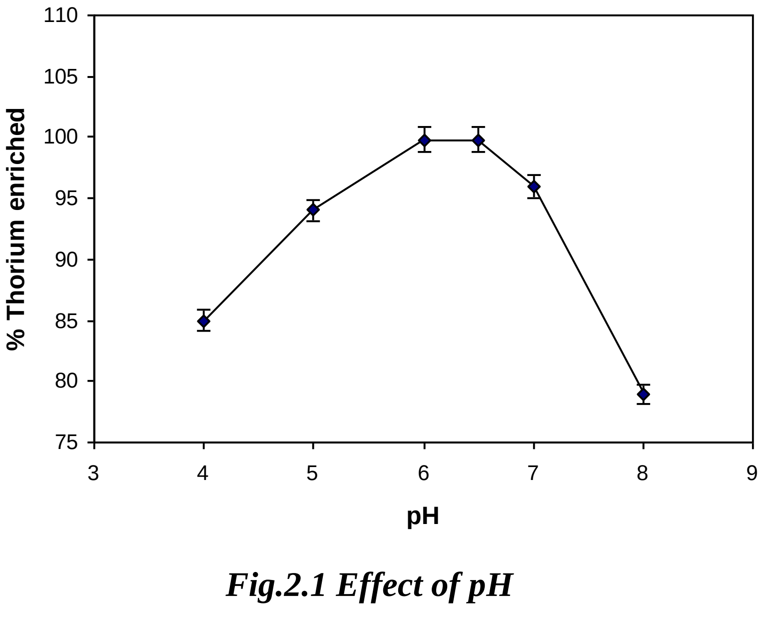

Fig.2.1 Effect of pH

2.2.2 Effect of DCQ Concentration in Benzophenone

Materials with different concentrations of DCQ in benzophenone (0.2-10%) were prepared and used for the preconcentration of thorium. The preconcentration and quantitation were carried out as described in section 2.2.1. The results obtained are shown in *Fig.2.2*. The enrichment of thorium onto DCQ embedded benzophenone was quantitative when the concentration of DCQ in benzophenone was $\geq$ 0.5%. So, 1.0% DCQ embedded benzophenone was used in subsequent studies.

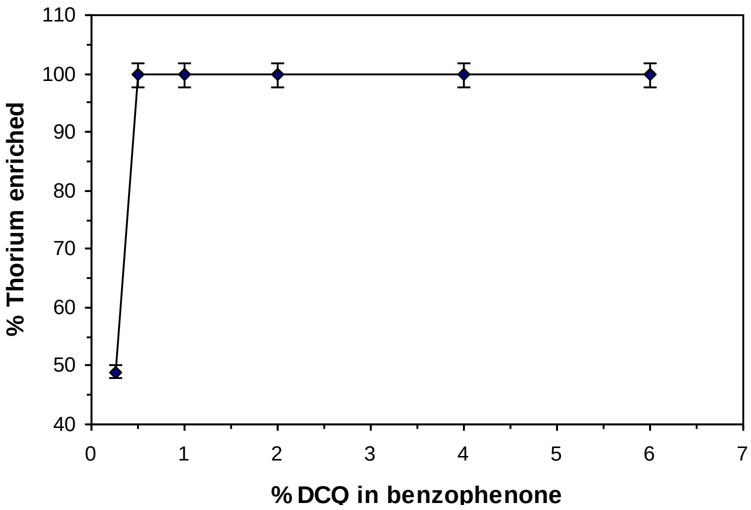

Fig.2.2 Effect of DCQ concentration in benzophenone

2.2.3 Effect of Amount of DCQ Embedded Benzophenone

The amount of solid phase extractant used during the preconcentration step was varied from 0.1 to 0.7 g per litre of the aqueous solution. The preconcentrated thorium onto DCQ embedded benzophenone was determined by Arsenazo III method. The results are summarized in *Table 2.2* which points out that the preconcentration of thorium onto DCQ embedded benzophenone was maximum when the amount of solid phase extractant was $\geq$ 0.2 g. 0.5 g of DCQ embedded benzophenone was employed for the quantitative preconcentration of thorium in the remaining studies.

2.2.4 Effect of Time of Preconcentration

The time required for the preconcentration of thorium onto DCQ embedded benzophenone was varied between 5 - 60 min. The preconcentration and quantitation were carried out as described in section 2.2.1. The results are shown in *Table 2.3* from which it is clear that stirring for 15 min. was enough for the quantitative preconcentration of thorium onto DCQ embedded benzophenone. So, preconcentration time was optimized at 15 min for the subsequent experiments.

Table 2.2 Effect of amount of DCQ embedded benzophenone

Amount of 5,7-Dichloroquinoline-8-ol embedded benzophenone (g)	Enrichment of thorium (%)
0.1	93.1 ± 0.3
0.2	99.2 ±0.3
0.3	99.5 ± 0.3
0.5	99.5 ± 0.3
0.7	99.7 ± 0.3

Table 2.3 Effect of time of preconcentration

Time of preconcentration (min)	Enrichment of thorium (%)
5	83.2 ± 0.2
10	97 ± 0.3
15	>99.8
20	>99.8
30	>99.8
60	>99.8

2.2.5 Effect of Aqueous Phase Volume

The effect of aqueous phase volume on preconcentration of thorium onto DCQ embedded benzophenone was studied in the range 25 - 1000 ml following the procedure described in section 2.2.1 and enrichment of thorium was established by Arsenazo III method. The results obtained are tabulated in *Table 2.4.* Results indicate that the enrichment of thorium is quantitative upto the sample volume of 1000 ml and thus enabling an enrichment factor of ~200.

2.2.6 Retention Capacity of 5,7-dichloroquinoline-8-ol embedded Benzophenone

This experiment was carried out by taking a solution containing 500 μg of thorium, 0.2 g of DCQ embedded benzophenone and 10 ml of 1.0 mol l^{-1} of sodium acetate - acetic acid buffer and diluted to 30 ml in a 125 ml separating funnel. After shaking for 30 minutes, the above solution was filtered. The amount of thorium left out in the filtrate was determined by Arsenazo III procedure. The maximum amount of thorium preconcentrated (retention capacity**)** was found to be 1.10 mg per g of the solid phase extractant material.

Table 2.4 Effect of aqueous phase volume

Aqueous phase volume (ml)	**Enrichment of thorium (%)**
25	>99.0
250	>99.0
500	>99.0
1000	99.5 ± 0.2

2.2.7 Choice of Solvent

Various solvents were tested for the dissolution of the SPE. This material was found to be soluble in water miscible solvents like acetone, dimethyl formamide (DMF), acetonitrile and dimethyl sulphoxide (DMSO). 2.0 ml of acetone or DMSO were enough for the dissolution of 0.5 g of thorium enriched SPE. On the other hand, 2.5 ml of acetonitrile and 5.0 ml of DMF were required for the complete dissolution of thorium enriched SPE. So, acetone was chosen as the solvent in further studies.

2.3 CALIBRATION GRAPH AND PRECISION STUDIES

A series of solutions containing varying amounts of thorium (1-200 μg per litre of solution) were added by 5.0 ml of 1.0 mol l^{-1} of sodium acetate-acetic acid buffer (pH 6.2 ± 0.2) and 0.5 g DCQ embedded benzophenone. The resulting solutions were subjected to preconcentration. The thorium content in the residue was determined by Arsenazo III procedure after dissolution in 5.0 ml of acetone. The detection limit corresponding to three times the standard deviation of the blank was found to be 0.5 μg l^{-1}.

The calibration graph is linear passing through the origin. The linear equation with regression (R) is

A = 0.0014 + 0.01596 C,

R = 0.99959

where A is the peak absorbance and C is the concentration of thorium in µg l^{-1}.

The standard deviation (σ) of the developed method was established by carrying out 10 separate determinations using 20 µg of thorium by following the general procedure. Calculations were made using the formula

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

X_n is the result obtained for n^{th} determination,

$\overline{X}$ is the mean or average of n determinations.

The relative standard deviation or coefficient of variation in given by $\frac{\sigma \times 100}{\overline{X}}$. The results are shown in *Table 2.5*.

Table 2.5 Precision studies

S.No	**Absorbance**	**Thorium found (µg) X_n**	**($X_n - \overline{X}$)**	**($X_n - \overline{X}$)^2**
1	0.320	19.81	0.74	0.5476
2	0.298	18.45	-0.62	0.3844
3	0.299	18.51	-0.56	0.3136
4	0.304	18.82	-0.25	0.0625
5	0.304	18.82	-0.25	0.0625
6	0.298	18.45	-0.62	0.3844
7	0.310	19.19	0.12	0.0144
8	0.315	19.50	0.43	0.1849
9	0.320	19.81	0.74	0.5476
10	0.312	19.32	0.25	0.0625

$\overline{X}$ = 19.07 $\Sigma (X_n - \overline{X})^2 = 2.564$

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

σ = 0.5337

Relative Standard Deviation (R.S.D) = 2.80 %

2.4 EFFECT OF DIVERSE IONS

Sample solutions containing 20 μg of thorium and various amounts of different metal ions were subjected to the preconcentration and quantitation as described under section 2.2.1. The tolerance limits (error < 3%) are given in *Table 2.6.* From the table it is clear that none of the ions except uranium interfere in the DCQ embedded benzophenone preconcentration procedure in conjunction with spectrophotometric determination using Arsenazo III as reagent.

2.5 SPECTRAL STUDIES

2.5.1 UV-Visible Absorption Spectra

UV-visible absorption spectra of DCQ embedded benzophenone (A) and thorium bonded DCQ embedded benzophenone (B) against benzophenone were recorded and shown in *Fig. 2.3.* As seen from the figure, there is a pronounced maximum at 390 nm in the case of thorium bonded DCQ embedded benzophenone. It can be suggested that thorium is enriched by the formation of a complex with DCQ present in benzophenone.

2.5.2 IR Spectra

The stretching frequency of the (C-O) bond in the IR spectrum of DCQ embedded benzophenone occurs at 1149 cm^{-1}. But in the case of thorium bonded DCQ embedded benzophenone, υ_{C-O} was found to be at 1122.7 cm^{-1}. The shift of vibrational frequency to lower value gives a strong evidence of the bond formation between thorium and DCQ (present in benzophenone). The appearance of a new peak at 439.8 cm^{-1} (corresponding to Th-O stretching frequency) in the spectrum of thorium bonded DCQ embedded benzophenone (which is absent in the spectra of benzophenone and DCQ embedded benzophenone) is an evidence for thorium being covalently bonded to DCQ.

Table 2.6 Effect of electrolytes and metal ions

S.No.	**Interferent ion**	**Compound taken**	**Tolerance limit**
1	Na(I)	NaCl	100
2	K(I)	KCl	100
3	Li(I)	LiCl	100
4	Ca(II)	$Ca(OH)_2$	100
5	Mg(II)	$MgCl_2.6H_2O$	100
6	Sr(II)	$SrCl_2.6H_2O$	100
7	Cd(II)	$Cd(NO_3)_2.4H_2O$	100
8	Mn(II)	$MnSO_4.H_2O$	100
9	Ni(II)	$NiSO_4.7H_2O$	50
10	Co(II)	$CoSO_4.7H_2O$	50
11	Zn(II)	$ZnSO_4.7H_20$	50
12	Cu(II)	$CuSO_4.5H_2O$	100*
13	V(V)	NH_4VO_3	50
14	Mo(VI)	$(NH_4)_2MoO_4$	50
15	Al(III)	$Al(NO_3)_3.9H_2O$	100
16	Sb(III)	Sb_2O_3	100
17	Fe(III)	$FeCl_3$	100
18	Cr(VI)	$K_2Cr_2O_7$	100
19	La(III)	La_2O_3	100
20	Eu(II)	Eu_2O_3	100
21	Lu(III)	Lu_2O_3	100
22	I^-	KI	100
23	SCN^-	KSCN	100
24	NO_3^-	$NaNO_3$	100
25	SO_4^{2-}	Na_2SO_4	100
26	AsO_4^{3-}	$Na_2HAsO_4.7H_2O$	100

*No interference at 100 fold level in presence of thiourea

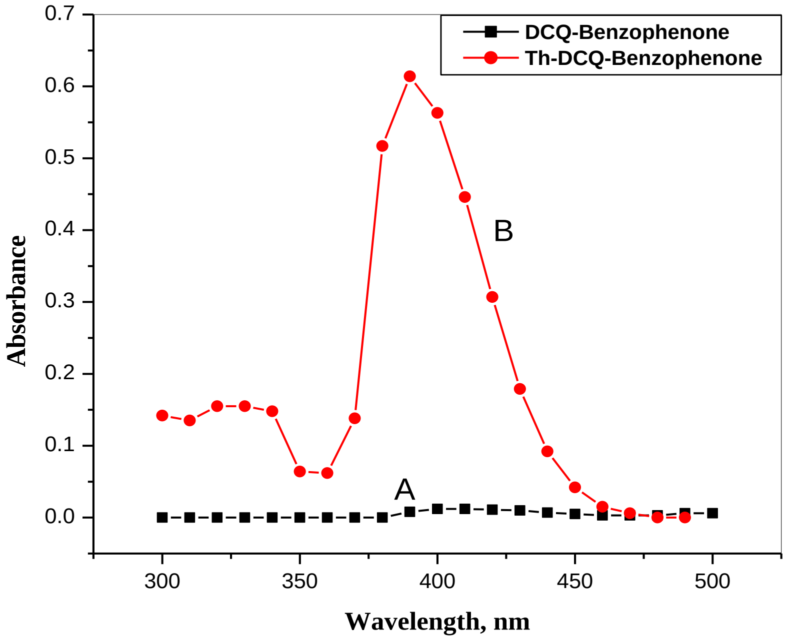

Fig.2.3 UV-visible absorption spectra of DCQ embedded benzophenone (A) and thorium bonded DCQ embedded benzophenone (B) against benzophenone

2.6 ANALYSIS OF RARE EARTH CHLORIDE SAMPLES

The developed preconcentration procedure in conjunction with spectrophotometry was tested for analyzing the rare earth chloride sample collected from Indian Rare Earths Limited (IRE), Alwaye. The sample was subjected to preconcentration by the developed procedure and the thorium content was subsequently established by Arsenazo III procedure. The results obtained are shown in *Table 2.7*. The amount of thorium in the IRE sample obtained by the developed method is comparable to the standard value obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Table 2.7 Analysis of rare earth chloride*

Sample	**Thorium found (μg ml^{-1})**			**Recovery (%)**
	Added	**Present method****	**Standard ICP-AES**	
Rare earth chloride	-	10.0 ± 0.1	9.95 ± 0.02	-
	5.0	15.1 ± 0.2	-	102.0
	10.0	20.0 ± 0.2	-	100.0

***Collected from Indian Rare Earths Limited, Alwaye.**
****Average of 3 determinations**

2.7 EXPERIMENTAL

2.7.1 Apparatus

A microcomputer based spectrophotometer consisting of Hitachi model 220 double beam spectrophotometer with an extended programme is used. A pair of matched 10 mm quartz cuvettes, which were periodically cleaned with $H_2SO_4 + HNO_3$ mixture and thoroughly washed with deionized water was used in this study. A LI-120 digital pH meter (ELICO, India) was used for adjusting the pH. FT-IR spectra were recorded using MAGNA IR-560 spectrometer (Nicolet, USA).

2.7.2 Chemicals

A stock solution of thorium(IV) was prepared by dissolving 0.6337 g of thorium nitrate hydrate (Fluka, Buchs, Switzerland) in deionized water and diluted to 250 ml after the addition of 5.0 ml of conc.HNO_3 to suppress hydrolysis. The solution was standardized by titrating with EDTA. Arsenazo III (0.1%, w/v) was prepared by dissolving 0.1 g of Arsenazo III (Fluka, Buchs, Switzerland) in 100 ml of deionized water. 1.0 mol l^{-1}sodium acetate-acetic acid buffer was used to maintain the pH of the aqueous phase. 5,7-dichloroquinoline-8-ol (Aldrich, Milwaukee, WI, USA) and benzophenone (E-Merck, India) were also used in the study. Acetone, hydrochloric acid and other reagents used were of analytical reagent grade.

2.7.3 Preparation of DCQ Embedded Benzophenone

5,7-dichloroquinoline-8-ol and benzophenone in the ratio 1:100 was dissolved in minimum amount of acetone. The acetone solution was poured as a fine stream into 500 ml of water with constant stirring at room temperature. The coprecipitated mixture was stirred for three hours and was allowed to settle for 10 min. Then it was filtered, washed with deionized water and dried in an oven at 40°C for several hours and then stored in an amber coloured bottle.

2.7.4 General Procedure for the Preconcentration and Determination of Thorium

A portion of the solution (1-200 μg) was diluted to 1.0 litre and the pH was adjusted to 6.2 ± 0.2 after the addition of 1.0 mol l^{-1} sodium acetate-acetic acid buffer and transferred to 2.0 litre beaker. DCQ (1.0%) embedded benzophenone (0.5 g) was added to the above solution and stirred for 15 minutes. The residue obtained after filtration was dissolved in 5.0 ml of acetone. 5.0 ml of 50% (v/v) hydrochloric acid and 2.5 ml of 0.1% Arsenazo III were added to the above solution and diluted to 25 ml with acetone. The absorbance of the thorium-Arsenazo III complex was measured at 660 nm.

2.7.5 Procedure for the Analysis of Rare Earth Chloride Samples

Suitable aliquots of Rare Earth chloride solution were subjected to the preconcentration and analysis procedure as described in section 2.7.4 after adjusting the pH to 6.2 ± 0.2. The thorium content of rare earth chloride sample was established by reference to the calibration curve prepared.

2.8 SUMMARY

Quinoline-8-ol and its halo derivatives embedded benzophenone were prepared by adding acetone solution of respective chelates and benzophenone as a fine stream into water. Thorium was found to be enriched quantitatively from 1.0 litre of aqueous solution in the pH range 6.0 - 6.5 only with 5,7-dichloroquinoline-8-ol embedded benzophenone. The filtered residue was subjected to direct analysis by Arsenazo III method after dissolution in acetone. Calibration graphs are linear over the range of 0 - 200 μg of thorium present in 1.0 litre of sample solution. Ten replicate determinations of 20 μg of thorium present in 1.0 litre of aqueous solution gave a mean absorbance of 0.320 with a relative standard deviation of 2.80%. The detection limit corresponding to three times the standard deviation of the blank was found to be 0.5 μg l^{-1}. The SPE procedure facilitates a 200 fold enrichment of thorium from dilute aqueous solution and do not require any separate elution step as it can be readily dissolved in acetone for subsequent quantitation by Arsenazo III method. The developed preconcentration procedure in conjunction with Arsenazo III method is highly selective as none of the extraneous cationic/anionic species (excepting uranium(VI)) including rare earth ions interfere at 100 fold levels. Furthermore, the developed method enables the reliable determination of trace amounts of thorium present in mixed rare earth chloride concentrate.

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CHAPTER 3

SPE PRECONCENTRATION AND DETERMINATION OF URANIUM(VI) USING DICYCLOHEXANO-18-CROWN-6 EMBEDDED BENZOPHENONE

Uranium is a naturally occurring element found at low levels in virtually all rocks, soils and water. Uranium is a potential energy resource. It provides 4% of world's renewable energy. Uranium is used in equal amounts, for nuclear weapons and nuclear power stations. Other uses of uranium are in medicine as radioisotopes. Uranium is used in helicopter and in air crafts as counter weights. In ceramic glazes small amount of uranium is added for color.

All isotopes and compounds of uranium are toxic and radioactive. Uranium and most of its byproducts including thorium, radium, radon and most of the radon daughters fall into the category of α-emitting substances. But uranium is considered more hazardous from the standpoint of chemical toxicity rather that its radioactivity. Uranium intake may lead to renal damages. Slight degenerative changes in lung histology were observed as a result of uranium exposure. The WHO, Health Canada and Australian drinking water guidelines fixed the maximum uranium concentration in drinking waters to be less than 9, 20 and 20 μg per litre .

Significant concentrations of uranium occur in some substances such as phosphate rock deposits and minerals such as lignite, and monazite sands. The concentration of uranium in phosphate rocks is in the range 0 - 0.12 mg per g. In sea water the uranium concentration is ~3.2 μg l^{-1}. So the recovery/removal of uranium has achieved considerable attention since long. The presence of huge levels of interfering matrix constituents, various preconcentration/or separation techniques are employed prior to its determination.

The crown ethers are an interesting class of complexing agents first synthesized by Pedersen in 1967 [1]. They are the macrocyclic ring systems containing at least one macrocyclic ring. In order to be a crown ether, a compound must be cyclic and must contain donor atoms such as oxygen. These oxygen atoms complex with the metal ions, even with large ions like group I ions that are not very good at forming complexes. The oxygen part of the molecule is puckered to give the crown arrangement, and the oxygen atoms with their lone pairs are nearly planar about the metal ions at the centre of the ring. The bonding of the metal ions to the polyether is largely electrostatic, and a close fit between the size of the metal ions and the size of the cavity in the centre of the polyether is essential. The size of the ring opening in the crown determines the size of the metal ions which may be accommodated [2]. The most versatile class of ion selective extractants is arguably the crown ethers, in which the macrocyclic cavity size, chelated ring size, macrocyclic rigidity and number and type of donor atoms may be tuned to provide a high degree of metal ion selectivity [3].

Pedersen [3] synthesized and investigated the unusual ability of crown ethers to form complexes with alkali metal salts. The stability of the crown ether-alkali metal complexes is at a maximum when there is good correspondence between the alkali metal ionic diameter and the size of the cavity in the crown ether. Thus, appropriately sized crown ether could be chosen to obtain selective extraction of particular cation of interest. The nature of substituent group on the macrocyclic ring is another important factor that influences the selectivity.

Solid phase extraction of lead using immobilized crown ether as an extractant coupled with flow injection FAAS determination (in-valve minicolumn preconcentration and separation) had been reported [4]. Yamini *et al* [5] proposed a simple method for the extraction and determination of ultra trace amounts of mercury ions using octadecyl bonded silica membrane disks modified with hexathia-18-crown-6 tetraone. Dibenzo-18-crown-6 modified octadecyl silica membrane disks were used for the selective separation of barium ion from alkali and alkaline earth metal ions [6]. Similar method had been applied for the solid phase extraction of strontium using decyl-18-crown-6 [7]. Thus, crown ether as modified SPEs are used for extraction of alkali metals and alkaline earth metals. Such a selectivity has often been rationalized a ‘hole size effect’ i.e., a correspondence between cation size and macrocyclic hole or cavity size. But, the relationship between cavity size and ionic diameter is not a determining factor in the complexation of UO_2^{2+} [8]. To our knowledge, there is no report for the solid phase extraction preconcentration of uranium using crown ether. Hence, in the present study, various solid phase extractants have been prepared using different crown ethers and benzophenone as solid support and used for the preconcentration of uranium(VI) from dilute aqueous solutions.

