

OFFLINE AND ONLINE SOLID PHASE EXTRACTION/PRECONCENTRATION OF INORGANICS

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By
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under the supervision of
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July 2005

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**OFFLINE AND ONLINE SOLID PHASE EXTRACTION/
PRECONCENTRATION OF INORGANICS**

**July
2005**



Dedicated to
Rev. Fr. Arul Devadhasan &
Late Rev. Fr. Lucas

DECLARATION

I hereby declare that the thesis entitled **“OFFLINE AND ONLINE SOLID PHASE EXTRACTION/PRECONCENTRATION OF INORGANICS”** embodies the results of bonafide research work carried out by me for the degree of **Doctor of Philosophy** in Chemistry under the Faculty of Science of the Cochin University of Science and Technology under the guidance of **Dr. T. Prasada Rao**, Regional Research Laboratory (CSIR), Thiruvananthapuram. I further declare that this thesis or a 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 thesis entitled '**Offline and Online solid phase extraction/preconcentration of inorganics**' embodies the results of bonafide research work done by **Mr. A. Maria Starvin** for the degree of **Doctor of Philosophy** in Chemistry under the Faculty of Science of Cochin University of Science and Technology under my guidance. The content of this thesis or a part thereof has not been submitted to any other university or institute for the award of any degree or diploma.

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ABSTRACT

Solid phase extraction (SPE) is a powerful technique for preconcentration/removal or separation of trace and ultra trace amounts of toxic and nutrient elements. SPE effectively simplifies the labour intensive sample preparation, increase its reliability and eliminate the clean up step by using more selective extraction procedures. The synthesis of sorbents with a simplified procedure and diminution of the risks of errors shows the interest in the areas of environmental monitoring, geochemical exploration, food, agricultural, pharmaceutical, biochemical industry and high purity metal designing, etc.

There is no universal SPE method because the sample pretreatment depends strongly on the analytical demand. But there is always an increasing demand for more sensitive, selective, rapid and reliable analytical procedures. Among the various materials, chelate modified naphthalene, activated carbon and chelate functionalized highly cross linked polymers are most important. In the biological and environmental field, large numbers of samples are to be analysed within a short span of time. Hence, online flow injection methods are preferred as they allow extraction, separation, identification and quantification of many numbers of analytes.

Chapter 1 deals with general introduction to solid phase extractive preconcentration and techniques adopted for the preconcentration.

Chapter 2 describes the determination of mercury (II) in Biological samples, such as hair using quinolin-8-thiol modified naphthalene as a solid phase extractant. The preparation of above mentioned material is very simple and the mercury (II) coprecipitated on naphthalene is simply dissolved in acetone for subsequent determination using dithizone procedure. Various parameters that influence the preconcentration of mercury (II) by solid phase extraction are systematically optimized and results obtained are discussed in this chapter.

Chapter 3 concerns with the removal of mercury (II) from hazardous wastes particularly brine sludge and effluent of chlor alkali industry with the use

of solid phase extractant 1-(2-thiazolylazo)naphthol (TAN) sorbed activated carbon. Various optimization studies are described in detail along with a flow chart.

Chapter 4 describes the selective preconcentration of uranium (VI) using Diarylazobisphenol modified activated carbon as solid phase extractant. The preparation of Diarylazobisphenol modified activated carbon is simple, and the uranium (VI) sorbed on Diarylazobisphenol modified naphthalene was eluted with suitable reagent for subsequent determination by spectrophotometry using Arsenazo III procedure. Various parameters that influence the preconcentration of uranium (VI) by solid phase extraction were systematically optimized, and its accuracy was tested by analyzing marine sediment reference material (MESS-3). Furthermore, the applicability of the procedure for determining uranium (VI) in soils and sediments are described.

Chapter 5 concerns with synthesis and characterization of the resin Amberlite XAD-4 functionalized with various β -diketones and its application in an off line preconcentration of thorium (IV) in column mode from a host number of other lanthanide elements (Rare earth chlorides). Since, Amberlite XAD-4 polymeric adsorbent has excellent physical, chemical and thermal stability, this SPE material can be reused via repeated cycles to preconcentratively separate thorium (IV) from dilute solutions. The influence of various cations and anions on the preconcentration of thorium (IV) has been studied. Furthermore, the thorium (IV) content in rare earth chloride has been established by using the above method.