3.1 PRELIMINARY INVESTIGATIONS

In the preliminary studies, dibenzo-18-crown-6, dicyclohexano-18-crown-6, 12-crown-4, benzo-12-crown-4 and 15-crown-5 embedded benzophenone were employed to extract uranium(VI) from aqueous solutions. Crown ether embedded benzophenone materials were prepared by dissolving appropriate amounts of different crown ethers and benzophenone in minimum amount of acetone and precipitating out the mixture from deionized water by stirring for 2 hours. The material was filtered in a Buchner funnel by suction, washed and dried. To the solution containing 25 μg of uranium(VI) present in 0.5 litre aqueous phase, whose pH was adjusted around 6.5, crown ether embedded benzophenone (0.5 g, 1.0%) was added and stirred for 5 minutes. The enriched uranium(VI) was eluted with 5.0 ml of 1.0 mol l^{-1} hydrochloric acid. The uranium(VI) content was established by Arsenazo III procedure [9]. Among the different crown ethers used, only dicyclohexano-18-crown-6 (DC18crown6) embedded benzophenone could enrich uranium(VI) quantitatively from aqueous solutions (cf.*Table 3.1*). So, for the subsequent studies, dicyclohexano-18-crown-6 embedded benzophenone was used as the solid phase extractant for enriching uranium(VI). Various parameters that influence preconcentration and elution of uranium(VI) were optimized systematically and are described in following pages.

Table 3.1 Various crown ethers and percent enrichment

Crown ether (1.0%) in benzophenone	**Percent enrichment of uranium (VI)**
Dibenzo-18-crown-6	48.0 ± 0.2
Dicyclohexano-18-crown-6	>99.0
12-crown-4	52.0 ± 0.2
Benzo-12-crown-4	66.7 ± 0.2
15-crown-5	55.8 ± 0.3

3.2 OPTIMIZATION OF PRECONCENTRATION AND ELUTION PARAMETERS

3.2.1 Preconcentration of Uranium(VI) as a Function of pH

The influence of pH on the preconcentration of uranium(VI) onto dicyclohexano-18-crown-6 embedded benzophenone was studied by varying the pH in the range 2.0 - 9.0. In these studies, the pH of the solution containing 25 μg of uranium(VI) in 0.5 litre of deionized water was adjusted with Dil.HCl or NaOH. Dicyclohexano-18-crown-6 embedded benzophenone (0.5 g) was added to this solution and stirred for 5 minutes. After filtration, the enriched uranyl ion was eluted by stirring with 5.0 ml of 1.0 mol l^{-1} of HCl. 5.0 ml of 1:1 HCl and 2.5 ml of 0.1% Arsenazo III were added to it and diluted to 25 ml with deionized water. The absorbance of the uranium(VI)-Arsenazo III complex was measured at 656 nm. Blanks were also prepared for each pH value. The results obtained are shown in *Fig.3.1*. The preconcentration of uranium(VI) onto dicyclohexano-18-crown-6 embedded benzophenone was quantitative in the pH range 6.0 - 7.0. So, in the subsequent work, the pH was adjusted to 6.5 ± 0.5 after the addition of 10 ml of 1.0 mol l^{-1} ammonium acetate buffer.

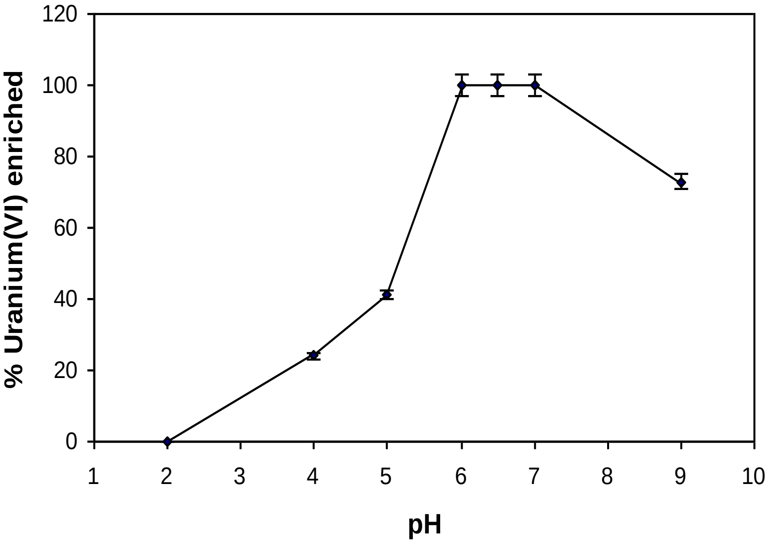

Fig.3.1 Effect of pH

3.2.2 Effect of Dicyclohexano-18-crown-6 Concentration in Benzophenone

The concentration of dicyclohexano-18-crown-6 in benzophenone was varied from 0.1 to 2.0%. The solid phase extraction and the determination of uranium(VI) were carried out as described in section 3.2.1. *Fig.3.2* shows that the preconcentration of uranium(VI) was quantitative when the crown ether concentration in benzophenone is $\geq$ 1.0%. For the subsequent studies, 1.0% dicyclohexano-18-crown-6 embedded benzophenone was used.

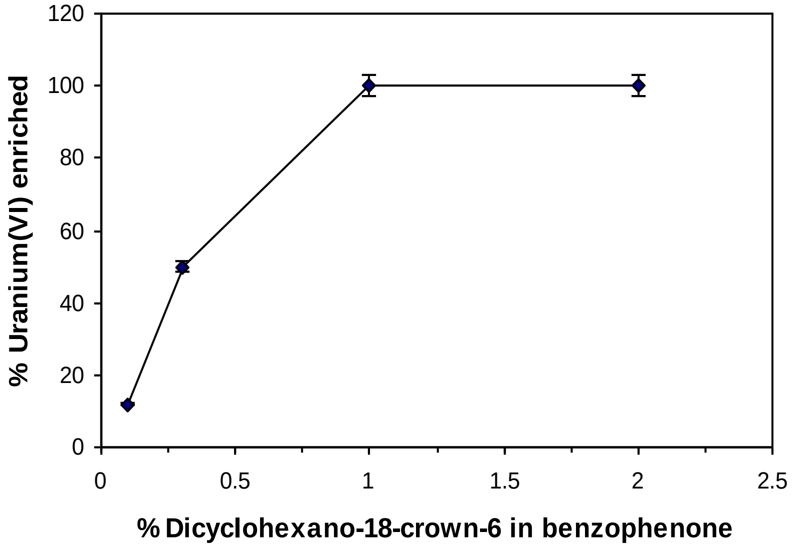

Fig. 3.2 Effect of Dicyclohexano-18-crown-6 concentration in benzophenone

3.2.3 Effect of Preconcentration Time

The effect of preconcentration time on the enrichment of uranium(VI) from aqueous solutions was studied in the range 5 - 30 min. The enriched uranium(VI) was quantified spectrophotometrically. The results are summarized in *Table 3.2* which indicates as low as 5 min of stirring time was enough for the quantitative preconcentration of uranium(VI) onto dicyclohexano-18-crown-6 embedded benzophenone. So, the time of preconcentration was fixed at 5 min.

Table 3.2 Effect of preconcentration time

Preconcentration time (min)	**Percent enrichment of uranium(VI)**
5	>99.0
10	>99.0
30	>99.0

3.2.4 Effect of Elution Time

The time required to desorb the uranium(VI) preconcentrated onto dicyclohexano-18-crown-6 embedded benzophenone was varied between 5 to 30 min. The results are given in T*able 3.3*. Elution for 5 min time was enough for the quantitative stripping of uranium(VI) that was previously preconcentrated with dicyclohexano-18-crown-6 embedded benzophenone. So, 5 min of elution was used for the desorption of uranium(VI) from the solid phase extractant.

Table 3.3 Effect of elution time

Elution time (min)	Percent enrichment of uranium(VI)
5	>99.0
10	>99.0
20	>99.0
30	>99.0

3.2.5 Effect of Volume of the Eluting Agent

It is very important that the analyte should be efficiently desorbed in a small volume so that a higher enrichment factor is obtained. The volume of HCl used for the elution of uranium(VI) from dicyclohexano-18-crown-6 embedded benzophenone was studied in the range 5-20 ml. The results are shown in *Table 3.4*. It is clear that a minimum of 5.0 ml of HCl is enough for the elution of uranium(VI) from the solid phase extractant.

Table 3.4 Effect of volume of the Eluting agent

Volume of eluting agent (ml)	Percent enrichment of uranium(VI)
5	>99.0
10	>99.0
20	>99.0

3.2.6 Effect of Concentration of the Eluting Agent

The concentration of hydrochloric acid used for the elution of the enriched uranium (VI) (25 µg) from dicyclohexano-18-crown-6 embedded benzophenone was varied in the range of 0.1 to 1.5 mol l^{-1}. The results are tabulated in *Table 3.5.* It can be concluded that 5.0 ml of 1.0 mol l^{-1} HCl is needed for the quantitative elution.

Table 3.5 Effect of concentration of the eluting agent

Conc. of the eluting agent (mol l^{-1})	**Percent enrichment of uranium(VI)**
0.1	55 ± 0.2
0.5	80 ± 0.2
1.0	$\geq$99.0
1.5	$\geq$99.0

3.2.7 Effect of Sample Volume

The preconcentration of uranium(VI) onto dicyclohexano-18-crown-6 embedded benzophenone was studied by varying the volume of the sample in the range of 25-1000 ml and keeping the total amount of loaded uranium(VI) at 25 µg under optimum conditions. The quantitation was carried out as described in section 3.2.1. The results obtained are shown in *Table 3.6. Q*uantitative preconcentration of uranium(VI) was observed upto 500 ml and thus enabling an enrichment factor of ~100.

Table 3.6 Effect of sample volume

Aqueous phase volume (ml)	**Percent enrichment of uranium(VI)**
25	>99.0
250	>99.0
500	>99.0
1000	97.5 ± 0.2

3.2.8 Retention Capacity of Dicyclohexano-18-crown-6 Embedded Benzophenone

To determine the retention capacity (maximum amount of uranium(VI) preconcentrated per g of the solid phase extractant) of the sorbent material, 0.2 g of dicyclohexano-18-crown-6 embedded benzophenone was saturated with uranium(VI) in batch mode under optimum conditions. The amount of uranium(VI) needed for saturation was determined spectrophotometrically after eluting it with a minimum volume of 1.0 mol l^{-1} HCl as mentioned in section 3.2.1. The maximum amount of uranium(VI) preconcentrated was found to be 2.42 mg per g of the solid phase extractant material.

3.3 STATISTICAL AND CALIBRATION PARAMETERS

The calibration curve was linear over the concentration range 0-100 μg of uranium(VI) present in 0.5 litre of solution. The detection limit corresponding to 3 times the standard deviation of the blank was found to be 2.0 μg l^{-1}. The linear equation with regression is as follows

$A = 0.0463\ C + 0.0015$

$R = 0.9993$

where A is the peak absorbance and C is the concentration in μg l^{-1}.

The standard deviation of the developed method was established by carrying out 10 separate determinations of 25 μg of uranium by the preconcentration and determination method as described in section 3.2.1 (cf.*Table 3.7*). All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

3.4 TOLERANCE OF ELECTROLYTES AND DIVERSE IONS

Sample solutions containing 25 μg of uranium(VI) and various amounts of different electrolytes and other cations were preconcentrated and determined under optimal conditions. The tolerance limits (error < 3%) are given in *Table 3.8.* From the table it is clear that none of the species tested interfere in the preconcentration procedure developed in conjunction with the spectrophotometric procedure using Arsenazo III as reagent. On the other hand, thorium interferes even at equal concentrations and has to be separated while analyzing thorium containing samples.

Table 3.7 Precision studies

S.No	**Absorbance**	**Uranium(VI) found (µg)** X_n	$X_n - \overline{X}$	$(X_n - \overline{X})^2$
1	0.043	23.89	-1.22	1.4884
2	0. 045	25.00	-0.11	0.0121
3	0. 047	26.11	1.00	1.0000
4	0. 045	25.00	-0.11	0.0121
5	0. 046	25.55	0.44	0.1936
6	0. 043	23.89	-1.22	1.4884
7	0. 046	25.55	0.44	0.1936
8	0. 047	26.11	1.00	1.0000
9	0. 045	25.00	-0.11	0.0121
10	0. 045	25.00	-0.11	0.0121

$\overline{X} = 25.11$ $\Sigma (X_n - \overline{X})^2 = 5.4124$

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

$\sigma = 0.7754$
Relative standard deviation = 3.088 %

Table 3.8 Effect of neutral electrolytes/diverse ions

Electrolyte/ion	**Remarks**
NaCl, $NaNO_3$, Na_2SO_4, KBr, $CaCl_2$ and $Mg(NO_3)_2$	No interference at 0.1 mol l^{-1} level
Li, Ca, Mg, Sr, Co, Ni, Mn, Zn, Cu, Pb, Cd, Fe(III), Bi(III), Al(III), Zr(IV), V(V) and Sb(V)	No interference at 100 fold level
La(III), Mo(VI) and As(V)	No interference at 100 fold level in presence of 1 g of NaF

3.5 SPECTRAL STUDIES

3.5.1 IR spectra:

The IR spectra of uranyl nitrate, benzophenone, dicyclohexano-18-crown-6 embedded benzophenone and uranyl bonded dicyclohexano-18-crown-6 embedded benzophenone were recorded and compared. The broad band centered around 950 cm^{-1} is assigned to $\nu_{U=0}$ in the spectrum of uranyl nitrate. This band is very well present in the spectrum of uranium bonded dicyclohexano-18-crown-6 embedded benzophenone. Again, there is a new peak in this case at 428 cm^{-1} (which corresponds to the UO_2^{2+}- O frequency) and is not there in the spectra of benzophenone or dicyclohexano-18-crown-6 embedded benzophenone. This subtle difference provides a definite evidence that uranyl ion forms complex with dicyclohexano-18-crown-6 prior to enrichment [10].

3.5.2 UV-Visible spectra

Fig.3.3 shows the UV-visible absorption spectrum of uranium(VI) adsorbed dicyclohexano-18-crown-6 embedded benzophenone against dicyclohexano-18-crown-6 embedded benzophenone. As seen from figure, there is a clear absorption maximum at 420 nm confirming the observation deduced from IR spectra i.e., uranium(VI) is bonded chemically during the enrichment by dicyclohexano-18-crown-6 embedded benzophenone.

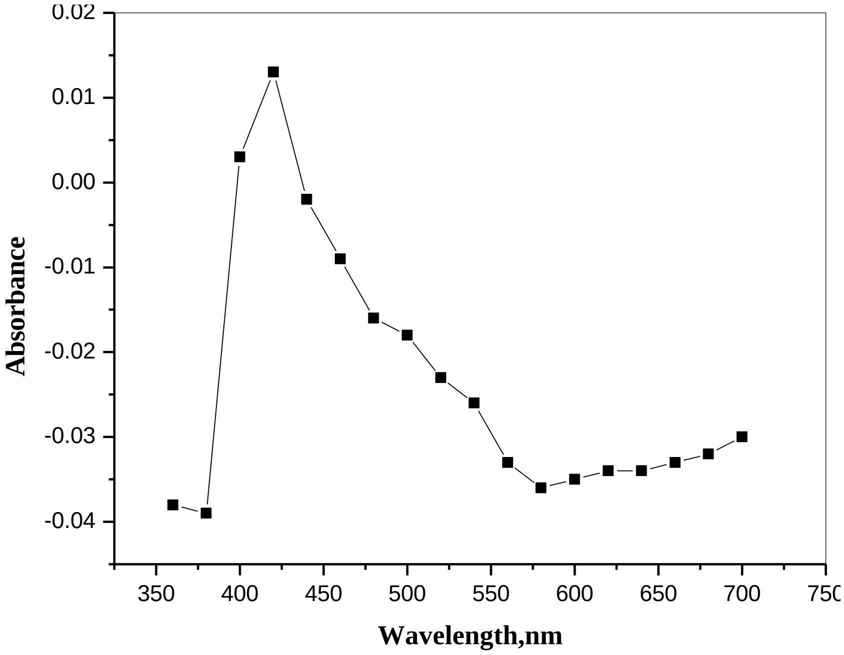

Fig. 3.3 UV-visible absorption spectrum of uranium(VI) adsorbed dicyclohexano-18-crown-6 embedded benzophenone against dicyclohexano-18-crown-6 embedded benzophenone.

3.6 APPLICATIONS

3.6.1 Analysis of Marine Sediment Reference Material (MESS-3)

The authenticity of the present method was ascertained by analyzing the marine sediment reference material (MESS-3) supplied by National Research Council, Canada. The uranium(VI) present in the sample was preconcentrated by the developed procedure and was subsequently determined by Arsenazo III procedure. The results are given in *Table 3.9*. Further, known amounts of uranium(VI) were added to the certified reference material before dissolution procedure. The recoveries were found to be good (cf.*Table 3.9*) indicating the suitability of the developed procedure for the determination of uranium(VI) in sediment samples.

3.6.2 Analysis of Soil and Sediment Samples

Soil samples from two stations in Trivandrum and sediments of Karamana River, Trivandrum and Arabian Sea (near Trivandrum coast) were collected and mineralized by following the procedure described in "Experimental". These samples were subjected to preconcentration using dicyclohexano-18-crown-6 embedded benzophenone and the uranium(VI) content was established by Arsenazo III procedure. The results obtained by the present method and that by Inductively coupled mass spectrometry (ICP-MS) are shown in *Table 3.10*, which indicate that the developed method can reliably be used for the analysis of soil and sediment samples

Table 3.9 Analysis of certified reference material (MESS-3) (supplied by National Research Council, Canada)

S. No.	**Uranium added (μg g^{-1})**	**Uranium(vi) found (μg g^{-1})**		**Recovery (%)**
		Present method*	**Certified**	
1	None	4.2 ± 0.1	4**	-
2	4.0	8.1 ± 0.2		97.5
3	8.0	12.2 ± 0.2		100

*Average of 3 determinations
**Information value

Table 3.10 Analysis of soil and sediment samples

S.No.	**Description of the sample**	**Uranium (μg g^{-1})**			**Recovery (%)**
		Added	**Found**		
			Present method*	**ICP-MS**	
1	Soil sample from station I	-	8.00 ± 0.2	7.96± 0.01	-
		8.00	16.00 ± 0.2		100.0
		16.00	24.10 ± 0.3		100.6
2	Soil sample from station II	-	7.00 ± 0.2	6.96± 0.01	-
		6.00	13.15 ± 0.2		101.7
		12.00	19.00 ± 0.3		100.0
3	Karamana river sediment, Trivandrum	-	5.00 ± 0.2	4.96± 0.01	-
		5.00	9.90 ± 0.2		98.0
		10.00	15.00 ± 0.2		100.0
4	Marine sediment from Arabian sea	-	8.10 ± 0.2	4.96± 0.01	-
		8.00	16.0 ± 0.2		98.0
		16.00	24.00 ± 0.2		100.0

*****Average of 3 determinations

3.7 EXPERIMENTAL

3.7.1 Apparatus

Absorbances were measured using Hitachi-220 microprocessor controlled double beam spectrophotometer (Hitachi, Japan). LI-120 digital pH meter

(ELICO, India) was used for pH measurements. FT-IR spectra (4000-400 cm^{-1}) were recorded using MAGNA IR-560 spectrometer (Nicolet, USA).Varian ultramass 700 Inductively coupled plasma mass spectrometer (Varian, USA) was used for analysis of soil and sediment samples.

3.7.2 Reagents

1) Uranium(VI) solution (1000 $\mu g\ ml^{-1}$): A stock solution of uranium(VI) was prepared by dissolving 0.5274 g of $UO_2(NO_3)_2.6H_2O$ (Loba Chemie, India) in deionized water (250 ml). conc.HNO_3 (~5 ml) was added to suppress hydrolysis. The solution was standardized by titrating with EDTA.

2) Arsenazo III (0.1% w/v): Arsenazo III reagent was prepared by dissolving 0.1 g of Arsenazo III (Fluka, Buchs, Switzerland) in 100 ml of deionized water.

3) Ammonium acetate buffer (1.0 mol l^{-1}) was prepared to maintain the pH of the aqueous phase at 6.5.

Crown ethers (Aldrich, USA) and benzophenone (E-Merck, India) were also used.

3.7.3 Preparation of Dicyclohexano-18-crown-6 Embedded Benzophenone

Dicyclohexano-18-crown-6 and benzophenone in the ratio 1:100 were dissolved in minimum amount of acetone. This acetone solution was poured as a fine stream into 500 ml of deionized water with constant stirring at room temperature. The co-precipitated mixture was stirred for 3 hour and was allowed to settle for 10 min. Then it was filtered, washed with deionized water and dried in an oven at $40^{o}C$ for several hours and then stored in an amber coloured bottle and kept in a desiccator.

3.7.4 General Procedure

A portion of solution of uranium(VI) (2-100 μg) was diluted to 0.5 litre and the pH was adjusted to 6.5 ± 0.5 after the addition of ammonium acetate buffer and transferred to 1.0 litre beaker. 0.5 g of dicyclohexano-18-crown-6 embedded benzophenone was added to the above solution and stirred for 5 min.

After filtration, the adsorbed uranyl ion was eluted by stirring with 5.0 ml of 1.0 mol l^{-1} of HCl. The determination of uranium(VI) was carried out spectrophotometrically after the addition of 5.0 ml of 1:1 HCl and 2.5 ml of 0.1% Arsenazo III in a total volume of 25 ml. The absorbance of the uranium(VI)-Arsenazo III complex was measured at 656 nm.

3.7.5 Procedure for Analysis of Marine Sediment Reference Material (MESS-3) and Soils and Sediments

About 0.5 g of the sample was treated with 5.0 ml of HF and 1.0 ml of Conc. H_2SO_4 at 150^oC on a hot plate. The process was repeated thrice. The residue is cooled and fused with 2.0 g of $KHSO_4$ at 800^oC in an electric bunsen for 30 min. The melt is then cooled, dissolved in 50 ml of water, and diluted to 100 ml. Preconcentration of uranium(VI) onto dicyclohexano-18-crown-6 embedded benzophenone and determination by Arsenazo III were carried out as described in general procedure given above after addition of 1.0 g each of sodium fluoride and thiourea.

3.8 SUMMARY

Solid phase extractants were prepared using benzophenone embedded with different crown ethers. Among the various crown ethers used, only dicyclohexano-18-crown-6 could quantitatively enrich uranium(VI). After eluting with 5.0 ml of 1.0 mol l^{-1} HCl, the enriched uranium(VI) was subjected to spectrophotometric determination by following Arsenazo III procedure. Calibration graphs are linear over the range 0-100 µg of uranium(VI) present in 0.5 litre of the sample solution. Ten replicate determinations of 25 µg of uranium(VI) present in 0.5 litre of aqueous solution gave an absorbance of 0.045 with a RSD of 3.088%. The detection limit corresponding to 3 times the standard deviation of the blank was found to be 2.0 µg l^{-1} .The SPE procedure facilitates a 100 fold enrichment of uranium(VI) from dilute aqueous solutions. The developed preconcentration procedure in conjunction with Arsenazo III method allows the selective determination of uranium(VI) in presence of various neutral electrolytes and a number of cationic and anionic species. The accuracy of the developed preconcentration procedure was good as the uranium(VI) content of the certified reference material determined by the present method matches with the certified value and also gave quantitative recoveries. In addition, the developed procedure enables a reliable determination of uranium(VI) in soils, river sediments and marine sediments .The uranium content of these samples obtained by the present method is in well agreement with ICP-MS values.

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CHAPTER 4

1-(2-PYRIDYLAZO)-2-NAPHTHOL(PAN) EMBEDDED BENZOPHENONE/NAPHTHALENE AS SOLID PHASE EXTRACTANT FOR THE PRECONCENTRATION OF URANIUM(VI)

Naphthols form stable complexes with various inorganics. By proper control of pH of the solution or the use of masking/sequestering agents, a greater degree of selectivity is usually achieved. So naphthols, in addition to their use as spectrophotometric reagents [1-3] have been widely used as chelating and/or sorbent extraction agents in analytical chemistry. The naphthol reagents include 1-(2-thiazolylazo)-2-naphthol (TAN), 1-(2-pyridylazo)-2-napthol (PAN) and 1-nitroso-2-naphthol.

As a versatile chelating agent, 1-(2-pyridylazo)-2-naphthol (PAN) can react with several metal ions to form water insoluble coloured chelate complexes and has been widely employed in liquid-liquid extractive separation and extractive photometric analysis [4-6]. Hafez *et al* [7] studied the use of chemically modified chloromethylated polystyrene-PAN for the preconcentration and separation of total mercury. Lead, cadmium, copper and zinc [8] were determined by AAS in high salt content samples after simultaneous separation on polyethylene powder impregnated with PAN. Taher [9] developed a method for the determination of indium after column preconcentration of indium- PAN complex onto naphthalene. Bhagavathy *et al* [10] for the first time developed a SPE procedure for the multielement preconcentration of yttrium and fourteen lanthanides using PAN modified naphthalene. Ponce *et al* [11] reported the preconcentration of rare earths using silica gel loaded with PAN. A cloud point extraction preconcentration of uranium was performed with PAN in presence of non-ionic surfactant Triton X-114 [12]. Vacha and Sommer [13] reported the sorption of urnayl ions on columns with the macroporous sorbent Amberlite XAD-4 modified with PAN. The preconcentration and removal of uranyl ion from aqueous solutions were achieved by using micellar enhanced ultrafiltration with PAN and Triton X-100 [14].

However, a thorough literature survey indicated that there is no report on SPE preconcentration of actinides and in particular for uranium using benzophenone/naphthalene as solid phase extractant. In the present study, uranium(VI) is selectively preconcentrated using PAN embedded benzophenone/naphthalene.

4.1 PRELIMINARY STUDIES

It was found that 1-(2-pyridylazo)-2-naphthol (PAN) embedded benzophenone/naphthalene can extract uranium(VI) from weakly alkaline solutions. PAN embedded benzophenone/naphthalene (solid phase extractant) was prepared by dissolving 1.0 g of PAN and 10 g of benzophenone/naphthalene in minimum amount of acetone and precipitating it out from deionized water by stirring for 3 hours. The resulting material was filtered, washed and dried. The pH of the solution containing 25 µg of uranium(VI) present in 1.0 litre aqueous phase was adjusted to 10. 0.5 g of PAN embedded benzophenone/naphthalene was added to the above solution and stirred for 10 minutes. The residue obtained after filtration was dissolved in 2.5 ml of acetone. 5.0 ml of 50% (v/v) hydrochloric acid and 2.5 ml of 0.1% Arsenazo III were added to the above solution and diluted to 25 ml with acetone. The absorbance of the uranium(VI)-Arsenazo III complex was measured at 656 nm. It was observed that uranium(VI) was quantitatively enriched with PAN embedded benzophenone/naphthalene. Various parameters like pH, aqueous phase volume, amount of solid phase extractant etc were optimized systematically.

4.2 OPTIMIZATION OF ANALYTICAL PARAMETERS

4.2.1 Effect of pH

The pH of the solution containing 25 µg of uranium(VI) present in 1.0 litre of deionized water was adjusted with Dil.HCl or NaOH in the range 8.0 to 11.5. 0.5 g of PAN embedded benzophenone/naphthalene was added to this solution and stirred for 10 minutes. The residue obtained after filtration was dissolved in 2.5 ml of acetone. 5.0 ml of 50% (v/v) hydrochloric acid and 2.5 ml of 0.1% Arsenazo III were added to the above solution and diluted to 25 ml with acetone. The absorbance of the uranium(VI)-Arsenazo III complex was measured at 656 nm. Blank determinations were also carried out for each pH value. The results obtained are shown in *Fig.4.1*. The preconcentration of uranium(VI) onto the developed solid phase extractant was quantitative in the pH range 10.5-11.0. In the subsequent work, the pH was adjusted to 10.7 ± 0.2 after adding 10 ml of 1.0 mol l^{-1} NH_3-NH_4Cl buffer.

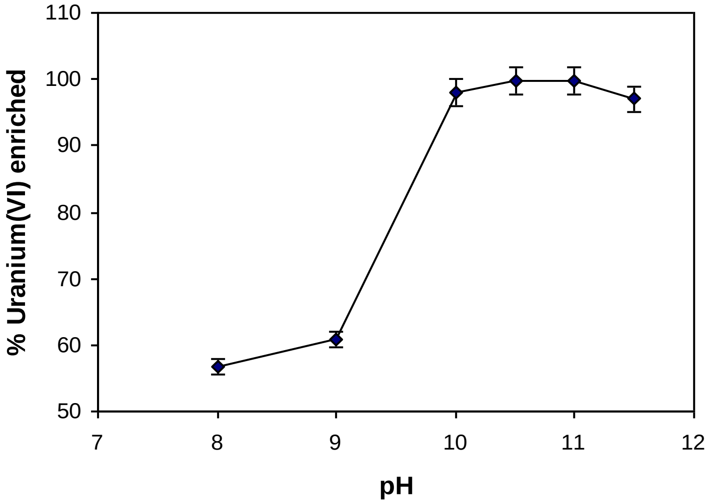

Fig. 4.1 Effect of pH

4.2.2 Effect of PAN Concentration in Benzophenone/Naphthalene

The concentration of PAN in benzophenone/naphthalene was varied in the range 1 - 10%. The preconcentration and determination were carried out as described earlier. The results are depicted in *Fig.4.2*. The preconcentration of uranium(VI) onto PAN embedded benzophenone/ naphthalene was quantitative when the concentration of PAN in benzophenone/naphthalene was $\geq$ 8%. Hence, the concentration of PAN in benzophenone/naphthalene was maintained as ~10% in subsequent studies.

4.2.3 Effect of Amount of PAN embedded Benzophenone / Naphthalene

The amount of solid phase extractant for the preconcentration procedure was varied from 0.1 to 1.0 g. The enrichment of uranium(VI0 was determined by the general procedure. The results are shown in *Table 4.1*. Results point out that the preconcentration of uranium(VI) onto PAN embedded benzophenone/ naphthalene was quantitative when the amount of SPE was $\geq$ 0.5 g. Hence for the subsequent work, 0.5 g PAN embedded benzophenone/naphthalene was used for preconcentration of uranium(VI).

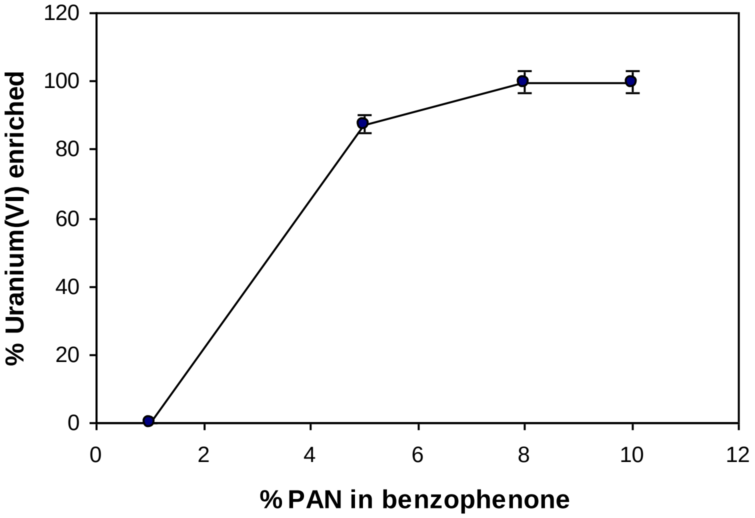

Fig. 4.2 Effect of PAN concentration in benzophenone/napthalene

Table 4.1 Effect of amount of PAN embedded benzophenone/naphthalene

Amount of PAN embedded benzophenone / naphthalene (g)	Percent enrichment of uranium(VI)
0.1	0
0.2	30.0 ± 0.1
0.3	62.0 ± 0.2
0.5	>99.0
0.7	>99.0
1.0	>99.0

4.2.4 Effect of time of preconcentration

The percent enrichment of uranium(VI) was found to be varying as the time of stirring during preconcentration was varied between 5 to 45 minutes. The enrichment of uranium(VI) corresponding to different time of preconcentration are summarized in *Table 4.2*. The preconcentration of uranium(VI) was quantitative even with 10 min and so preconcentration time was optimized at 10 minutes.

Table 4.2 Effect of time of preconcentration

Time of stirring (min)	Percent enrichment of uranium(VI)
5	28.0 ± 0.1
10	>99.0
15	>99.0
30	>99.0
45	>99.0

4.2.5 Effect of Sample Volume

The sample volume was varied in the range 25-1000 ml. The preconcentration and quantitation were carried out as described in section 4.2.1. and the results are summarized in *Table 4.3*. Quantitative preconcentration of uranium(VI) was observed upto 1000 ml and thereby enabling an enrichment factor of 400.

Table 4.3 Effect of aqueous phase volume

Sample volume (ml)	Percent enrichment of uranium(VI)
25	>99.0
50	>99.0
100	>99.0
500	>99.0
1000	98.5 ± 0.2

4.2.6 Retention Capacity of the Solid Phase Extractant

0.2 g of PAN embedded benzophenone was added to a solution containing 1.0 mg of uranium(VI) and 10 ml of 1.0 mol l^{-1} NH_3-NH_4Cl buffer (pH 10.7). The above solution was transferred to a 125 ml separating funnel. After shaking for 30 min the solution was filtered. The amount of uranium(VI) left out in the filtrate was determined spectrophotometrically by Arsenazo III procedure. The maximum amount of uranium(VI) preconcentrated by using PAN embedded benzophenone was found to be 2.388 mg per g of the solid phase extractant material which is higher than 5,7-dichloroquinoline-8-ol embedded naphthalene (1.881 mg per g) of the SPE [15].

4.2.7 Choice of Solvent

Various solvents like acetone, dimethyl formamide (DMF), acetonitrile, dimethyl sulphoxide (DMSO) were tested for the dissolution of SPE after enrichment of uranium(VI). 2.0 and 4.0 ml of acetone or DMF was enough for dissolution of 1.0 g of SPE containing benzophenone and naphthalene respectively. 3.3 ml of DMSO and 4.2 ml of acetonitrile were required to dissolve 1.0 g of SPE containing benzophenone. However, 5.0 and 10 ml of acetonitrile and DMSO were required for the dissolution of 1.0 g of SPE containing naphthalene. So, PAN embedded benzophenone was preferred over PAN embedded naphthalene and 2.5 ml of acetone was used for dissolution of the uranium(VI) enriched SPE.

4.3 CALIBRATION GRAPH

Calibration graph was plotted by varying uranium(VI) concentration in the range 2-200 µg. To each of these solutions, 10 ml of 1.0 mol l^{-1} NH_3-NH_4Cl buffer and 0.5 g PAN embedded benzophenone were added and made upto 1000 ml and the resulting solution was stirred for 10 min. Uranium(VI) content in the residue was determined by Arsenazo III procedure after dissolution of uranium(VI) enriched SPE in 2.5 ml of acetone.

The linear equation with regression is $A= 0.00094 + 0.0045C$

where A is the peak absorbance and C is the concentration. The regression coefficient is 0.99992. The detection limit corresponding to 3 times the standard deviation of the blank was found to be 2.0 µg l^{-1}.

4.4 PRECISION STUDIES

The standard deviation of the developed method was established by carrying out ten separate determinations using 25 µg of uranium(VI) (see *Table 4.4*). Calculation was made using the formula given in chapter 2.

Table 4.4 Precision studies

S.No	**Absorbance**	**Uranium(VI) found (µg) X_n**	**$(X_n - \overline{X})$**	**$(X_n - \overline{X})^2$**
1	0.044	24.44	-0.50	0.2500
2	0.045	25.00	0.06	0.0036
3	0.046	25.56	0.62	0.3874
4	0.045	25.00	1.06	0.0036
5	0.046	25.56	0.62	0.3874
6	0.047	26.11	1.17	1.3689
7	0.043	23.89	-1.05	1.1025
8	0.044	24.44	-0.50	0.2500
9	0.044	24.44	-0.50	0.2500
10	0.045	25.00	0.06	0.0036

$\overline{X} = 24.94$ $\Sigma\,(X_n - \overline{X})^2 = 4.007$

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

$\sigma = 0.6674$

Relative standard deviation = 2.68 %

4.5 TOLERANCE LIMITS OF CATIONS

Sample solutions containing 25 µg of uranium(VI) and various amounts of different metal ions (added individually) were examined by the SPE procedure described in section 4.2.1. Selective enrichment of 25 µg l^{-1} of uranium(VI) was possible in presence of 100 fold amounts of Li, Ca, Mg, Sr, Fe(II), Ni(II), Fe(III). Bi(III), Te(IV), As(V) and Sb(V). Further, 100 fold amounts of Cu(II), Cd(II) and Zn(II) in presence of 1.0 g of thiourea and La(III),V(V) and Mo(VI) (in presence of 2.0 g of NaF) do not affect the preconcentrative separation of 25 µg l^{-1} of uranium (VI).

4.6 SPECTRAL STUDIES

The UV-visible absorption spectra of benzophenone (A), PAN embedded benzophenone (against acetone) (B) and uranium(VI) bonded PAN embedded benzophenone (against PAN embedded benzophenone) (C) are given in *Fig.4.3*. There is a clear cut absorption maximum at 580 nm in the third case which indicates uranium(VI) is bonded chemically during enrichment of uranium(VI) by PAN embedded benzophenone.

IR spectra of benzophenone, PAN embedded benzophenone and uranium(VI) bonded PAN embedded benzophenone were recorded. The presence of a band at 438 cm^{-1} in the spectrum of uranium(VI) bonded PAN embedded benzophenone(which is absent in the other cases) indicates that uranium(VI) is enriched to PAN embedded benzophenone.

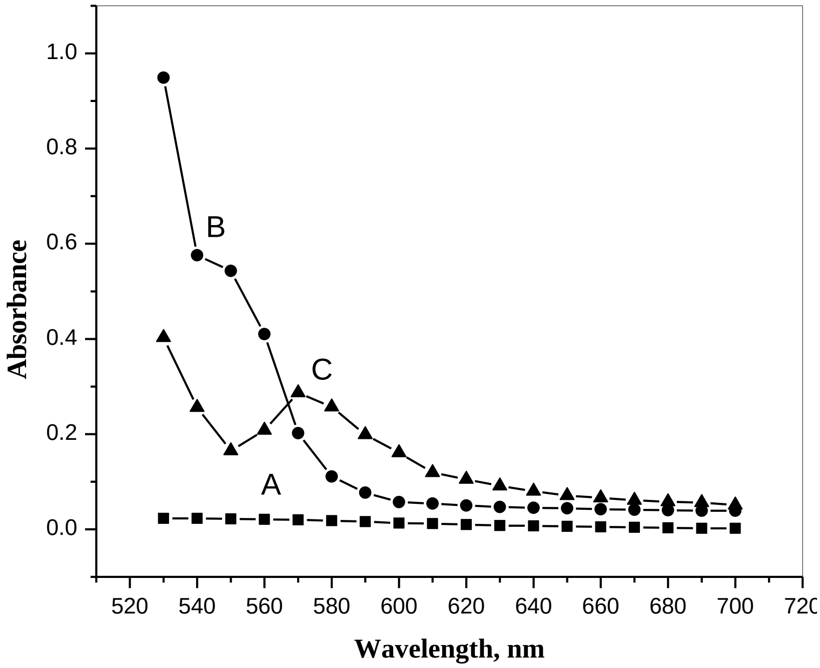

***Fig.4.3** UV-visible absorption spectra of benzophenone (A) and PAN embedded benzophenone (against acetone) (B) and uranium(VI) bonded PAN embedded benzophenone (against PAN embedded benzophenone) (C)*

4.7 APPLICATIONS

4.7.1 Analysis of the Marine Sediment Reference Material (MESS-3)

The accuracy of the developed preconcentration procedure was established by analyzing marine sediment reference material (MESS- 3) supplied by National Research Council, Canada. The sediment sample was mineralized by following the dissolution procedure described in "Experimental". The uranium(VI) present in the sample was preconcentrated with PAN embedded benzophenone and determined by Arsenazo III procedure. The results obtained are shown in *Table 4.5.* The amount of uranium(VI) established by the developed procedure is comparable to the information value given by NRC, Canada. Further, known amounts of uranium(VI) were added to certified reference material before dissolution step. The recoveries (see *Table 4.5*) were found to be good indicating that developed procedure is suitable for the determination of uranium(VI) in sediment samples.

Table 4.5 Analysis of certified reference material (MESS-3)

S.No.	Uranium added ($\mu g\ g^{-1}$)	Uranium(VI) found ($\mu g\ g^{-1}$)		Recovery (%)
		Present method*	Certified value	
1	**-**	**4.1± 0.1**	**(4)****	**-**
2	**5.0**	**9.1± 0.1**		**100**
3	**10.0**	**14.2 ± 0.1**		**102**

***average of 3 determinations**
****Information value**

4.7.2 Analysis of Soil and Sediment Samples

Soil samples collected from 2 stations in Trivandrum and sediment collected from Karamana river and Arabian sea were brought into solution by fusing with $KHSO_4$ after fuming with HF and H_2SO_4 to remove silica. The preconcentration and determination of uranium(VI) were carried out by following the procedure described section 4.2.1. The results obtained were compared with the results obtained by Inductively coupled plasma mass spectrometry (ICP-MS) (see *Table 4.6*). The good agreement between the two indicate that the developed method can be reliably used for the analysis of uranium(VI) in soil and sediment samples**.**

Table 4.6 Analysis of soil and sediment samples

S.No.	**Description of the sample**	**Uranium (μg g^{-1})**			**Recovery (%)**
		Added	**Found**		
			Present method*	**ICP-MS**	
1	Soil sample from station I	-	6.67 ± 0.2	6.96 ± 0.01	-
		6.00	12.65±0.2		99.7
		12.00	18.60 ± 0.3		99.4
2	Soil sample from station II	-	8.00 ± 0.2	7.96 ± 0.01	-
		8.00	16.05 ± 0.3		100.6
		16.00	24.00 ± 0.3		100.0
3	Karamana river sediment, Trivandrum	-	5.00 ± 0.2	4.96 ± 0.01	-
		5.0	10.00 ± 0.2		100
		10.0	15.10± 0.3		101
4	Marine sediment from Arabian sea,Trivandrum	-	8.33± 0.2	8.22 ± 0.01	-
		8.00	16.25 ± 0.3		99.0
		16.00	24.40 ± 0.3		100.4

*Average of 3 determinations

4.8 EXPERIMENTAL

4.8.1 Apparatus

A Hitachi 220 (Tokyo, Japan) double beam microprocessor based spectrophotometer was used for measuring absorbances. A LI-120 digital pH meter [ELICO, India] was used for pH measurements. A MAGNA FT-IR-560 spectrophotometer [Nicolet, USA] was used to obtain IR spectra. A Varian ultramass 700 Inductively coupled plasma mass spectrometer (Varian, USA) was used for the analysis of soil and sediment samples.

4.8.2 Reagents

1) Uranium(VI) solution (1000 µg ml^{-1}): A stock solution of uranium (VI) was prepared by dissolving 0.5274 g of $UO_2(NO_3)_2.6H_2O$ (Loba Chemie, India) in 250 ml of deionized water. Conc.HNO_3 (~5 ml) was added to suppress hydrolysis. The solution was standardized by titrating with EDTA.

2) Arsenazo III (0.1%, w/v): 0.1% solution was prepared by dissolving 0.1 g of Arsenazo III (Fluka, Buchs, Switzerland) in 100 ml of deionized water.

3) Ammonia-ammonium chloride buffer (1.0 mol l^{-1}) was used to maintain the pH.

1-(2-pyridylazo)-2-naphthol [Aldrich, USA], benzophenone, naphthalene [E-Merck, India] were also used. Acetone, hydrochloric acid and other reagents used were of analytical reagent grade.

4.8.3 Preparation of PAN embedded Benzophenone

1-(2-pyridylazo)-2-naphthol (PAN) and benzophenone taken in the ratio of 1:10 was dissolved in minimum amount of acetone. The resultant solution was poured as a fine stream into 500 ml of water with constant stirring at room temperature, stirred for further 3 hour and was allowed to settle. Then it was filtered , washed with deionized water, dried in oven at $40^{o}C$ for several hours and then stored in an amber coloured bottle.

4.8.4 General Procedure

A portion of uranium(VI)(2 - 200 µg) was diluted to 1.0 litre and the pH was adjusted to 10.7±0.2 after adding 10 ml of NH_3-NH_4Cl buffer and transferred to a 2.0 litre beaker. 0.5 g of PAN embedded benzophenone was added to the above solution and stirred for 10 min. The residue obtained after filtration was dissolved in 2.5 ml of acetone. 5.0 ml of 50% (v/v) hydrochloric acid and 2.5 ml of 0.1% Arsenazo III were added to the above solution and diluted to 25 ml with acetone. The absorbance of the uranium(VI)-Arsenazo III complex was measured at 656 nm.

4.8.5 Procedure for the Analysis of Marine Sediment Reference Material (MESS-3), Soils and Sediments

0.5 g of the sample was taken in a platinum crucible and treated with 5.0 ml hydrofluoric acid, 1.0 ml of Conc. H_2SO_4 at 150^oC on a hot plate. The process was repeated thrice. The residue was cooled and fused with 2.0 g $KHSO_4$ at 800^oC in an electric bunsen for 30 min. The melt was cooled and dissolved in 50 ml water and was made upto 100 ml. To 50 ml of the above solution 1.0 g of thiourea and 2.0 g sodium fluoride were added and the pH was adjusted to 10.7 ± 0.2 after addition of 5.0 ml of NH_3 - NH_4Cl. The preconcentration and subsequent determination were carried out by following the procedure described in section 4.8.4. The uranium(VI) content of soil, river and marine sediment materials were established by reference to the calibration curve.