Chapter 6 concerns with the development of on-line flow injection-flame atomic absorption spectrometry (FI-FAAS) technique for the determination of cobalt and nickel at $\mu\text{g/l}$ level, using commercially available C_{18} bonded silica gel microcolumn loaded with orthodihydric phenols. The preconcentration and elution sequence is highly reproducible. One minute loading allows a sampling frequency of 30/h. In addition, a linear relationship was observed between loading time and enrichment factor and thus enhancing sensitivity at the expense of

number of samples that can be analysed in an hour. The validity of the developed method carried out by analyzing certified Hair reference materials soil and sediments for cobalt and nickel. Again, the developed method has been applied successfully to the analysis of real human hair, soils and sediment samples collected at various geographical locations.

Chapter 7 concerns the conclusions and suggestions for the future work based on the results obtained in the present investigations.

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CHAPTER 1

INTRODUCTION

1.2 TRACE ANALYSIS

The study of trace elements is of great importance because of (i) their importance for the growth and development of living being and (ii) their environmental toxicity. Many metallic and non-metallic elements like Co, Ni, Cu, Zn etc are essential for growth of life along with C, H₂, O₂, N₂, Na, K. Yet, the presence of these elements or their compounds in excess is hazardous for the metabolic processes of life. Selenium which is required in exiguous amounts by living organisms may be toxic if it exceeds certain levels and cause cancer in cattle. Cadmium was reorganized as an occupational hazard a century ago, on the basis of its acute toxicity.

Some elements which are found in the body tissues have no apparent physiological role and are found to be non-toxic. Examples include rubidium, strontium, titanium, niobium, boron, germanium and lanthanum. Various elements which have been used in medicine in non-nutritional roles include lithium, bismuth, antimony, bromine, platinum and gold. On the other hand lead, cadmium, mercury, arsenic, uranium etc. and their compounds are generally now identified as toxic.

Industrial wastes as well their products containing metallic elements are let into the environment indiscriminately which are hazardous to life. Though necessary steps are taken, pollution from industries is high and day-by-day it increases with the development of modern technology and taking a leading role in toxicology due to their fast reaction kinetics. Therefore trace analysis plays a vital role both in industry and government to monitor the environment, to protect the health and safety of the work force and to enforce regularity limits.

Powerful analytical tools were developed for the trace element determination because of the rapid growth in instrumentation. But it is often impossible to apply directly the various determination techniques of trace analysis, even after decomposition or dissolution of the sample because of i) the concentrations of desired elements well below the detection limit, i.e. too low a concentration to give reliable data and ii) the selectivity, i.e. determination of particular analyte in presence of extraneous species. Hence, preconcentration and/or separation prior to determination is an inevitable process in modern day trace analysis.

1.3 PRECONCENTRATION

Preconcentration also called enrichment is a generic term for various processes employed to increase the ratio of the amount of a desired trace element to that of the original matrix and is converted into a new matrix which is suitable for the determination. Preconcentration improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitates calibration. In general, it can be referred to as the enrichment process consisting of either stripping the major components from the minor ones or extraction of the analyte into a second phase of less volume than the original. Enrichment is attained by the use of various preconcentration techniques based on physical, physico-chemical and chemical principles. Enrichment techniques generally employed in analytical chemistry are volatilization, coprecipitation, floatation, liquid-liquid extraction, ion exchange, reversed phase extraction chromatography, electrophoresis, and solid phase extraction.

Also, preconcentration is inherent in some techniques, i.e. in sample decomposition, in dry ashing, in selective dissolution, in hydride generation, in cold vapour mercury determination by AAS, in stripping voltammetry or in electro-deposition. However, solid phase extraction, as a preconcentration technique represented a real advantage in sample enrichment, against the high cost

of the sophisticated instrumental techniques and requiring skilled people for maintenance and interpretation of the data. It reduces consumption and exposure to hazardous solvents, thus environmentally friendly. Consequently, solid-phase extraction is a widely used strategy in view of the numerous advantages mentioned above and also discussed subsequently.

1.3.1 Precipitation

Precipitation is one of the oldest chemical techniques for the separation and concentration of ions. A massive effort has been made over the years to find specific precipitation agents and to minimize coprecipitation, the completeness of the precipitation of the ions is much more important. The solubility of many common precipitates is sufficiently great to prevent quantitative precipitation of the ions of interest at concentrations less than few ppm. For example, nickel in this concentration range can be precipitated quantitatively with dimethyl glyoxime. In many cases, however, quantitative precipitation may be achieved by the addition of a coprecipitant [1-3]. The major advantages of precipitation methods are that they are simple and that uniform deposits on membrane filter can be obtained.