4.9 SUMMARY

PAN embedded benzophenone/naphthalene SPE materials were used to enrich uranium(VI) from 1.0 litre of the aqueous solution in the pH range 10.5-11.0. Uranium(VI) enriched PAN embedded benzophenone/naphthalene was dissolved in 2.5 ml of acetone and subjected to analysis by using Arsenazo III method. Calibration graphs are linear in the range 2 - 200 μg of uranium(VI) present in 1.0 litre of sample solution. Ten replicate determination of 25 μg of uranium (VI) present in 1.0 litre of aqueous solution gave a mean absorbance of 0.045 with a standard deviation of 2.68%. The detection limit corresponding to 3 times the standard deviation of the blank was found to be 2.0 μg l^{-1}. The developed SPE procedure facilitate a 400 fold enrichment of uranium(VI) from dilute aqueous solutions and do not require any elution as it can be readily dissolved in acetone for subsequent quantitation by Arsenazo III method. The retention capacity of PAN embedded benzophenone/napththalene SPE was found to be 2.39 mg per g. The developed preconcentration procedure in conjuction with Arsenazo III spectrophotometric method is highly selective as none of the extraneous ions other than thorium interferes. The method has been validated by successfully analyzing marine sediment reference material.

Furthermore, the developed preconcentration procedure was found to be suitable for analyzing soil and sediment samples as the results obtained by the present method compare favorably with standard ICP-MS values.

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CHAPTER 5

OFFLINE COLUMN PRECONCENTRATION OF URANIUM(VI) WITH 1-(2-THIAZOLYLAZO)-2-NAPHTHOL (TAN) SORBED ACTIVATED CARBON

A number of solid sorbents such as chelating resins [1-3], cellulose [4], C_{18} bonded silica membrane discs [5], silica gel [6,7], glass beads [8-10], silica frit [11], metal hydroxides [12], polymer supports [13,14] and activated carbon [15,16] were used as sorbents for solid phase extractive preconcentration of inorganics. Of these activated carbon is preferred for the preconcentrative separation of inorganics and organics in view of its high surface area, ready availability, ease of elution and application to enrichment at trace, micro and macro levels.

It was noticed, in general, that activated carbon (AC) as such does not enrich metal ions quantitatively when present in trace and ultra trace levels. But very many reports are there in which activated carbon was used for the preconcentration of a large number of inorganics as their chelate complexes. Narin *et al* [17] developed a simple column preconcentration method for the determination of copper, manganese, cobalt, lead, nickel and chromium after preconcentration of their pyrocatechol violet complexes onto activated carbon. Niazi *et al* [18] reported a method by which the preconcentration of lead onto activated carbon was achieved in presence of anthralinic acid. Bhagavathy *et al* [19] described a method for the determination of traces of rare earths using energy-dispersive X-ray fluorescence spectrometry (EDXRF) after preconcentration of their quinoline-8-ol complexes onto activated carbon.

However, reports on preconcentration with chelating agent impregnated activated carbon are rare. Uzawa *et al* [20] developed a method for the determination of gallium by AAS after preconcentration with quinoline-8-ol impregnated activated carbon. 1,2-cyclohexanediondioxime functionalized activated carbon was used for the preconcentration of trace amounts of copper and lead and subsequent determination by tungsten metal furnace AAS [21]. To our knowledge, there is no report concerning the preconcentration of trace and ultra trace amounts of uranium with chelating agent sorbed activated carbon as solid phase extractant.

1-(2-thiazolylazo)-2-naphthol (TAN) is widely used as an analytical reagent in UV-visible spectrophotometry as it can form coloured chelates with several metal ions. Puri *et al* [22] reported a highly selective, sensitive, economical and rapid method for the trace determination of zinc using TAN as an analytical reagent and ammonium tetraphenylborate(ATPB)-naphthalene as an adsorbent There is no report pertaining to the use of TAN as chelating agent for preconcentration of uranium(VI) onto solid supports including activated carbon.

In the present work, TAN sorbed activated carbon was used as solid phase extractant for the column preconcentration of trace and ultratrace amounts of uranium(VI).

5.1 PRELIMINARY STUDIES

During the preliminary studies it was found that TAN sorbed activated carbon could very well adsorb uranium(VI) quantitatively from aqueous solutions. A solution containing 25 µg of uranium(VI) present in 1.0 litre deionized water whose pH was maintained at 6.5 after the addition of 10 ml of 1.0 mol l^{-1} ammonium acetate buffer, was passed through a column containing 0.1 g of 1-(2-thiazolylazo)-2-naphthol sorbed activated carbon. The uranium(VI) thus adsorbed was then eluted from the solid phase extractant with 5.0 ml of 1.0 mol l^{-1} HCl and the uranium(VI) content was established spectrophotometrically by Arsenazo III procedure. The enrichment was found to be quantitative under these conditions. Various parameters like pH, TAN concentration in SPE, amount of solid phase extractant, sample flow rate, eluent flow rate, eluent concentration and aqueous phase volume were optimized systematically and the results obtained are described below.

5.2 OPTIMIZATION OF VARIOUS EXPERIMENTAL PARAMETERS

5.2.1 Fabrication of the column

The glass column (vensil, size: 7.0 mm diameter and 20 cm length) was packed with 0.1 g of TAN sorbed activated carbon. It was first washed with 25 ml of 1.0 mol l^{-1} HCl and then with deionized water until it is free from acid, after each cycle of preconcentration and elution experiments the column is regenerated by washing with 20 ml of 1.0 mol l^{-1} HCl and conditioned by passing acetate buffer of pH~5 (see *Fig.5.1*).

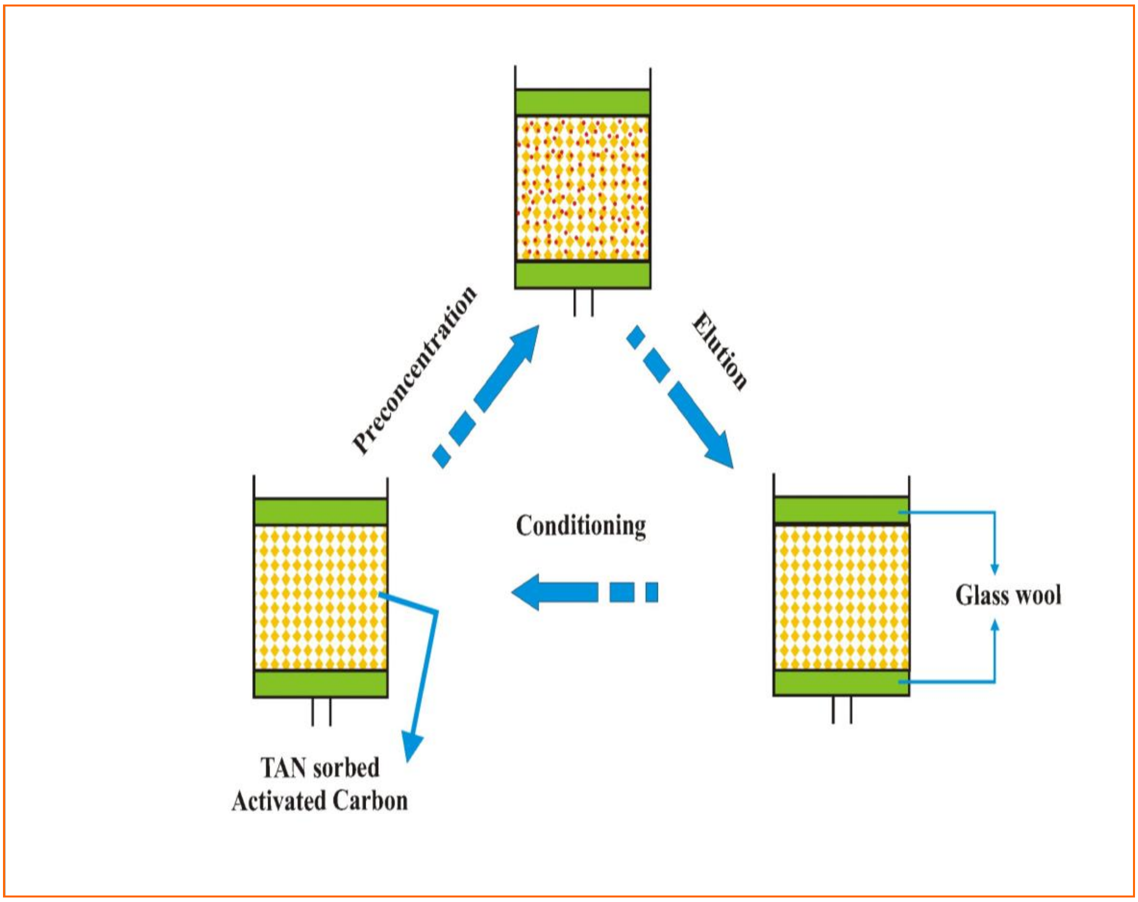

Fig.5.1 Schematic representation of off-line column preconcentration

5.2.2 Effect of pH

The preconcentration of uranium(VI) onto TAN sorbed activated carbon was carried out in different pHs ranging from 4.0 to 9.0 in steps of 1.0. In these investigations, the pH of the solution containing 25 µg of uranium(VI) in 1.0

litre of deionized water was adjusted with Dil. HCl or NaOH. The solution was passed through a column containing 0.1 g of 1.0% TAN sorbed activated carbon at a flow rate of 2.0 ml per min. The uranium(VI) adsorbed on TAN sorbed activated carbon was eluted with 5.0 ml of 1.0 mol l^{-1} HCl, treated with 5.0 ml of 50% (v/v) HCl and 2.5 ml of 0.1% Arsenazo III and diluted to 25 ml with deionized water. The absorbance of the uranium(VI)-Arsenazo III complex was measured at 656 nm. Blanks were prepared for each pH value. The results obtained are shown in *Fig.5.2*. The preconcentration of uranium(VI) onto TAN sorbed activated carbon was quantitative in the pH range 6.0 - 7.0. So, in the subsequent work, the pH was adjusted to 6.5 ± 0.5 after the addition of 10 ml of 1.0 mol l^{-1} ammonium acetate buffer.

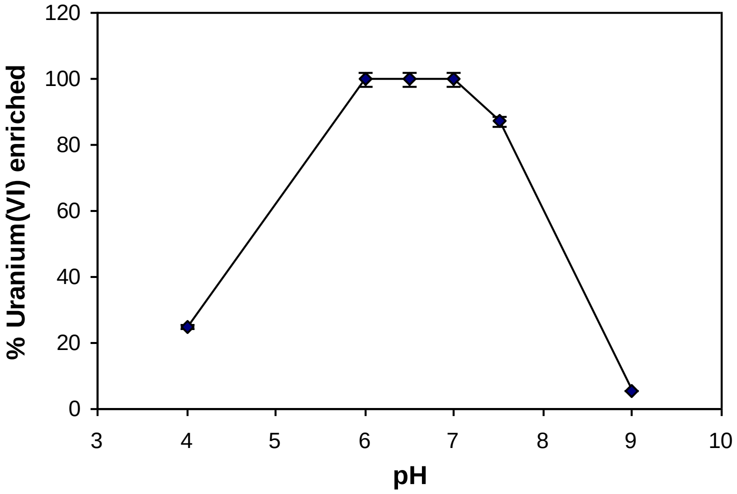

Fig.5.2 Effect of PH

5.2.3 Effect of 1-(2-thiazolylazo)-2-naphthol Concentration in Activated Carbon

The concentration of TAN in activated carbon was varied from 0.1 to 5.0%. The preconcentration and determination of uranium(VI) was carried out as described in “Effect of pH”. The results are shown in *Fig.5.3* from which it is clear that the preconcentration of uranium(VI) onto TAN sorbed activated carbon was quantitative when the concentration of TAN in activated carbon was ≥ 1.0%. Hence, 1.0% TAN sorbed activated carbon was used in subsequent studies.

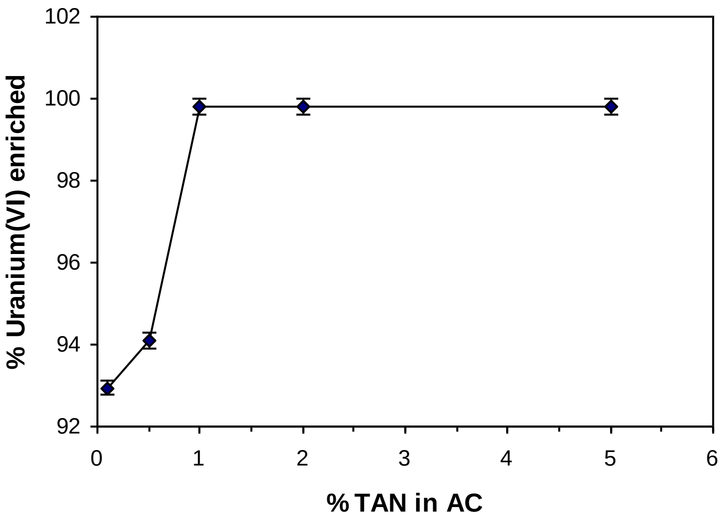

Fig.5.3 Effect of TAN concentration in activated carbon

5.2.4 Effect of Amount of 1-(2-thiazolylazo)-2-naphthol Sorbed Activated Carbon

The amount of solid phase extractant was varied from 0.02 to 0.5 g. The preconcentration and determination were carried out. The results are shown in *Table 5.1* which clearly indicate that the preconcentration of uranium(VI) onto TAN sorbed activated carbon was maximum when the amount of SPE was ≥0.1 g. So, for the subsequent work, 0.1 g TAN sorbedd activated carbon was used for quantitative preconcentration of uranium.

Table 5.1 Effect of amount of solid phase extractant

Amount of TAN sorbed activated carbon (g)	Percent enrichment
0.02	67.0 ± 0.2
0.05	98.0 ± 0.2
0.1	>99.0
0.2	>99.0
0.5	>99.0

5.2.5 Effect of Sample Flow Rate

The preconcentration of uranium(VI) onto TAN sorbed activated carbon was studied at different flow rates. Solutions containing 25 µg of uranium(VI) in 1.0 litre was passed through the column at flow rates varying between 0.2 to 4.0 ml min^{-1}.The preconcentrated uranyl ions was eluted with 5.0 ml of 1.0 mol l^{-1}

HCl . The metal content of the eluate was determined spectrophtometrically. It was found that 0.2-2.0 ml min^{-1} flow rate was suitable for the optimum loading of uranium(VI) onto the solid phase extractant (cf.*Table 5.2*). The flow rate slower than 1.0 ml min^{-1}is not preferred as it is time consuming. But at flow rates higher than 2.0 ml min^{-1} uranium(VI) does not equilibrate quantitatively with the column material . So 2.0 ml min^{-1}was chosen as the optimum flow rate.

Table 5.2 Effect of sample flow rate

Sample flow rate (ml min^{-1})	Percent enrichment
0.2	>99.0
0.5	>99.0
1.0	>99.0
2.0	>99.0
4.0	95 ± 0.2

5.2.6 Effect of Eluent Concentration

Hydrochloric acid of different concentrations in the range 0.1 to 2 mol l^{-1} was used for establishing the effect of eluent concentration on the elution of previously enriched uranium(VI) onto TAN sorbed activated carbon. The preconcentration and determination were carried out as described in section 5.2.2. The results are summarized in *Table 5.3*. The elution of uranium(VI) was quantitative and maximum when the eluent concentration was $\geq$ 0.5 mol l^{-1}. So, 1.0 mol l^{-1} hydrochloric acid was used for the elution of uranyl ion.

Table 5.3 Effect of eluent concentration

Eluent concentration (mol l^{-1})	Percent enrichment
0.1	84.5 ± 0.2
0.5	>99.0
1.0	>99.0
2.0	>99.0

5.2.7 Effect of Eluent Flow Rate

The flow rate on the elution of previously sorbed uranium(VI) on TAN sorbed activated carbon was varied in the range 0.2 - 4.0 ml min^{-1}. The preconcentration and determination were carried out using the general procedure. The results are summarized in *Table 5.4*. The elution of enriched uranium was quantitative upto the flow rate of 4.0 ml min^{-1}.

Table 5.4 Effect of eluent flow rate

Eluent flow rate (ml min^{-1})	Percent enrichment
0.2	>99.0
0.5	>99.0
1.0	>99.0
2.0	>99.0
4.0	>99.0

5.2.8 Effect of Eluent Volume

Solutions containing 25 µg of uranium(VI) present in 1.0 litre was preconcentrated at optimal conditions. The volume of the eluent (1.0 mol l^{-1} HCl) required for the effective desorption was studied by varying its volume in the range 1.0 to 10.0 ml. The uranium(VI) content in the eluate was determined spectrophotometrically. The results are given in *Fig.5.4*. It was found that 5.0 ml of HCl was sufficient for the quantitative enrichment.

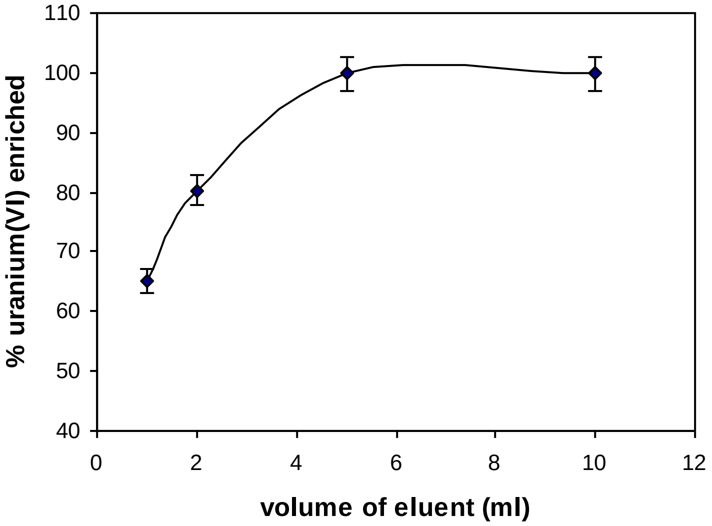

Fig.5.4 Effect of eluent volume

5.2.9 Effect of Aqueous Phase Volume

The preconcentration of uranium(VI) on TAN sorbed activated carbon was studied by varying the volume of the uranyl ion solution from 25 to1000 ml keeping the total amount of loaded metal ion constant at 25 µg under optimum conditions. The enriched uranyl ion was eluted with HCl, and measured spectrophotometrically. Quantitative recoveries of uranium(VI) were obtained upto 1000 ml. The results are summarized in the *Table 5.5*. As the preconcentrated uranium(VI) was eluted with 5.0 ml of 1.0 mol l^{-1} HCl, the preconcentratation factor achieved was ~200.

Table 5.5 Effect of aqueous phase volume

Aqueous Phase volume (ml)	Percent enrichment
25	>99.0
100	>99.0
250	>99.0
500	>99.0
1000	>99.0

5.2.9 Sorption Capacity of TAN Sorbed Activated Carbon

This experiment was carried out by taking a solution containing 1.0 mg of uranium(VI), 0.2 g of TAN sorbed activated carbon and 5.0 ml of 1.0 mol l^{-1} ammonium acetate (pH 6.5) in a 125 ml separating funnel. The resulting mixture was shaken for 30 minutes and filtered. The amount of uranium(VI) left out in the filtrate was determined by Arsenazo III procedure. The retention capacity of TAN sorbed activated carbon was found to be 4.86 mg per g of SPE.

5.3 EFFECT OF DIVERSE IONS

The possible preconcentrative separation of uranium(VI) from various inorganic ions likely to be present in soils and sediments were tested. The results obtained are shown in *Table 5.6* from which it is clear that the selective preconcentrative separation of uranium(VI) from concomitant species is possible. The presence of Cu(II), Cd(II) and Zn(II) (in presence of 1.0 g of thiourea) and La(III), V(V), and Mo(VI) (in presence of 2.0 g of NaF) did not affect the preconcentration and subsequent elution.

Table 5.6 Effect of diverse ions on uranium (VI) preconcentration
(Uranium (VI) - 15 µg l^{-1}, interfering ion- 1.0 mg l^{-1})

Metal ion	Remarks
Na, K, Li, Ca, Mg, Sr, Fe (III), Ni (II), Fe (II), Bi (III), Te (IV), As (V) and Sb (V)	No interference
Cu (II), Cd (II) and Zn (II)	No interference in the presence of 1 g of thiourea
La (III), V(V), and Mo (VI)	No interference in the presence of 2 g of NaF

5.4 LINEARITY, SENSITIVITY AND PRECISION

Under the optimum conditions, the calibration curve was linear over the concentration range of 0 - 200 µg of uranium(VI) present in 1.0 litre of solution. Ten replicate determinations of 25 µg of uranium(VI) present in 1.0 litre of solution gave a mean absorbance of 0.045 with relative standard deviation of 2.22% (cf.*Table 5.7*). The detection limit (corresponding to 3 times the standard deviation of the blank) and the enrichment factor were calculated to be 2 µg l^{-1} and 200 respectively.

The linear equation with regression is, $A=0.446 + 0.0016C$,where A is the absorbance and C is the concentration of uranium(VI) in µg l^{-1}.The correlation coefficient (R) is 0.9974.

5.5 APPLICATIONS

5.5.1 Analysis of Marine Sediment Reference Material

The accuracy of the developed preconcentration procedure was tested by analyzing marine sediment reference material (MESS-3) supplied by National Research Council, Canada. The sediment sample was mineralized and the uranium(V1) present in the sample was preconcentrated by using TAN sorbed activated carbon by following the procedure described in "Experimental". The results obtained are shown in *Table 5.8* from which it is clear that the amount of uranium present in marine sediment sample determined by the developed

Table 5.7 Precision studies

S.No	**Absorbance**	**Uranium(VI) found (µg) X_n**	**$X_n - \overline{X}$**	**$(X_n - \overline{X})^2$**
1	0.045	25.00	0.05	0.0025
2	0.044	24.44	-0.51	0.2601
3	0.046	25.56	0.61	0.3721
4	0.045	25.00	0.05	0.0025
5	0.046	25.56	0.61	0.3721
6	0.044	24.44	-0.51	0.2601
7	0.045	25.00	0.05	0.0025
8	0.043	23.89	-1.06	1.1236
9	0.046	25.56	0.61	0.3721
10	0.045	25.00	0.05	0.0025

$\overline{X} = 24.95$ $\Sigma\,(X_n - \overline{X})^2 = 2.770$

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

$\sigma = 0.5548$

Relative standard deviation = 2.22 %

Table 5.8 Analysis of reference material [MESS-3] [supplied by the National Research Council of Canada]

S.No.	**Uranium added (µg g^{-1})**	**Uranium found (µg g^{-1})**		**Recovery (%)**
		Present method*	**Certified value**	
1	-	4.2 ± 0.2	(4)	-
2	5.0	9.1 ± 0.2	-	98.0
3	10.0	14.1 ± 0.2	-	99.0

*Average of 3 determinations

method is comparable to the information value given by NRC, Canada. Further, known amounts of uranium(VI) were added to standard reference material before mineralization step. The recoveries were found to be good indicating the reliability of the developed procedure for determination of uranium(VI) in soil and sediment samples.

5.5.2 Analysis of Soil and Sediment Samples

The developed column preconcentration procedure using TAN sorbed activated carbon was extended to the analysis of real samples. Soil samples collected from two stations in Trivandrum, sediment of Karamana river, Trivandrum and marine sediment collected from Arabian sea were subjected to the analysis ofuranium (VI) using the procedure described in section 5.2.2. The results obtained by the present method agree well with standard ICP-MS values (See *Table 5.9*) which indicate that the developed method can reliably be used for the analysis of soil and sediment samples.

5.6 EXPERIMENTAL

5.6.1 Apparatus

A microcomputer based spectrophotometer system was used. This consists of a Hitachi model 220 double beam spectrophotometer with an extended programme.

A pair of matched 10 mm quartz cuvettes which were periodically cleaned with H_2SO_4 + HNO_3 mixture and thoroughly washed with deionized water was used in this study. A LI-120 digital pH meter (ELICO, India) was used for adjusting the pH. A Varian ultra mass 700 inductively coupled plasma mass spectrometer (Varian, USA) was used for referal analysis of soil and sediment samples.

Table 5.9 Analysis of soil and sediment samples

S.No.	**Description of the sample**	**Uranium ($\mu g\ g^{-1}$)**			**Recovery (%)**
		Added	**Found**		
			Present method*	**ICP-MS**	
1	Soil sample from Station I	-	6.80 ± 0.2	6.96 ± 0.01	-
		6.00	12.75 ± 0.2		99.2
		12.00	18.80 ± 0.2	-	100.0
2	Soil sample from Station II	-	8.05 ± 0.2	7.96 ± 0.01	-
		8.00	16.05 ± 0.2	-	100.0
		16.0	24.00 ± 0.3	-	99.7
3	Karamana river sediment	-	5.00 ± 0.2	4.96 ± 0.01	-
		5.00	10.00 ± 0.2	-	100.0
		10.00	15.05 ± 0.2	-	100.5
4	Marine sediment from Arabian Sea	-	8.25 ± 0.2	8.22 ± 0.01	-
		8.00	16.25 ± 0.3	-	100.0
		16.00	24.30 ± 0.3	-	100.3

*****Average of 3 determinations

5.6.2 Reagents

A stock solution of uranium(VI) was prepared by dissolving appropriate amount of $UO_2(NO_3)_2.6H_2O$ (Aldrich, USA) in distilled water. Conc. HNO_3 (~5.0 ml) was added to 100 ml of solution to suppress hydrolysis. This solution was standardized by titrating with EDTA. Arsenazo III (Fluka, Buchs, Switzerland), 0.1% solution was prepared by dissolving 0.1 g of the reagent in 100 ml of distilled water. 1.0 mol l^{-1} ammonium acetate buffer was prepared to maintain the pH of the aqueous phase. Reagents like 1-(2-thiazolylazo)-2-naphthol (Aldrich, USA), activated carbon (Aldrich, USA) were used throughout the study. Acetone, hydrochloric acid and other reagents (Merck, India) used were of analytical reagent grade. The reference material MESS-3 (Marine sediment reference material supplied by National Research Council, Canada) certified for trace elements was used for quality assurance.

5.6.3 Preparation of 1-(2-thiazolylazo)-2-naphthol Sorbed Activated Carbon

To a suspension of 10 g of activated carbon in 1.0 litre of deionized water, acetone solution of TAN (0.1 g in 5.0 ml) was added as fine stream with constant stirring at room temperature. The resulting mixture was stirred for 3 hours and was allowed to settle for 10 min. Then it was filtered, washed with deionized water and dried in an oven at $60^{o}C$ for several hours and then stored in an amber coloured bottle.

5.6.4 General Procedure

A portion of solution (2 – 200 µg) of uranium(VI) was diluted to 1.0 litre with deionized water and the pH was adjusted to 6.5 after adding 10 ml of 1.0 mol l^{-1} ammonium acetate buffer. TAN sorbed activated carbon (0.1 g) was packed in a column (7.0 mm diameter) and the sample solution was passed through the column at a flow rate of 2.0 ml min^{-1}. The uranium(VI) bonded to TAN sorbed activated carbon was eluted with 5.0 ml of 1.0 mol l^{-1} HCl at a flow rate of 4.0 ml min^{-1}. To this solution, 5.0 ml of 50% (v/v) HCl and 2.5 ml of 0.1% Arsenazo III were added and diluted to 25 ml with deionized water. The absorbance of uranium(VI)-Arsenazo III complex was measured at 656 nm.

5.6.5 Procedure for the Analysis of Certified Reference Material (MESS-3), Soils and Sediments

To 0.5 g of sample, 5.0 ml of HF and 1.0 ml of Conc. H_2SO_4 were added and heated at $150^{o}C$ on a hot plate. The process was repeated thrice. The residue was cooled and fused with 2.0 g $KHSO_4$ at $800^{o}C$ in an electric Bunsen for 30 min. The melt was cooled and dissolved in 50 ml of deionized water, 1.0 g of thiourea and 2.0 g of sodium fluoride were added and preconcentration and determination were carried out by following the procedure described in section 5.6.4. The uranium content of soil, river and marine sediment samples were established with reference to a calibration graph.

5.7 SUMMARY

TAN sorbed activated carbon SPE material was prepared by adding acetone solution of TAN to the suspension of activated carbon in deionized water. The resulting SPE material, after filtration and drying, was packed into a column. Traces of uranium(VI) (2-200 µg) was found to be enriched quantitatively in the pH range 6.0 - 7.0 onto TAN sorbed activated carbon as determined by Arsenazo III method. Ten replicate determinations of 25 µg of uranium(VI) present in 1.0 litre of aqueous solution gave a mean absorbance of 0.045 with a RSD of 2.22%. The detection limit corresponding to 3 times the standard deviation of the blank and enrichment factor were found to be 2.0 µg l^{-1} and 200 respectively. The retention capacity of TAN sorbed activated carbon was found to be 4.86 mg per g of SPE.

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CHAPTER 6

ION IMPRINTED POLYMER PARTICLES AS THE SOLID PHASE EXTRACTANT FOR THE RECOVERY OF URANIUM(VI) FROM SYNTHETIC NUCLEAR SPENT FUEL

Uranium is the most important fuel in nuclear power reactors. Enriched uranium is used as a material of high density in the aeronautics industry, as radiation shielding, as an additive for catalysts or steels and in glass and ceramic industries. The principal uranium deposits occur in Australia and Canada which constitute 28 and 14% of world deposits respectively. Australia and Canada are the major countries that export U_3O_8. However, these exports are limited to signatories of nuclear non-proliferation treaty which allow international inspection to verify that U_3O_8 is used only for peaceful purposes. In view of this, countries with deposits of as low as 0.1% uranium are being mined. One way of solving the problem in a long term perspective is to recover uranium from sea water or from nuclear spent fuels. The typical composition of nuclear spent fuel is given in *Table 6.1*, from which it is clear that as high as 20 g l^{-1} of uranium is present along with several other inorganic species. Hence, the selective recovery of uranium from nuclear spent fuel is an important option to serve the futuristic needs of any country producing nuclear power.

Table 6.1 Composition of spent nuclear fuel of pressurized heavy water reactor (PHWR)

Constituent	**Concentration (mg l^{-1})**
U	20,000
La	263.8
Ce	532.5
Nd	862.5
Sm	163.8
Pr	243.8
Gd	165.0
Tb	5.0
Dy	2.0
Y	99.0
Ru	463.8
Pd	267.5
Na	3000.0
Ba	308.8
Ni	100.0
Cr	100.0
Mn	181.3
Co	127.5
Mo	731.3
Zr	771.3

Ion exchange and liquid-liquid extraction (LLE) techniques are traditionally employed for recovering uranium. LLE is always preferred over ion exchange because of its simplicity, rapidity, ready adaptability to scale up and easy recovery of analyte and extractant [1]. However, despite these positive features, they do possess inherent limitations such as finite aqueous phase solubility, low enrichment factors, third phase formation and cumbersome disposal of organic solvents. In order to overcome these problems, solid phase extraction (SPE) has come to the forefront in recent years [2]. However, most of the SPE methods are non-selective and do not find favour for selective recovery of uranium from a host of inorganic species that coexist in nuclear spent fuel.

Ion imprinted polymers (IIP) for solid phase extraction has of late come to reckoning for selective recovery of inorganics as this technique provides higher enrichment factors and selectivity coefficients [3]. Dai *et al* [4] had prepared mesoporous sorbent materials by ion imprinting technique for selective recovery of uranyl ions using bifunctional ligands such as amines and sulphonic acids. The invention of John *et al* [5] relates to the detection and extraction of uranyl ions by polymer imprinting wherein complexable functionality is of the formula CTCOOH where T is a hydrogen or any halogen (preferably chlorine), methyl and halogen substituted forms thereof or CCOOH or PhCOOH. However, the inventions of Dai *et al* [4] and John *et al* [5] pertain to recovery of uranium from aqueous solutions only. Bae *et al* [6] and Gladis and Rao [7-10] had utilized vinyl benzoate and quinoline-8-ol or its derivatives – vinyl pyridine as complexable functionalities during the preparation of ion imprinted polymeric resins and particles respectively and these polymers had been used for recovery of uranium from sea water. However, these IIPs are not suitable for recovery of uranium from nuclear spent fuel which contains free acidity. Recently, Say *et al* [11] had selectively removed uranium using glutamic acid ion imprinted polymeric beads from weakly acidic solutions (pH 3.5) containing Fe(III), Th(IV) and Mn(II). As seen from the above account, none of the researchers attempted selective recovery of uranium from a host of coexisting inorganic species from weakly acidic to acidic solutions using IIPs.

Oxy-imines, more commonly abbreviated as oximes, constitute an important class of chelating agents [12,13]. They find extensive applications as highly selective reagents for the separation and/or spectrophotometric determination of a large number of metal ions [12,14,15]. Amidoxime modified polymers have been employed for recovery of uranium from sea water [16, 17]. A polymeric sorbent containing amidoxime functional group can extract uranium(VI) when the pH of the solution is ~ 8.0 and so it cannot be used for recovery of uranium from acidic solutions. On the other hand, salicylaldoxime (SALO) has been used for the liquid-liquid extraction of uranium(VI) from weakly acidic solutions (pH ~3.5) [18]. Hence, SALO is an ideal candidate in preparing uranyl IIP particles which can be used for the selective recovery of uranium from a host of other coexisting inorganic species and that too from weakly acidic solutions. In the present work, uranium(VI) imprinted polymer particles using U(VI) – SALO – VP were prepared and the possible application to the recovery of the uranium from synthetic nuclear spent fuel samples was investigated.

6.1 SYNTHESIS OF URANIUM(VI) IMPRINTED POLYMER (IIP) AND CONTROL POLYMER (CP) PARTICLES

1**)** The preparation of ternary pre-polymer complex of uranium(VI), 4-vinyl pyridine and salicylaldoxime (SALO).

2) Co-polymerization of the ternary complex with styrene (monomer) and divinyl benzene (cross-linking monomer) (see *Fig. 6.1*).

The imprint ion (U(VI)) was complexed with salicylaldoxime and/or 4-vinyl pyridine in 10 ml of 2-methoxyethanol. These binary/ternary complexes in porogen were mixed with styrene (monomer) and divinyl benzene (crosslinking monomer) in presence of AIBN as initiator. The polymerization mixtures were cooled to 0^oC and purged with N_2 for 10 min, sealed and thermally polymerized in an oil bath at ~80°C while stirring for 3 hours. The resulting polymer materials were then dried, ground and sieved to get the ion imprinted polymer particles. Control polymer particles were similarly prepared by omitting the imprint ion. The principles of the design and preparation of ion imprinted polymers are summarized in *Fig.6.2.*

The composition of the different ion imprinted polymers and control polymers used in the present study are given in *Table 6.2.*

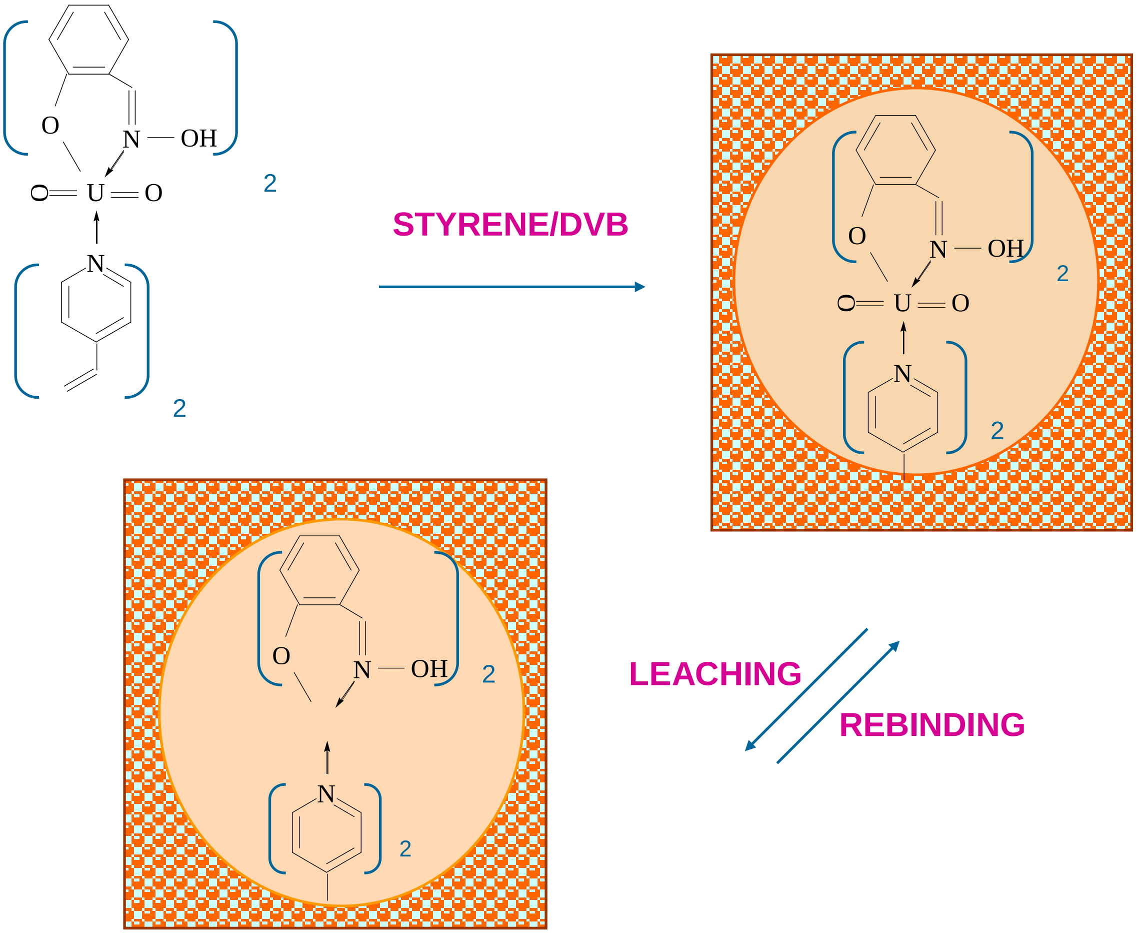

Fig.6.1: Scheme for the synthesis of U(VI) ion imprinted polymers

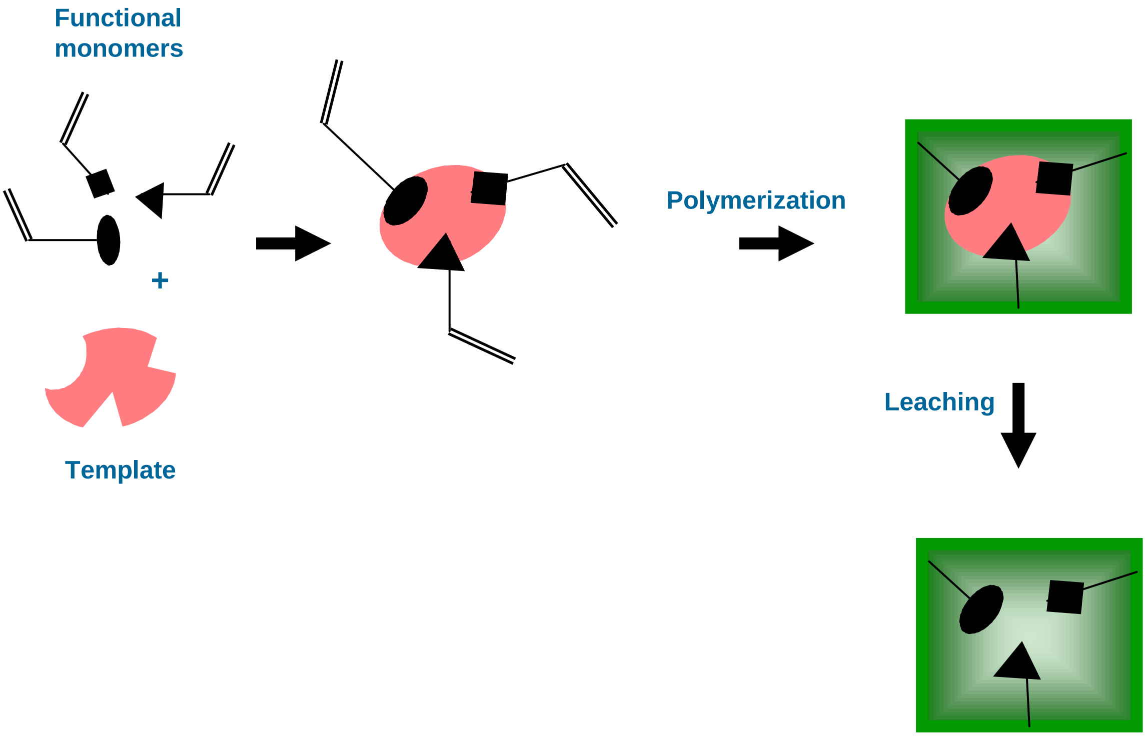

Fig.6.2 Schematic diagram of ion imprinting technology

Table 6.2. Preparation of control and uranium(VI) imprinted polymers

Polymer		Imprint ion U(VI) (mM)	SALO (mM)	VP (mM)	Styrene (mM)	DVB (mM)	AIBN (mg)
Styrene	CP_1	-	2	2	20	-	50
	IIP_1	1	2	2	20	-	50
DVB	CP_2	-	2	2	-	20	50
	IIP_2	1	2	2	-	20	50
SALO (binary)	CP_3	-	4	-	20	20	50
	IIP_3	1	4	-	20	20	50
VP (binary)	CP_4	-	-	4	20	20	50
	IIP_4	1	-	4	20	20	50
Ternary	CP_5	-	2	2	20	20	50
	IIP_5	1	2	2	20	20	50

6.1.2 Pretreatment of Polymer Particles to Leach the Imprint Ion

The imprint ion (U(VI)) was leached out from 2.0 g of the polymer particles by stirring with 100 ml of 6.0 mol l^{-1} HCl for 5 hours to obtain leached

IIP particles for possible selective extraction of uranium(VI) from dilute aqueous solutions. CP particles were also subjected to similar pretreatment.

6.2 ENRICHMENT OF URANIUM(VI) USING ION IMPRINTED POLYMER PARTICLES

A series of solution containing 25 μg of uranium(VI) was diluted to 500 ml and the pH was adjusted to 3.5 ± 0.3 after the addition of 5.0 ml of 1.0 mol l^{-1} sodium acetate-acetic acid buffer. Leached polymer particles (0.1 g) were added to the above solution and stirred for 10 min. The uranium(VI) preconcentrated onto the polymer particles were eluted with 10 ml of 1.0 mol l^{-1} HCl by stirring for 10 min. The uranyl ion content was determined spectrophotometrically using Arsenazo III method [19]. Suitable aliquots of eluent were taken and 2.5 ml each of Conc. HCl and 0.1% Arsenazo III were added and diluted to 25 ml. The absorbance of uranium(VI) – Arsenazo III complex was measured at 656 nm.

The results given in *Table 6.3* convey the imprinting effect (higher extraction percentage with IIPs than CPs) in the case of all binary and ternary complexes of uranium(VI). Further, the preconcentration of uranium(VI) was quantitative in the case of IIP_5 corresponding to U(VI) - SALO – VP ternary complex. The binary complexes i.e, IIP_3 (U(VI) -SALO) and IIP_4 (U(VI) -VP) did not preconcentrate uranium(VI) quantitatively. The higher percent enrichment of uranium(VI) with ternary mixed ligand complex compared to individual binary complexes is probably due to the availability of more number of interaction sites in the ternary complex. Hence, IIP_5 and CP_5 particles were used in further studies.

6.3 EFFECT OF TEMPLATE TO MONOMER AND CROSS LINKING MONOMER RATIO

Three sets of polymers were prepared by varying the template to styrene (monomer) to DVB (crosslinking monomer) ratio as 1:10:10; 1:20:20 and 1:40:40. The preconcentration studies were carried out with each polymer. The results on percent extraction of uranium(VI) are shown in *Table 6.4*. It was confirmed that the polymer having the particular ratio of 1:20:20 alone gave quantitative recovery. Other two polymers in which the ratio is too high or too low did not enrich uranium quantitatively. When the ratio is low, the polymer matrix is not sufficient to trap the salicylaldoxime ligand during leaching of uranium(VI). Similarly, when the ratio is too high, the effective number of binding sites per unit weight of the polymer particles decreases with increase of polymer matrix resulting again in a decrease in percent enrichment.

Table 6.3. Percent recovery of uranium(VI) using CP and IIP particles

S. No.	CP	Recovery (%)	IIP	Recovery (%)
1	CP_1	17.6 ± 0.2	IIP_1	49.8 ± 0.4
2	CP_2	27.9 ± 0.3	IIP_2	29.5± 0.3
3	CP_3	28.0 ± 0.3	IIP_3	51.3 ± 0.4
4	CP_4	47.1 ± 0.3	IIP_4	82.1 ± 0.7
5	CP_5	13.2 ± 0.2	IIP_5	> 99.0

Table 6.4. Percent recovery of uranium(VI) with CP or IIP prepared using different template - styrene– DVB combinations

S.No.	Template: styrene:DVB	CP	Recovery (%)	IIP	Recovery (%)
1	1:10:10	CP_6	23.9 ± 0.3	IIP_6	79.6 ± 0.5
2	1:40:40	CP_7	18.4 ± 0.2	IIP_7	91.8 ± 0.8
3	1:20:20	CP_5	13.2± 0.2	IIP_5	> 99.0

6.4 CHARACTERIZATION STUDIES

6.4.1 FT-IR Studies

The FT-IR spectra of CP (leached and unleached), IIP (leached and unleached) were recorded. All have similar IR spectra indicating that all the polymers have similar backbone. >C = N stretching vibration is generally observed in the range 1400 - 1600 cm^{-1} [20]. Here, in the IR spectra of both CP and IIP (leached and unleached) there is a prominent absorption peak in the range 1489 – 1496 cm^{-1}, which indicates the presence of salicylaldoxime in the polymer matrix before and after leaching. N-O stretching frequency is usually observed in the range of 1055 – 870 cm^{-1} [21]. The presence of an absorption peak in 989 - 991 cm^{-1} establishes the fact that SALO is kept intact in the polymer matrix even after leaching. A weak band near 802 cm^{-1} is present in spectrum of unleached ion imprinted polymer only. This is of the O=U=O symmetric stretching [6].

6.4.2 X-ray diffraction Studies

The XRD patterns of ternary complex (A),unleached IIP (B),leached IIP (C) and CP (D) are given in *Fig.6.3.*

The peaks obtained at 2θ values 42.12, 43.84, 49.10, and 50.92 in the ternary complex are very much present in the unleached IIP. Again, these peaks are absent in the leached one indicating that the uranium(VI) is completely removed from the material during leaching. This observation is similar to previous reports published by Gladis *et al* [8-10].

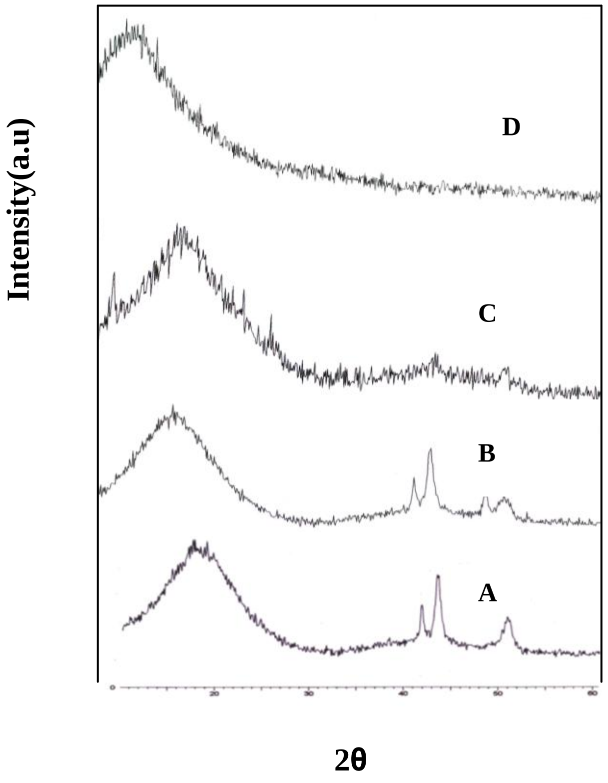

Fig.6.3 ***X-ray diffraction patterns of ternary complex(A), unleached and leached uranium(VI) IIP (B&C) and CP (D)***

6.4.3 SEM Studies

The morphology of the crushed polymers prepared by thermal polymerization was assessed by SEM (micrograph shown in *Fig.6.4*). As seen from the micrograph, the polymer particles are agglomerated in irregular shapes analogous to the results reported for thermal polymerization [22].

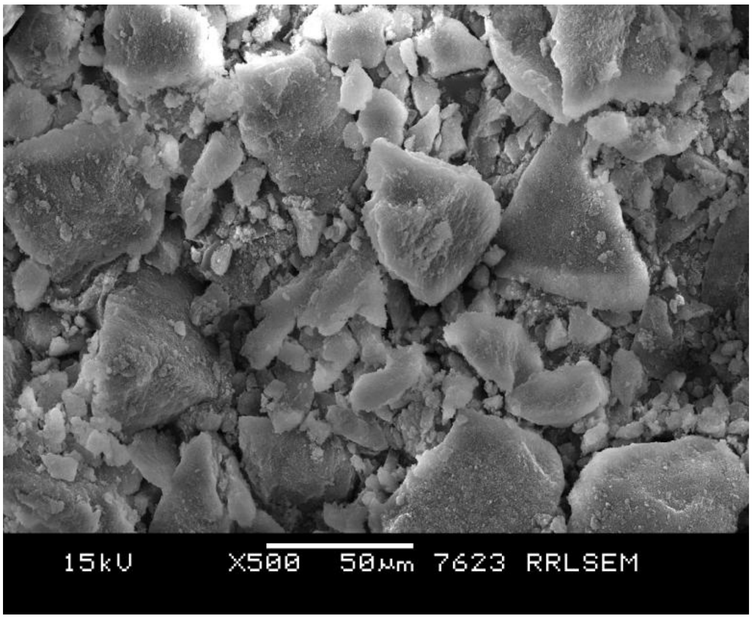

Fig.6.4 SEM photograph of leached uranium(VI) IIP particles prepared using uranium-salicyladoxime- 4-vinyl pyridine template

6.5 OPTIMIZATION OF EXPERIMENTAL VARIABLES

6.5.1 Effect of Leachant

HCl (6.0 mol l^{-1}), HNO_3 (6.0 mol l^{-1}), H_2SO_4 (3.0 mol l^{-1}) and Na_2CO_3 (1.0 mol l^{-1}) were used as leachants during the pretreatment of the polymer particles. The preconcentration using IIP_5 and determination were carried out as described in section 6.2. The results are shown in *Table 6.5*. It was found that hydrochloric acid could be used for the leaching out of the imprint ion from the polymer.

Table 6.5 Effect of leachant

Leachant (mol l^{-1})	**% Recovery by IIP_5**
HCl (6.0 mol l^{-1})	> 99.0
HNO_3 (6.0 mol l^{-1})	15.2 ± 0.2
H_2SO_4 (3.0 mol l^{-1})	28.6 ± 0.2
Na_2CO_3 (1.0mol l^{-1})	32.5 ± 0.3

6.5.2 Effect of Leachant Concentration and Leaching Time

The effect of HCl concentration (1.0-10.0 mol l^{-1}) and leaching time (3-9 h) were studied and the percent enrichment of uranium(VI) by IIP_5 particles are given in *Table 6.6* and *Table* 6*.7*. It is seen that the percent recovery of uranium(VI) was quantitative when leachant concentration was in the range 5.0-10.0 mol l^{-1} and a minimum of 5 hours was needed for the effective removal of the imprint ion.

Table 6.6 Effect of leachant concentration

Leachant (HCl) concentration (mol l^{-1})	**% Recovery by IIP_5**
1.0	31.8 ± 0.3
3.0	46.2 ± 0.4
5.0	> 99.0
6.0	> 99.0
10.0	> 99.0

Table 6.7 Effect of leaching time

Leaching time (h)	**% Recovery by IIP_5**
3	28.2 ± 0.2
4	47.2 ± 0.4
5	> 99.0
6	> 99.0
8	70.7 ± 0.6

6.5.3 Effect of pH

The influence of pH on the preconcentration of uranium(VI) was studied in the range 1.0 - 7.0. The preconcentration of uranium(VI) was constant and maximum in the pH range 3.2 to 5.0 (See *Fig.6.5*). For comparison, the percent recovery of uranium(VI) with CP_5 is also included in *Fig.6.5*. The imprinting effect is clearly observed in all pH conditions. The decrease in percent recovery of uranium(VI) at pHs <3.2 is attributed to competition of H^+ ions with uranium(VI) to form complex with SALO. Hence, the pH was adjusted to 3.5 ± 0.3 in all subsequent studies after the addition of 5.0 ml of 1.0 mol l^{-1} sodium acetate – acetic acid buffer.

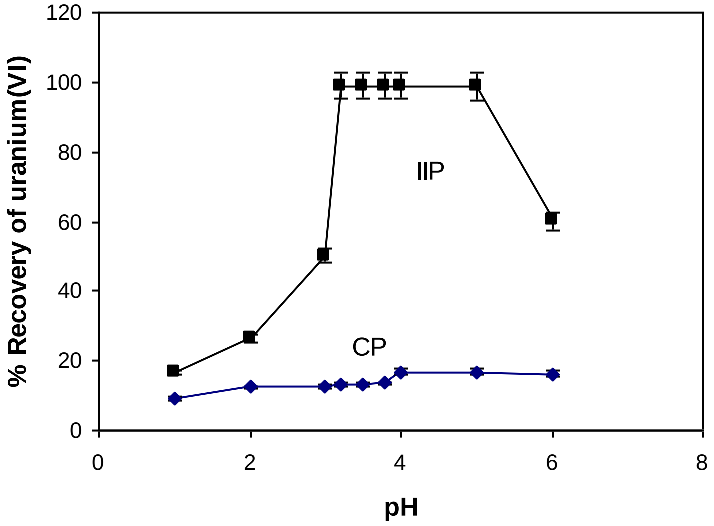

Fig.6.5 Effect of pH on the preconcentration of uranium(VI) using CP_5 and IIP_5 particles

6.5.4 Effect of Amount of Polymer Particles

Fig.6.6 shows the percent recovery of uranium(VI) with different amounts of CP_5 and IIP_5 particles. Again, as in case of pH studies, imprinting effect was noticed in all the instances. As low as 0.08 g of IIP_5 particles were enough for quantitative recovery of uranium(VI). Hence, 0.1 g of IIP_5 particles was used in all subsequent studies.

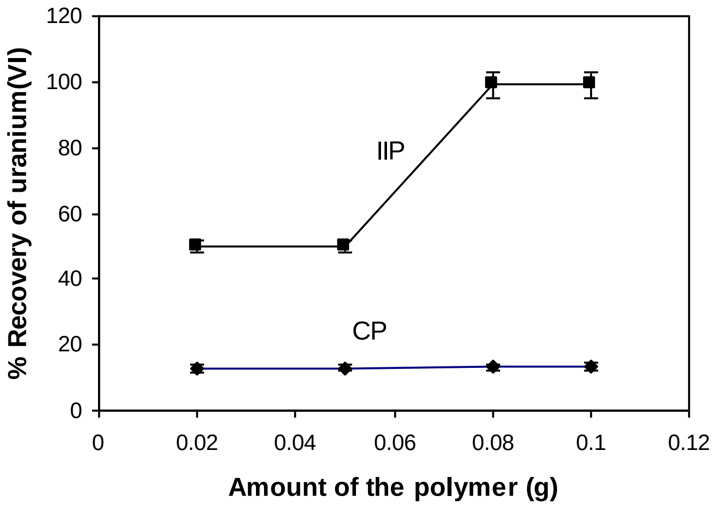

Fig.6.6 Effect of amount of polymer on the preconcentration of uranium(VI) using CP_5 and IIP_5 particles

6.5.5 Effect of Time of Preconcentration and Elution

The influence of time of preconcentration and elution on the recovery of 25 µg of uranium(VI) present in 500 ml of solution was studied. The results are depicted in *Fig.6.7*. It is seen that as low as 10 min of preconcentration was enough to load the uranium(VI) to the solid phase. Again, 10 min. of elution was required for effective recovery of the preconcentrated uranium(VI) using IIP_5 particles.

6.5.6 Effect of Sample Volume

The volume of the aqueous phase was varied from 25-1000 ml during preconcentation to estimate the effect of it on the percentage extraction of uranium(VI) by CP_5 and IIP_5. It can be seen from the *Table 6.8* that the change of aqueous phase volume from 25-500 ml did not affect the preconcentration efficiency of 25 µg of uranium(VI) using 0.1 g of IIP_5.

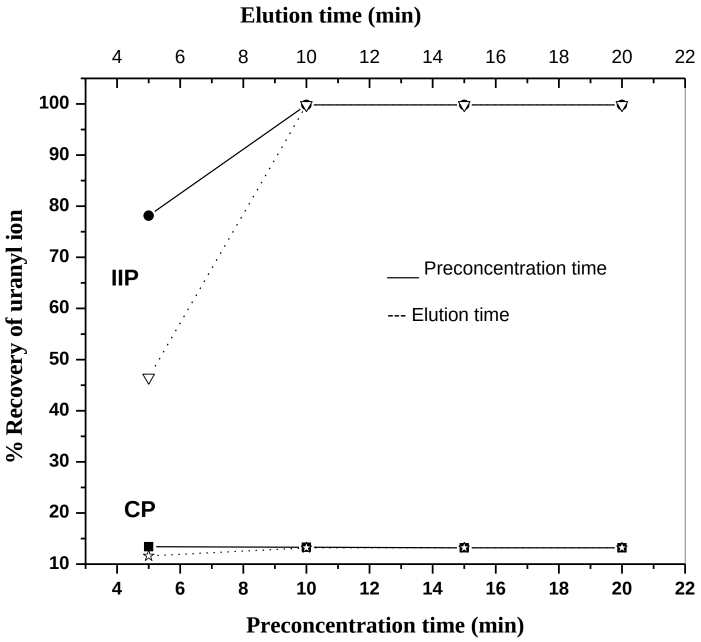

Fig.6.7 Effect of time of preconcentration and elution on the preconcentration of uranium(VI) using CP_5 and IIP_5 particles

6.5.7. Choice of Eluting Agents

The choice of appropriate eluting agent is extremely important for ensuring the selective separation/extraction of uranium(VI). The enriched uranium(VI) on the CP_5 and IIP_5 were eluted with various mineral acids like HCl (1.0 mol l^{-1}), HNO_3 (1.0 mol l^{-1}) and H_2SO_4 (0.5 mol l^{-1}). The percent extraction of uranyl ion using CP_5 and IIP_5 is tabulated in *Table 6.8.* Hydrochloric acid alone could elute the previously enriched uranium(VI) from the polymer particles quantitatively.

6.5.8 Effect of Concentration and Volume of the Eluent

The effect of concentration of hydrochloric acid on the elution of the previously enriched uranium(VI) was tested by varying the concentration over the range 0.1 to 2.0 mol l^{-1}. 1.0 mol l^{-1} HCl could elute the preconcentrated uranium(VI) and the same was recommended in subsequent studies.

It is very important that the analyte should be efficiently desorbed in a small volume so that a higher enrichment factor is resulted. For this reason, volume of hydrochloric acid used was varied from 5.0 to 20 ml. The results are given in *Table 6.8.* From the table it is clear that single elution with 10 ml of eluent is required for eluting the previously enriched uranium(VI) from the polymer particles and thus providing an enrichment factor of ~50.

Table 6.8 Influence of various parameters on the percent recovery of uranium(VI) by CP_5 and IIP_5 particles

S.No.	**Parameter**	**Recovery (%)**	
		CP_5	**IIP_5**
1	**Aqueous phase volume (ml)**		
	25	13.2± 0.2	> 99.0
	100	13.2 ± 0.2	> 99.0
	250	13.2 ± 0.2	> 99.0
	500	13.2 ± 0.2	> 99.0
	1000	10.5± 0.2	68.2 ± 0.2
2	**Nature of eluent**		
	1 mol l^{-1} HCl	13.2 ± 0.2	> 99.0
	1 mol l^{-1} HNO_3	12.4 ± 0.2	70.6 ± 0.6
	0.5 mol l^{-1} H_2SO_4	8.6 ± 0.2	24.4± 0.3
3	**Eluent (HCl) concentration (mol l^{-1})**		
	0.1	12.4 ± 0.2	26.4 ± 0.3
	0.5	14.4 ± 0.2	80.1 ± 0.7
	1.0	13.2 ± 0.2	> 99.0
	2.0	13.3 ± 0.2	> 99.0
4	**Eluent volume (ml)**		
	5	10.4 ± 0.2	35.5 ± 0.3
	10	13.2 ± 0.2	> 99.0
	20	13.0 ± 0.2	> 99.0

6.6 CALIBRATION GRAPH AND PRECIION STUDIES

Under the optimum conditions described above, the calibration curve is linear over the concentration range 0 – 100 μg of uranium(VI) present in 500 ml of aqueous solution. The linear equation with regression is as follows

$$A = 0.0495 + 0.0018C$$

where correlation coefficient = 0.99955, A is the absorbance and C is the concentration in microgram of uranium(VI) in 500 ml. The enrichment factor and the corresponding lowest concentration below which the recoveries become non-quantitative are 50 and 10 μg l^{-1} respectively. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range. Ten replicate determinations of 25 μg of uranium(VI) present in

500 ml solution gave a mean absorbance of 0.045 with a relative standard deviation of 2.716% (see *Table 6.9*).

Table.6.9 Precision studies

S.No	**Absorbance**	**Uranium(VI) found (µg) X_n**	$X_n - \overline{X}$	$(X_n - \overline{X})^2$
1	0.043	23.89	-1.22	1.4884
2	0. 045	25.00	-0.11	0.0121
3	0. 045	25.00	-0.11	0.0121
4	0. 046	25.55	0.44	0.1936
5	0. 046	25.55	0.44	0.1936
6	0. 044	24.44	-0.67	0.4489
7	0. 046	25.55	0.44	0.1936
8	0. 047	26.11	1.00	1.0000
9	0. 044	24.44	-0.67	0.4489
10	0. 046	25.55	0.44	0.1936

$\overline{X} = 25.11$ $\Sigma (X_n - \overline{X})^2 = 4.1848$

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

$\sigma = 0.6819$

Relative standard deviation = 2.716 %

6.7 SELECTIVITY STUDIES

The selectivity of CP_5 and IIP_5 particles towards uranium over other inorganic ions that usually coexist with uranium in nuclear spent fuel was determined. The selectivity coefficient ($S_{U(VI)}/{}_{M}{}^{n+}$) is defined as

$$S_{U(VI)}/{}_{M}{}^{n+} = \frac{D_{U(VI)}}{D_{M}n+} \qquad (1)$$

where $D_{U(VI)}$ and $D_{M^{n+}}$ are the distribution ratios of the uranium(VI) and other inorganic species respectively. These distribution ratios were calculated using the formula

$$D_{M^{n+}} = \frac{C^{i}_{M^{n+}} - C^{f}_{M^{n+}}}{C^{f}_{M^{n+}}} \times \frac{v}{m} \qquad (2)$$

where $C^{i}_{M^{n+}}$ and $C^{f}_{M^{n+}}$ are the concentrations of inorganic ions in aqueous phase before and after extraction, v the volume of the solution and m is the mass of the polymer.

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

$$\%E = \frac{C^{i}_{M^{n+}} - C^{f}_{M^{n+}}}{C^{i}_{M^{n+}}} \times 100 \qquad (3)$$

Under the optimum conditions of preconcentration of uranium(VI), 50 μg each of individual inorganic species (which are likely to coexist with uranium in nuclear spent fuel) were equilibrated with 0.1 g of CP_5 or IIP_5 particles and the preconcentrated amounts of these elements were ascertained by spectrophotometry or FAAS after elution with 10 ml of 1.0 mol l^{-1} HCl. The percent extraction, distribution ratio and selectivity coefficients of uranium(VI) with respect to other inorganics using CP_5 and IIP_5 particles are shown in *Table 6.10.* As seen from the table, the selectivity coefficients for IIP_5 particles are much higher compared to CP_5 particles. This observation is attributed to significant imprinting effect. It is clear from *Table 6.10* that uranium(VI) can be recovered selectively from several inorganic species.

6.8 RETENTION EFFICIENCY OF THE POLYMER PARTICLES

The maximum amount of uranium(VI) preconcentrated per gram viz retention/binding capacity of CP_5 or IIP_5 was calculated by saturating 0.1 g of polymer particles with 40 - 600 mg l^{-1} of uranium(VI) in 25 ml of solution under optimal conditions. The results are shown in *Fig.6.8.* It can be seen that the retention capacity increases with increase of initial uranium(VI) concentration and reaches a plateau at 14.3 (CP_5) and 98.5 (IIP_5) mg per g of the polymer when the uranium(VI) concentration is greater than 480 mg l^{-1}. As seen from the *Fig.6.8*, the retention capacities for IIP_5 particles are higher than CP_5 at all initial concentrations of uranium(VI).

Table 6.10 Percent extraction (%E), distribution ratio (D) and selectivity coefficient ($S_{U(VI)}/_{M}{}^{n+}$) of CP_5 and uranium(VI) IIP_5 particles

Metal ion	**Analysis procedure**	**%E**		**D (x 5x 10^3)**		**$S_{U(VI)}/_{M}{}^{n+}$**	
		CP_5	**IIP_5**	**CP_5**	**IIP_5**	**CP_5**	**IIP_5**
U(VI)	Spectrophotometry	13.2	> 99	0.15	99	-	-
Th(IV)	”	52.3	49.0	1.10	0.96	0.14	103
La(III)	”	63.9	28.6	1.77	0.40	0.08	248
Nd(III)	”	48.8	9.7	0.95	0.11	0.16	900
Sm(III)	”	64.4	16.2	1.81	0.19	0.08	521
Gd(III)	”	52.2	12.0	1.10	0.14	0.14	707
Ce(IV)	”	45.2	36.6	0.82	0.58	0.18	171
Zr(IV)	”	41.5	37.5	0.71	0.60	0.21	165
Pd(II)	FAAS*	0.3	10.6	0.003	0.12	50	825
Cu(II)	”	0.5	2.0	0.01	0.02	15	4950
Zn(II)	”	14.1	2.9	0.16	0.03	0.94	3300
Co(II)	”	0.9	1.4	0.01	0.01	15	9900
Ni(II)	”	2.9	10	0.03	0.11	1.4	900
Mn(II)	”	3.5	4.5	0.04	0.05	3.0	1980
Pb(II)	”	22.7	71.4	0.29	2.49	0.52	40
Cd(II)	”	< 0.1	6.0	0.001	0.06	150	1650
Fe(III)	”	42.9	57.7	0.74	1.36	0.20	73
Cr(VI)	”	< 0.2	7.2	0.002	0.08	751	237
Au(II)	”	1.5	< 0.3	0.01	0.003	15	$3.3x10^4$

*FAAS – Flame atomic absorption spectrometry

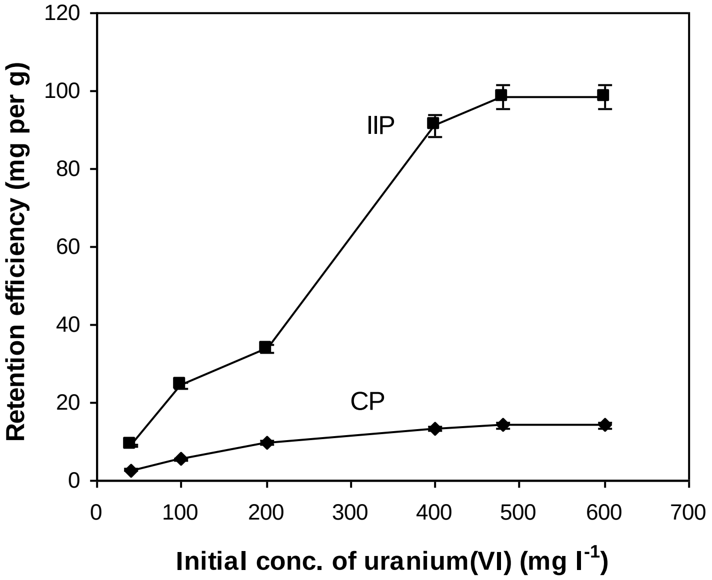

Fig.6.8 Retention efficiency of CP_5 and IIP_5 particles as a function of uranium(VI) concentration

6.9 RECOVERY OF URANIUM FROM SYNTHETIC NUCLEAR SPENT FUEL

The recovery of 0.25 - 400 mg of uranium present in 500 ml of a solution of synthetic nuclear spent fuel (prepared based on the composition listed in *Table 6.1*) was tested using 0.1 g of IIP_5 particles under the optimal experimental conditions. The results on the percent recovery of uranium is shown in *Table 6.11*. It was concluded that uranium which is present to an extent of ~150 mg l^{-1} can be selectively recovered from synthetic nuclear spent fuel.

Table 6.11 Recovery of uranium from synthetic nuclear spent fuel

S.No.	Amount of uranium(VI) in synthetic spent nuclear fuel (mg 0.5 l^{-1})	% Recovery of uranium(VI)
1	0.25	>99.0
2	0.50	>99.0
3	10	>98.5
4	50	>98.5
6	300	>98.0
7	400	62.5 ± 0.5

6.10 EXPERIMENTAL

6.10.1 Instrumentation

A Shimadzu UV 2401 PC controlled spectrophotometer (Shimadzu, Japan) and an LI-120 digital pH meter (ELICO, India) were used for absorbance and pH measurements respectively. A Perkin Elmer AAnalyst –100 flame atomic absorption spectrometer (Perkin Elmer, USA) was used for determining inorganic species which are likely to coexist with uranium in nuclear spent fuel. FTIR spectra were recorded in the frequency range 4000 - 400 cm^{-1} by KBr pellet method using Prestige – 21 IR Spectrometer (Shimadzu, Japan). The surface morphology of the IIP particles was studied using scanning electron microscope (SEM) (JEOL, Model JSM 5600 LV). The X- ray diffraction (XRD) patterns were obtained using Cu K_α X-raysource and Philips PW 1710 diffractometer (Holland).

6.10.2 Reagents and Materials

A stock solution (1000 $\mu g\ ml^{-1}$) of uranium(VI) was prepared by dissolving appropriate amount of uranyl nitrate ($UO_2(NO_3)_2.6H_2O$) (Aldrich, USA) in deionized water. Salicylaldoxime (SALO) and Arsenazo III were purchased from Aldrich, USA. The concentration of uranium(VI) was monitored spectrophotometrically by forming binary complex with Arsenazo III (0.1 g of reagent was dissolved in 100 ml of deionized water). 1.0 mol l^{-1} sodium acetate – acetic acid buffer (pH 3.5) was prepared to maintain the pH of the aqueous phase (3.5 ± 0.3) during preconcentration. Styrene, 4-vinyl pyridine (VP), divinyl benzene (95%) (DVB) and 2, 2'-azobisisobutyronitrile (AIBN) were obtained from Aldrich, USA. All other chemicals were of analytical reagent grade.

6.10.3 Preconcentration Procedure

A portion of the solution containing 5-250 μg of uranium(VI) was diluted to 500 ml and the pH was adjusted to 3.5 ± 0.3 after the addition of 5.0 ml of 1.0 mol l^{-1} sodium acetate-acetic acid buffer. Leached polymer particles (0.1 g) were added to the above solution and stirred for 10 min. The uranium(VI) preconcentrated onto polymer particles were eluted with 10 ml of 1.0 mol l^{-1} HCl by stirring for 10 min. The uranium(VI) content was determined spectrophotometrically using Arsenazo III method. Suitable aliquots of eluent were taken and 2.5 ml conc. HCl and 2.5 ml of 0.1% Arsenazo III were added and diluted to 25 ml. The absorbance of uranium(VI) – Arsenazo III complex was measured at 656 nm.

6.10.4 Recovery of Uranium from Synthetic Nuclear Spent Fuel

Nuclear spent fuel was prepared synthetically as per the composition listed in *Table 6.1*. The recovery of 0.25 - 400 mg of uranium present in 500 ml of solution of synthetic nuclear spent fuel was tested using 0.1 g of IIP_5 particles under the optimal experimental conditions described above.

6.11 SUMMARY

Thanks to its predetermined selectivity, ion imprinted polymers find extensive applications in solid phase extraction/preconcentration of valuable metals. Ion imprinted polymer particles were prepared using binary and mixed ligand ternary complexes of uranium(VI) imprint ion. These pre-polymer complexes were copolymerized with styrene and divinyl benzene in presence of AIBN. Finally, the uranium(VI) was leached out from the polymer. Control polymers were also prepared and subjected to the same pretreatment.

The methodology described in this chapter for the preconcentration of uranium(VI) offers simple and fast means for the preconcentrative separation of uranium(VI) from the ambience of a large number of inorganic species. Studies revealed that the polymer comprising of mixed ligand ternary complex alone could enrich uranium(VI) quantitatively. It is again obvious from the results that the uranyl ion imprinted particles are quite potential as solid phase extractant as it offers a high binding capacity of 98.5 mg per g of the polymer.

Further it was demonstrated that the uranium(VI) imprinted material is suitable for the recovery of uranium from weakly acidic nuclear spent fuel.

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CHAPTER 7

ONLINE SPE PRECONCENTRATION OF ZINC IN FRACTIONATED SOIL SAMPLES AND DETERMINATION USING FAAS

Solid phase extraction (SPE) is currently used as a preconcentration/ separation procedure when the concentration of analytes in complex materials are low. SPE has become the method of choice in many laboratories for the analysis of complex real samples because of the ease of automation, low reagent consumption, absence of emulsion formation and flexibility [1]. Further, SPE is often regarded as environmentally friendlier as large volumes of toxic solvents are not used unlike in liquid-liquid extraction [2,3]. Flow injection (FI) on-line SPE preconcentration and matrix separation is a powerful technique which effectively enhances the selectivity, sensitivity and precision of flame atomic absorption spectrometry (FAAS) [4,5].

The growing interest in the use of flow injection analysis (FIA) in conjunction with FAAS technique was highlighted in several reviews. The FI manifold for online loading and elution sequences is shown in *Fig 7.1*. FIA is mainly used for online preconcentration based on sorbent extraction in which a sample (for the determination of the element of interest) and a suitable chelating reagent are allowed to mix up and passed through a micro column packed with suitable sorbent material for adsorbing the metal chelates selectively. The sorbed metal chelates were eluted with suitable solvents, pumped through the peristaltic pump. The total operations are computer controlled. This leads to better precision in addition to enhancement in the sensitivity, reproducibility and sample throughput.

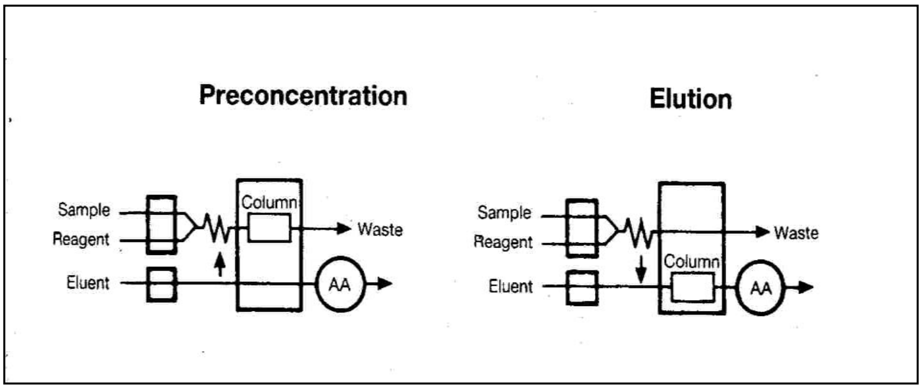


Fig.7.1 FI manifold diagram

Zinc is an essential element for the growth of human beings and animals. Experiments showed that zinc deficient animals require 50% more food to gain the same weight as an animal supplied with sufficient zinc. Zinc is a micro nutrient and activates enzymes in plants and hence zinc is an important requirement for the satisfactory growth of plants. Zinc is also essential for the maintenance of certain growth substance (auxin) and is involved in protein synthesis. Zinc deficiency results in chlorosis and interveinal yellowing on young leaves, reduces leaf size and shortens internodes in addition to various growth abnormalities. Excess zinc may cause iron deficiency in some plants [6]. Hence, the routine monitoring of zinc in soils, which lie in the range of 1-80 mg/kg, is utmost important [7].

FIA-FAAS method proposed for molybdenum was based on the on line solid phase extraction of its quinoline-8-ol complex onto C_{18} bonded silica gel micro column [8]. Yebra *et al* [9] determined copper in sea water by using FIA-FAAS containing minicolumn packed with Amberlite XAD-4 impregnated with 1-(2-pyridylazo-2-naphthol). Karthikeyan *et al* [10] reported on-line FIA-FAAS method for the determination of copper, cadmium and lead in marine samples after adsorption of their dithizone complexes onto C_{18} bonded silica gel. Further, a rapid and sensitive online FIA-FAAS procedure was described for multielement (iron, cobalt, nickel, manganese and zinc) determination after complexing them with 5,7-dichloroquinoline-8-ol and passing through C_{18} bonded silica gel microcolumn [11].

The salient features of various FIA procedures developed for the determination of ultra trace amounts of zinc are summarized in *Table 7.1.* The systematic investigations carried out using 1-(2-thiazolylazo)-2-naphthol (TAN) as chelating agent led to the development of rapid, reliable, precise and sensitive online FIA-FAAS procedure for the ultratrace determination of zinc.

Table 7.1 ***Summary of FIA procedures developed for determination of zinc since 1990***

S.No	**Detection technique**	**Detection limit (ng ml^{-1})**	**Linear range (μg ml^{-1})**	**Application**	**Ref.**
1.	UV-Visible	-	-	-	[12]
2.	Fluorescence	3	-	-	[13]
3.	Flame AAS	-	-	-	[14]
4.	Flame AAS	100	0.1-0.5	-	[15]
5.	Flame AAS	1	-	-	[16]
6.	Flame AAS	-	-	-	[17]
7.	Flame AAS	0.5	0.0005-0.05	Marine sediment and sea plant	[11]
8.	ICP AES	-	-	-	[18]
9.	ICP AES	3.6	0.01-20	-	[19]
10.	Flame AAS	0.15	0.0005-005	Soil samples	Present method

7.1 PRELIMINARY STUDIES

In preliminary studies, pump 1 of FIA was used for pumping sample and reagent through the microcolumn packed with C_{18} bonded silica gel for the online preconcentration. Pump 2 was used for pumping eluent through the column (see *Fig.7.1*). Manifold valve was changed to load or elute position through computer control. A typical FIA-gram will be displayed by plotting absorbance against time of elution using FIA-FAAS software.

Studies were conducted by passing zinc and 1-(2-thiazolylazo)-2-naphthol (TAN) solutions through microcolumn packed with C_{18} bonded silica gel for 60s. The effluent of microcolumn was found to have no zinc revealing that zinc-TAN complex is sorbed quantitatively on the column material. By pumping acidified methanol through pump 2 results in considerable enhancement in the zinc signal compared to conventional nebulization.

A detailed evaluation of various parameters responsible for the online SPE and determination using FAAS were carried out using TAN as the chelating agent for SPE of zinc onto C_{18} bonded silica gel.

7.2 OPTIMIZATION OF ANALYTICAL VARIABLES

7.2.1 pH Conditions

The influence of pH on the SPE of zinc with TAN was investigated by varying the pH in the range 8.0 - 11.0. In this study 5.0 μg l^{-1}solution of zinc was mixed with TAN solution, (adjusted to different pH values) and passed through a microcolumn packed with C_{18} bonded silica gel. The sorbed complexes were eluted with acidified methanol and aspirated into air-acetylene flame for the measurement of absorbance at 213.9 nm. The results obtained are given in *Fig. 7.2* which demonstrated that the complex formation and sorption efficiency are maximum in the pH range 9.5 - 10.5. Therefore the pH of the TAN reagent was adjusted to ~10.0 in the subsequent work.

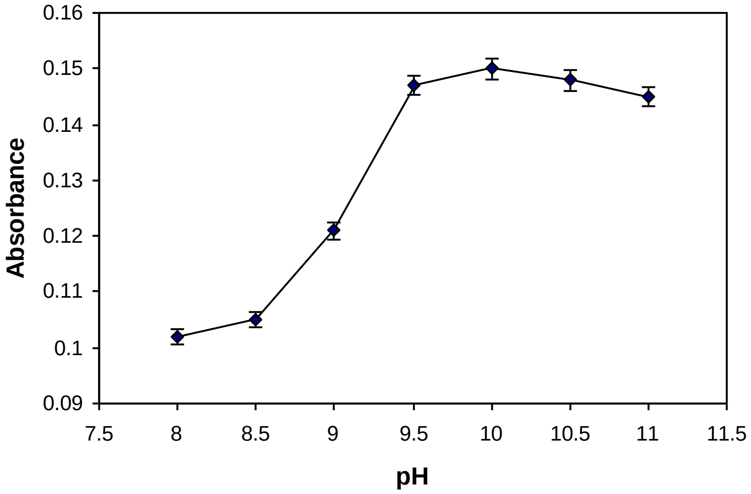


Fig.7.2 Effect of pH

7.2.2 Influence of Ammonia Concentration

The concentration of ammonia was varied in the range 0.1 - 1.0 mol l^{-1}. The preconcentration and determination were carried out as described in section 7.2.1. From *Fig.7.3*, it is clear that no significant influence on the retention efficiency was observed for the concentration range 0.5-1.0 mol l^{-1}. Therefore, TAN was prepared in 0.5 mol l^{-1} ammonia solution for the later studies.

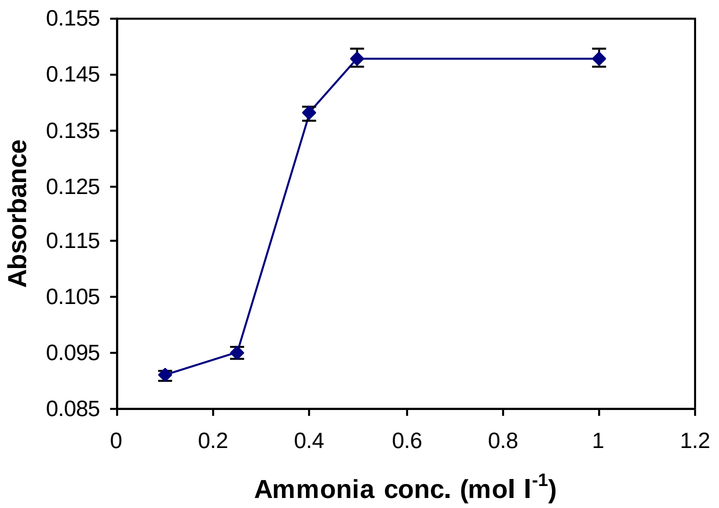


Fig.7.3 Effect of concentration of ammonia

7.2.3 Concentration of TAN

In order to study the influence of TAN concentration in the complex formation, the concentration of TAN was varied from 0.002 to 0.01%. Sample and reagent were pumped simultaneously through the column during loading, eluted with acidified methanol, and fed to the nebulizer of FAAS. No significant influence on retention efficiency was observed for TAN concentration in the range 0.005 – 0.01% (see *Fig.7.4*). Therefore, 0.005% TAN was used in the later work.

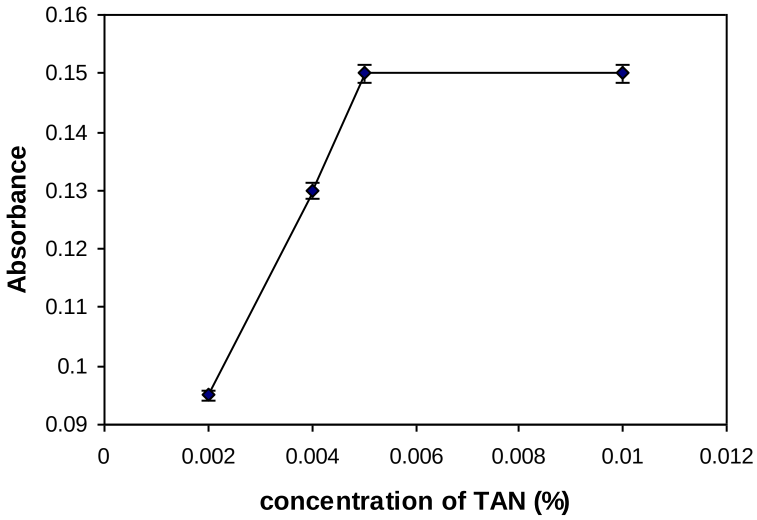


Fig. 7.4 Effect of TAN concentration

7.2.4 Selection of Eluent and its Acidity

In order to choose the best eluent for the desorption of zinc preconcentrated on C_{18} bonded silica gel, various water miscible solvents (acidified to pH >2.0) such as methanol, dimethyl formamide, dimethyl sulphoxide and acetonitrile were tested. Methanol gave the highest absorbance compared to other solvents and hence the same was chosen for subsequent studies. The optimum acidity of the methanol eluent was investigated by varying nitric acid concentration in the range 0.001 - 0.1 mol l^{-1}. 0.01 to 0.1 mol l^{-1} of nitric acid in methanol was found to elute sorbed zinc quantitatively from C_{18} bonded silica gel microcolumn. Hence, in subsequent studies methanol acidified to ~0.01 mol l^{-1} with nitric acid was used.

7.2.5 Influence of Loading time

For establishing a linearity with respect to preconcentration time, the sample solution was passed through a micro column for different preconcentration times ranging from 30 to 300 s (*Fig. 7.5).* The preconcentrated zinc was eluted with acidified methanol and introduced into the nebulizer for its determination. Linearity was observed over the entire range. However, an optimum time of 60 sec was selected for rapid analysis with reasonable sensitivity and sufficient sampling frequency.

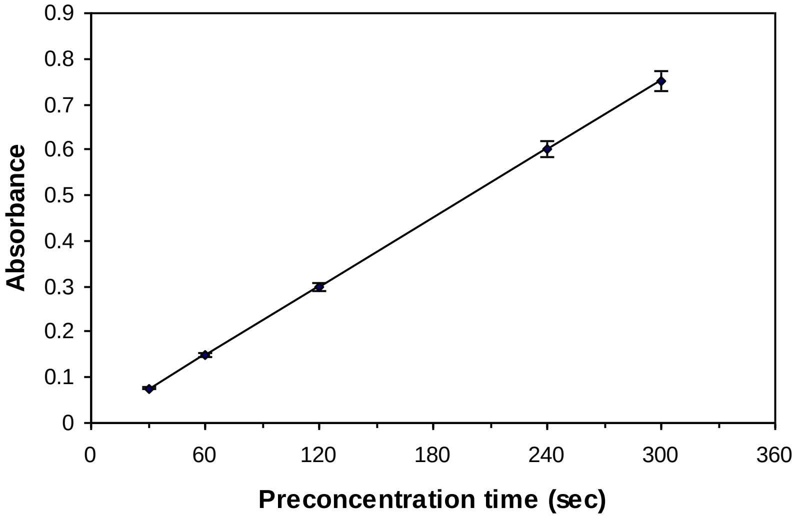


Fig .7.5 Effect of preconcentration time

7.3 OPTIMIZATION OF FIA PARAMETERS

7.3.1 FI Flow Condition Optimization

High sample loading flow rates are important for efficient preconcentration and high sample throughput. In general, FI sample flow rates are limited due to the back pressure produced by the column and/or sorption efficiency which decreases with the decreasing flow rate. No degradation insorption efficiency was observed upto a loading flow rate of 10.0 ml min^{-1} of the sample and reagent which is the highest flow rate that can be handled with reproducibility by the peristaltic pump and the type of column used in this work. The reagent flow rate should not be too low so as to ensure good mixing of the reagent and sample solutions. Optimum sample and reagent flow rates were found to be 7.0 and 3.0 ml min^{-1} and these flow rates were used in subsequent experiments.

An optimum elution flow rate of 4.0 ml min^{-1} was selected, which provides optimum sensitivity and elution peaks with minimum tailing. No provision was made to compensate for the lower flow rate delivered by the FI system, however, the transfer capillary to the nebulizer (PTFE, 0.3 mm i.d) restricted the uptake rate to values close to the flow rate provided by the FI system. Operating the nebulizer at this flow rate does not lower the sensitivity in proportion to the decrease in flow rate because of the potential improvements in the nebulizer efficiency under starved conditions [11, 20]. The lower sample flow rate in the FI mode in comparison to the conventional free uptake of the nebulizer is also beneficial for the droplet diameter distribution, which results in smaller droplets and is therefore less prone to vaporization interferences.

7.3.2 Performance of Online Preconcentration System

The characteristic data for the performance of the on-line preconcentration system are summarized in *Table 7.2*. The efficiency of SPE was investigated by analyzing the previously collected column eluent from a standard solution of zinc and using the same preconcentration technique. From the results obtained by the repeated preconcentration, a retention efficiency of >99% was calculated for zinc. Further, loading time of 1.0 min allows a sampling frequency of 30 per hour. Higher sensitivities can be obtained by modifying the method i.e, using a longer preconcentration period at the expense of lower sample throughput.

Table 7.2 Analytical performance data

Linear range	0.5-50 μg l^{-1}
Sensitivity enhancement[a]	120
Concentration efficiency[a]	120
Precision(RSD[b])(at 5.0 μg l^{-1})	1.55%
Sample consumption	7.0 ml
Loading time	60s
Sample frequency	30 h^{-1}
Detection limit(3σ)	0.15 μg l^{-1}

a. compared to conventional nebulization
b. n = 10

7.3.3 Calibration Graph

Calibration graph was obtained using zinc solutions of different concentrations. Detailed FIA programme for on-line preconcentration and elution is described in section 7.3.1. The calibration plot is a straight line in the range 0.5 - 50 µg l^{-1} of zinc passing through the origin. The linear equation with regression is as follows.

$A=0.00085+0.0299C$

Correlation coefficient is 0.9985,

where A is the absorbance and C is the concentration of zinc in μg l^{-1}. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

7.3.4 Sensitivity and Precision

The precision of the developed procedure was established by carrying out ten replicate determinations using 5.0 µg l^{-1} zinc by following the general procedure. The results are shown in *Table 7.3*. The overall precision of ten successive determinations of 5.0 µg l^{-1} of zinc was calculated to be 1.55% which indicates that the SPE-elution sequence is highly reproducible. The detection limit corresponding to 3 times the standard deviation of the blank was found to be 0.15 µg l^{-1} for zinc.

Table 7.3 Precision studies

S.No	**Absorbance**	**Zn found (µg) X_n**	**$X_n - \overline{X}$**	**$(X_n - \overline{X})^2$**
1	0.151	5.0	-0.051	0.0026
2	0.155	5.13	0.079	0.0062
3	0.154	5.09	0.039	0.0015
4	0.153	5.07	0.019	0.0004
5	0.148	4.9	-0.151	0.0228
6	0.155	5.13	0.079	0.0062
7	0.151	5.0	-0.051	0.0026
8	0.155	5.13	0.079	0.0062
9	0.149	4.93	-0.021	0.0004
10	0.155	5.13	0.079	0.0062

$\overline{X} = 5.051$ $\Sigma (X_n - \overline{X})^2 = 0.0551$

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

$\sigma = 0.0782$

Relative Standard Deviation (R.S.D) = 1.55%

7.4 INTERFERENCE STUDIES

The tolerance of maximum concentrations of coexisting ions usually present in soil samples and neutral electrolytes in the determination of 5.0 µg l^{-1} of zinc was systematically studied by the FIA-FAAS procedure. Any deviation greater than 3% from the standard absorbance value was taken as interference. The maximum concentration of neutral electrolytes and coexisting ions which do not cause reduction in FIA-FAAS signal of zinc are: NaCl (0.1 mol l^{-1}), $NaNO_3$ (0.1 mol l^{-1}), Na_2SO_4 (0.1 mol l^{-1}), Fe, Zn, Co, Ni or Mn (50 μg ml^{-1}) and Cr or Mo (200 μg ml^{-1}). These observations suggest that the developed procedure can reliably be used for the determination of zinc in soil samples.

7.5 APPLICATIONS

The determination of distinct chemical species, often referred to as speciation, is now widely acknowledged to be of vital importance in environmental analysis. Whilst it is often possible to define a particular compound or oxidation state when dealing with solution, for example, natural water, it is far more difficult to characterize the actual form of an element in solids such as soil [21]. Pickering [22] has summarized the series of reagents used for fractionation of soil samples ranging from water to a strong chemical such as concentrated acid. Owing to the variety of the different fractionation procedures, the results were not comparable, as they were highly dependent on the procedure employed. In 1987, the Community of Bureau of Reference (BCR, now Standards, Measurements and Testing Programme) consisting of various European experts have started a programme to harmonize the methodology and reported (in 1994) a sequential fractionation scheme adopted in different stages [23,24].

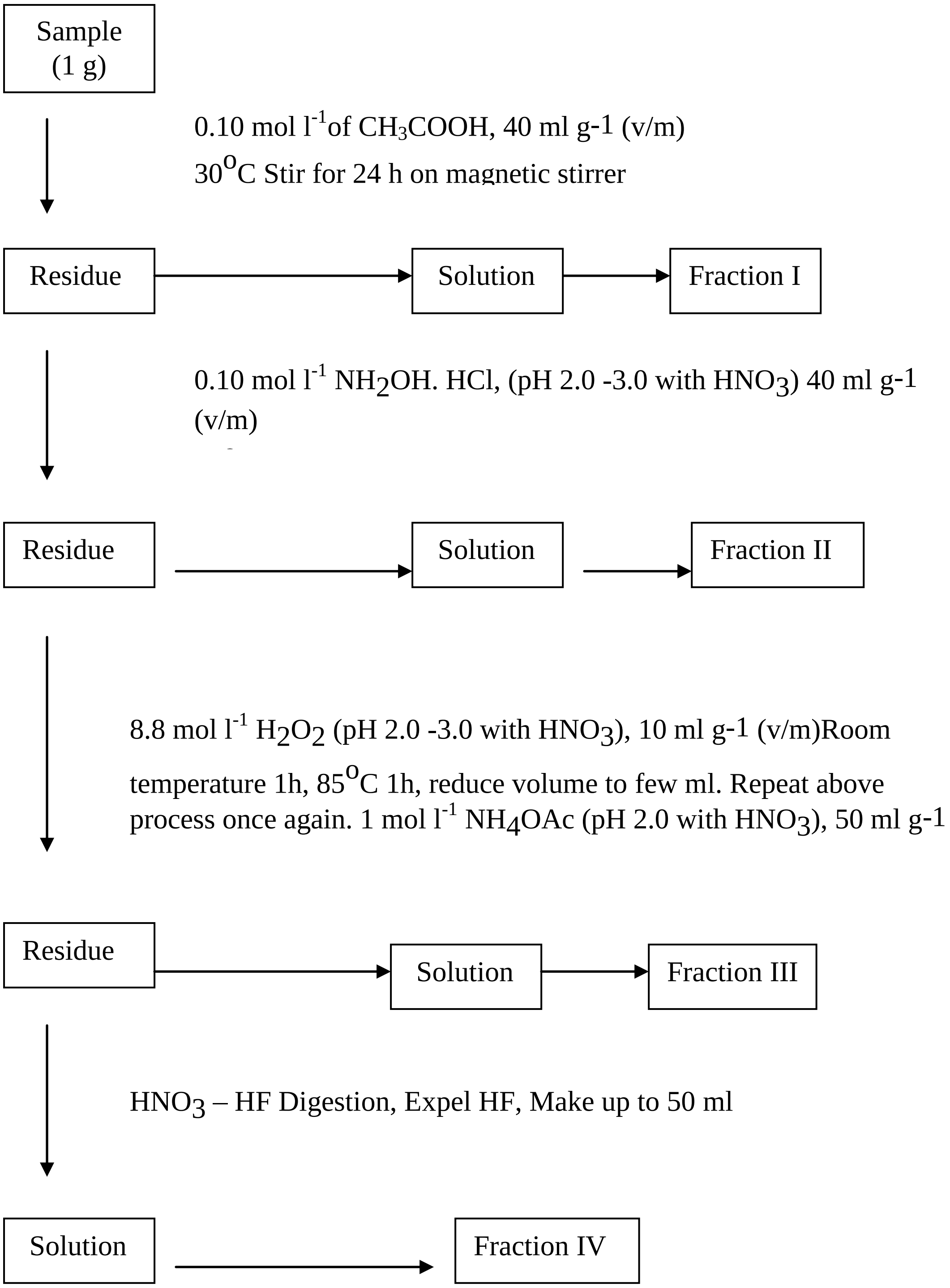
The soil samples collected from 12 stations were dried, powdered and subjected to modified BCR fractionation procedure (see S*cheme 7.1*). The applicability of the developed on-line FIA-FAAS was tested by analyzing four different fractions of soil samples. The results obtained by the developed FIA-FAAS procedure using direct and standard addition methods for zinc are summarized in *Table 7.4* from which following observations can be deduced.

1. The total amount of zinc present in soil samples varies from 0.185 (Mango garden at Stiles India, Mangapuram) to 0.991 μg per g of soil sample (voltarek electrodes, G.mandyam).
2. In all the samples fraction IV contains considerable amount of zinc compared to fractions I-III indicating that zinc is present not as exchangable/acetic acid soluble or bound to iron/manganese oxides or bound to organic matter which is leached under oxidizing conditions respectively.
3. In samples 2,4,9,10,11 and 12 considerable amount of zinc is leached in Fraction III indicating that zinc is bound to organic matter. Zinc content in Fraction II of samples 3&4 is not detectable by the present method indicating the absence of zinc bound to iron/manganese oxides.
4. Only one sample collected near Grindwell norton factory do not contain even traces of exchangeable/acetic acid soluble zinc.

7.6 EXPERIMENTAL

7.6.1 Instrumentation

A Perkin Elmer® Model AAnalyst™ 100 atomic absorption spectrometer (Perkin Elmer instruments, Shelton, CT, USA) with deuterium background correction and Lumina make zinc hollow cathode lamp were used. The instrumental parameters such as hollow cathode lamp current, wavelength and spectral band pass were 30 mA, 213.9 nm and 0.7 nm respectively. A standard air-acetylene nebulizer burner system was operated at an air flow rate 4.0 l min^{-1} and an acetylene flow rate of 1.0 l min^{-1}. The burner height was adjusted to about 30 mm from the base for optimum sensitivity. The nebulizer uptake rate was adjusted to provide optimum response for conventional sample aspiration (see *Fig.7.6*).



Scheme 7.1 Schematic diagram of the sequential extraction procedure to determine extractable trace metals in soils.

*Table 7.4 Analysis of Zn in soil samples (μg g-1)**

Sample Description	**Acetic Acid fraction (I)**		**Hydroxylamine HCl fraction (II)**		**H_2O_2 Fraction(III)**		**HF**
	Direct	**SA**	**Direct**	**SA**	**Direct**	**SA**	**Dir**
1. Near Madhu Industries, Agarala	0.060 ± 0.002	0.058 ± 0.002	0.009 ± 0.002	0.010 ± 0.002	0.02 ± 0.002	0.021 ± 0.002	0.11 0.0
2.Near Spartek Ceramics, Magapuram	0.050 ± 0.002	0.048 ± 0.002	0.039 ± 0.002	0.040 ± 0.002	0.291 ± 0.004	0.290 ± 0.005	0.06 0.0
3.Near Mango garden at Stiles india, Mangapuram	0.009 ± 0.002	0.010 ± 0.002	<0.002	<0.002	0.027 ± 0.002	0.025 ± 0.002	0.14 0.0
4.Mungilipattu fertile land	0.029 ± 0.002	0.028 ± 0.002	0.023 ± 0.002	0.022 ± 0.002	0.041 ± 0.002	0.040 ± 0.002	0.31 0.0
5.Near Sugar Factory G.Mandyam	0.008 ± 0.002	0.009 ± 0.002	<0.002	<0.002	0.120 ± 0.003	0.122 ± 0.003	0.26 0.0

Sample Description	**Acetic Acid fraction (I)**		**Hydroxylamine HCl fraction (II)**		**H_2O_2 Fraction(III)**		**HI**
	Direct	**SA**	**Direct**	**SA**	**Direct**	**SA**	**Dir**
6. Near Steel Factory	0.008 ± 0.002	0.008 ± 0.002	0.044 ± 0.002	0.040 ± 0.002	0.025 ± 0.002	0.025 ± 0.002	0.43 0.0
7.Near AmaraRaja Batteries	0.081 ± 0.003	0.080 ± 0.003	0.040 ± 0.002	0.040 ± 0.002	0.070 ± 0.003	0.069 ± 0.003	0.12 0.
8.Near Grindwell Norton factory	<0.002	<0.002	0.160± 0.004	0.158 ± 0.004	0.081 ± 0.003	0.080 ± 0.003	0.39 0.
9.Near Water Distilleries, G.Mandyam	0.161 ± 0.003	0.160 ± 0.003	0.166 ± 0.004	0.165 ± 0.004	0.213 ± 0.004	0.215 ± 0.004	0.41 0.0
10. Near Voltark Electrodes, G.Mandyam	0.106 ± 0.002	0.105 ± 0.002	0.140 ± 0.003	0.145 ± 0.003	0.319 ± 0.008	0.320 ± 0.008	0.42 0.0
11. Near Mango Garden Renigunta.	0.063 ± 0.002	0.161 ± 0.002	0.094 ± 0.002	0.095 ± 0.002	0.128 ± 0.003	0.130 ± 0.003	0.42 0.0
12. Near S.V. Sugars G.Mandyam	0.072 ± 0.002	0.075 ± 0.002	0.077 ± 0.002	0.074 ± 0.002	0.138 ± 0.003	0.140 ± 0.003	0.28 0.

*** Average of 3 determination, SA=Standard addition method**

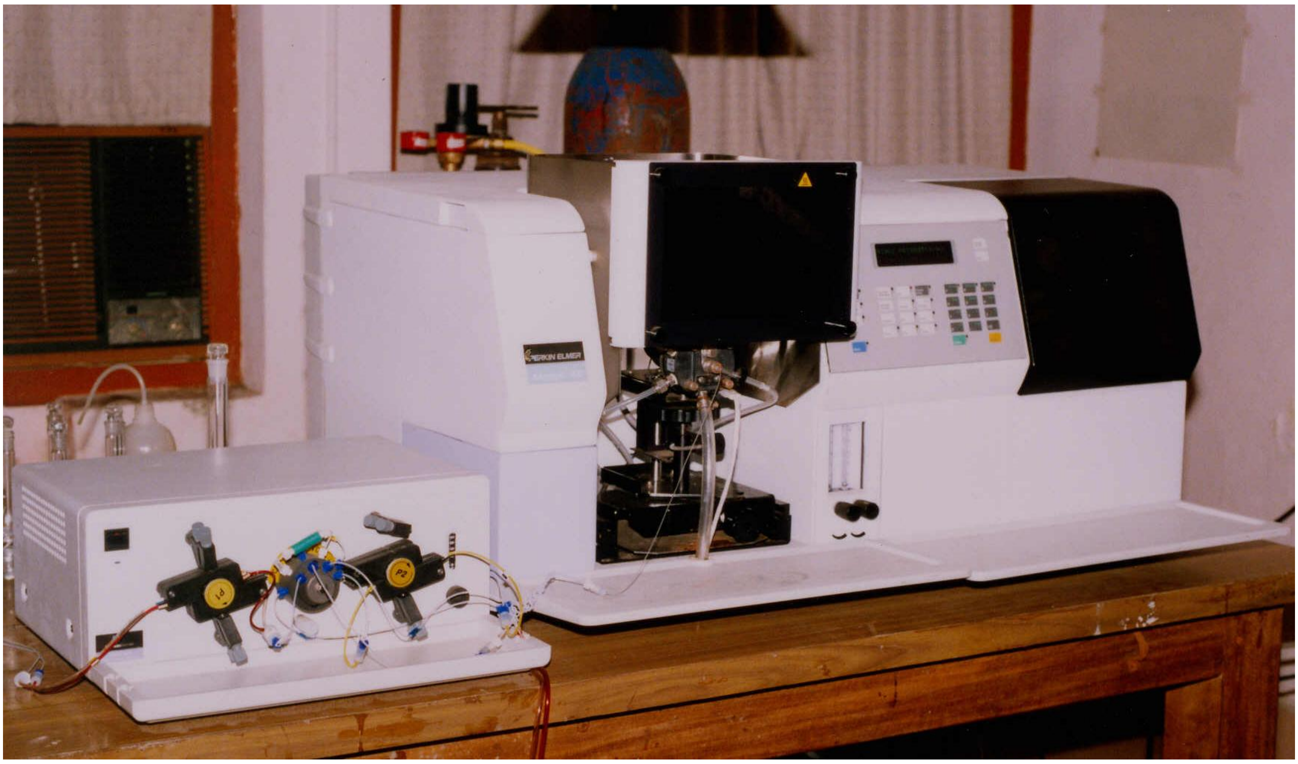


Fig.7.6: Flow Injection-FAAS for online preconcentration & Determination

A Perkin Elmer FIAS^{TM}-400 flow injection system connected to the spectrometer was used for the on-line preconcentration of zinc. The automatic operation of the injection valve and two multichannel peristaltic pumps were programmed using the spectrometer software (Winlab^{TM} V.3.0). Tygon® pump tubes were used to propel the sample and reagent solutions. PTFE tubing of 0.3 mm i.d was used for all connections in order to minimize dead volume. A commercially available conical shaped microcolumn of 50 μl capacity (Perkin Elmer Instruments, Shelton, CT, USA) packed with 20 mg of C_{18} bonded silica gel (40-60 μM) was used. Time resolved absorbance signals of zinc were displayed on the computer monitor and printed with peak height and integrated absorbance values.

7.6.2 Reagents

Stock standard solution of 1 mg ml^{-1} of zinc was prepared by dissolving appropriate amounts of zinc sulfate (Aldrich,USA) in deionized water. This solution was standardized by using EDTA titration procedure and the working solutions were prepared by suitable dilution.

1-(2-thiazolylazo)-2-naphthol (TAN) 0.005% (Aldrich, Milwaukee, WI.USA) was prepared in 0.5 mol l^{-1}of ammonia solution.

Methanol acidified to pH >2 with A.R. nitric acid was used for elution of the zinc adsorbed on the microcolumn. 0.5 mol l^{-1} (pH~10) NH_3-NH_4Cl buffer was used for pH adjustment.

7.6.3 General Procedure

The FIAS programme was run as given in *Table 7.5* to pump sample and TAN containing buffer solution. The zinc and TAN solutions were mixed on-line and loaded through the microcolumn for 60 sec. The sorbed complex was eluted with acidified methanol using pump 2 and aspirated to FAAS for measurement of absorbance signal at 213.9 nm. The complete operation programme is depicted in *Table 7.5*.

Table 7.5 Sequence of opearations for online FI sorbent extraction preconcentration for the determination of zinc by FIA-AAS

Stages of operation	**Time (s)**	**Pump 1 (ml min^{-1})**	**Pump 2 (ml min^{-1})**	**Valve position**	**Pumped medium**	
					Pump 1	**Pump 2**
prefill	20	7.0 3.0	4.0	elute	Sample, TAN	methanol
load	40	7.0 3.0	off	load	Sample, TAN	–
wash tubings	20	7.0 3.0	4.0	load	Sample, TAN	methanol
elution	20	off	4.0	elute	off	methanol

7.6.4 Analysis of Soil Samples

7.6.4.1 Fractionation Procedure

The soil samples collected from 12 different stations were dried and ground to fine powder. About 1.0 g of soil sample was weighed and then fractionated as per S*cheme 7.1*. The four fractions collected for each sample was subjected to online SPE preconcentration and flame AAS determination of zinc.

7.7 SUMMARY

A flow injection on-line SPE preconcentration system coupled to FAAS was developed for the determination of zinc at μg l^{-1} level. Zinc was complexed with TAN in the pH range of 9.5 – 10.5 in the flow injection system and adsorbed onto a C $_{18}$ bonded silica gel microcolumn. The preconcentrated zinc-TAN complex was eluted with acidified methanol and injected directly into the nebulizer of FAAS for measurement. The developed procedure is precise, rapid and allows the analysis of 30 samples per hour with a loading time of 1.0 min. Again, flow injection provides a simple means of total automation, eliminating manual operations resulting in a better precision of 1.55% during the ten successive determinations of 5.0 μg l^{-1} of zinc solution. The on-line FI manifold used in the present study permits high sampling loading rates, resulting in a higher preconcentration/enrichment factor of 120 with 1.0 min loading time compared to conventional FAAS. No significant interference was observed from neutral electrolytes and coexisting ions that are usually present in soil samples. The FI-FAAS method was applied successfully in the analysis of soil samples which were fractionated as per the modified BCR methodology (now Standards, Measurements and Testing Programme).

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CHAPTER 8

CONCLUSIONS

Preconcentration techniques adopted by various researchers are based on physical, physio-chemical and chemical principles. Hitherto, liquid-liquid extraction (LLE) is most often used due to its simplicity, rapidity and ready adaptability to scale up and easy recovery of analyte and extractant. Recently, solid phase extraction (SPE) is replacing LLE due to the several advantages it offers. These include,

i) higher enrichment factors
ii) absence of emulsion
iii) low costs due to low consumption of reagents
iv) flexibility
v) ease of automation and
vi) environmental friendly.

The introductory part of the thesis brings out the need of developing newer preconcentrative separation procedures for inorganics based on solid phase extraction for the determination of toxic/nutrient elements present at trace levels.

Due to the greater flexibility, operational stability and simplicity of the equipments required, offline SPE is still playing a significant role in analytical chemistry. 5,7-dichloroquinoline-8-ol and dicyclohexano-18-crown-6 embedded benzophenone SPE materials were prepared and had been used for trace enrichment of thorium(IV) (Chapter 2) and uranium(VI) (Chapter 3) respectively. The metal enriched SPE materials were subjected to analysis using Arsenazo III spectrophotometric method. The developed procedures had been successfully employed for the analysis of thorium(IV) in mixed rare earth chloride concentrate and uranium(VI) in soil and sediment samples.

Offline batch and column preconcentration procedures were developed for separation of uranium(VI) in presence of various neutral electrolytes and coexisting ionic species that are likely to present in soil and sediment samples using 1-(2-pyridylazo)-2-naphthol (PAN) embedded bezophenone/naphthalene (Chapter 4) and 1-(2-thiazolylazo)-2-naphthol (TAN) sorbed activated carbon (Chapter 5). The accuracy of the developed preconcentrative separation procedures were tested by analyzing marine sediment certified reference material supplied by National Research Council, Canada. In addition, the developed procedures permit the analysis of soils and sediment samples using simple, low cost and readily available spectrophotometer. The results obtained by the developed methods compare favorably with standard ICP-MS values. The retention capacities of various SPE materials prepared are in the order TAN sorbed activated carbon > PAN embedded benzophenone/naphthalene > DC18C6 embedded benzophenone > DCQ modified naphthalene for uranium(VI).

Molecular imprinting is a popular technology for the preparation of polymeric materials of high molecular recognition. Ion imprinted polymers (IIP) are particularly attractive in separation studies as they are having predetermined selectivity. Uranyl ion imprinted polymers were prepared using vinyl pyridine and salicylaldoxime (Chapter 6). Greater extraction efficiency of the imprinted polymers could be attributed to the imprinting effect noticed during the study. These polymers can be used for the recovery of uranium(VI) from a complex matrix as it offered high separation factor over most of the coexisting species. Retention capacity of the polymers was found to be high (98.5 mg per g). These ion imprinted polymers were used for the selective recovery of uranium from synthetic nuclear spent fuel.

Manually operated separation and preconcentration procedures (batch or column) are usually tedious and time consuming with the risk of losses and contamination. On the other hand, online flow injection SPE preconcentration approach has several virtues over the above mentioned offline SPE procedures. The flow injection online preconcentration coupled with flame AAS procedure developed during the present study allows the determination of zinc at $\mu g\ l^{-1}$ levels. Zinc is complexed with TAN in the flow injection system and adsorbed onto a C_{18} bonded silica gel microcolumn. The sorbed complex was eluted with acidified methanol and determined by FAAS. The developed method was successfully applied in the analysis of soil samples which were fractionated as per modified BCR (now Standards, Measurements and Testing programmes). The instrumentation adopted in the present study is simpler and of low maintenance costs compared to costlier ICP-AES or ICP-MS instruments.

8.1 ENVISAGED OUTCOME OF THE PRESENT INVESTIGATION

(i) Removal of toxic uranium(VI) present in various environmental matrices.
(ii) Recovery of uranium(VI) from synthetic nuclear spent fuel.
(iv) Chemical speciation of soils for a micronutrient like zinc.

8.2 FUTURE OUTLOOK

(i) Synthesis of new materials for SPE procedures.
(ii) Developing functionalized polymers and highly crosslinked sorbents.
(iii) Developing new molecularly/ion imprinted polymers in order to monitor a wider range of micropollutants in water samples by the selective SPE of specific groups of analytes.
(iv) Developing new polymers by imprinting uranium-macrocyclic complex template for recovery of uranium from strongly acidic conditions.
(iv) Standardization of chemical speciation methodology proposed in the work to suit Indian context.

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