1.3.2 Evaporation

Perhaps the simplest method of preconcentration of ions from solution is evaporation of the solvent and is yet least suited for thermally stable species. This technique has been applied to X-ray spectrometry using conventional wavelength dispersion technique [4] and proton induced X-ray emission [5].

1.3.3 Electrodeposition

A method that would appear to be extremely useful for preconcentration of metal ions is electrodeposition. Electrodeposition was used extensively for electrogravimetry, an early preconcentration method. Deposition of metals into mercury cathodes, followed by distillation of the mercury to yield the

concentrated metals, is one useful approach. Perhaps one of the most valuable and widely applied electrochemical preconcentration techniques is stripping analysis [6]. The advantages of electrodeposition are that contamination is negligible as few reagents need be added and the instrumentation is simple. Spontaneous deposition of the sample ions occurs when the two electrodes are shorted and the solutions joined by salt bridge. There have been some successful reports by preconcentration on graphite using laboratory – simulated fresh water samples [7] and using in situ deposition of metals from water. The saline nature of the ocean water provides an excellent, natural electrochemical cell. Small self-contained electrodeposition units have been designed for in situ sampling water. The major disadvantage of the electrodeposition is that they are by and large very slow, even though very little operator attention is required during the deposition.

1.3.4 Flotation

Flotation is the process by which finely divided solids are suspended in a solution and floated to the surface of the liquid. When hydrophilic substances are to be floated, they are generally rendered hydrophobic and precipitated at the interface by equilibrating with suitable immiscible organic solvents [8]. In some cases, desired trace elements in an aqueous solution are quantitatively collected on small amounts of inorganic or organic collector, precipitated and are then floated by bubbling with or without the aid of surfactant ions of opposite charge to the precipitate surfaces [9].

The flotation of the ternary ion associate praseodymium-5,7-dichlorooxine-Rhodamine 6G with hexane followed by dissolution of the floated precipitate in acetone after discarding the aqueous and hexane layers results in the development of highly sensitive spectrophotometric procedure ($\epsilon = 1.83 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) for the determination of traces of praseodymium [10].

Co-flotation with phenolphthalein or 2-naphthol as the collector and octadecylamine (ODA) and sodium dodecylsulphate (SDS) as the surfactants resulted in flotation of copper, cobalt, cadmium and nickel as their oxinates from

solutions of high salinity and synthetic seawater. The process was optimized by means of the COFLOT program. Yields > 90% were achieved for nickel, cobalt and cadmium with phenolphthalein as collector but the yields of copper is low. However, the yields were much lower with 2-naphthol as collector. Flame AAS was used for the final measurements.

1.3.5 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 of ions of opposite sign. To concentrate dilute solutions, it is passed through a column of an appropriate ion exchange resin, the exchangeable ions will be exchanged. Then it is eluted with 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.

1.3.6 Liquid-liquid extraction

One of the most extensively studied and widely used technique for preconcentration is liquid-liquid extraction, in which a water immiscible solvent and an aqueous solution containing chelated metal ions are brought into contact in which the complexing agent forms a non-ionic or neutral chelate, which is more soluble in the organic solvent than in water. Some of the complexing agents are sodium diethyl dithiocarbamate (NaDDTC) and quinoline-8-ol. Some others such as dimethylglyoxime are highly specific. It is interesting to note that a great deal of research has been performed to develop methods for selective extractions with reagents such as phosphinic oxide. There is no single chelating agent that is specific extractant. However, Pohl [11-13] and Ather [14, 15] have proposed several multicomponent systems that cover a wide range of elements.

1.3.7 Solid phase extraction (SPE)

SPE involves partitioning between a liquid and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After all the sample has been passed through the sorbent, retained analytes are subsequently recovered upon by elution with an appropriate solvent. The first experimental applications of SPE started fifty years ago [15,16]. However, its growing development as an alternative approach to liquid-liquid extraction for sample preparation started only in the mid 1970's . It has been extensively used in the past fifteen years for the preconcentration of organic micropollutants, especially pesticides, in water samples [17]. However, numerous studies have also shown the great potential of this technique for inorganic analytes.

1.3.7.1 Basic principles

An SPE method always consists of three to four successive steps, as illustrated in Fig.1.1. First, the solid sorbent is conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial as it enables the wetting of the packing material and the solvation of functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent. The nature of the conditioning solvent depends on the nature of the solid sorbent. Typically, for reversed phase sorbent (such as octadecyl-bonded silica), methanol is frequently used, followed with water or aqueous buffer whose pH and ionic strength are similar to that of the sample. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps. Otherwise, the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned.

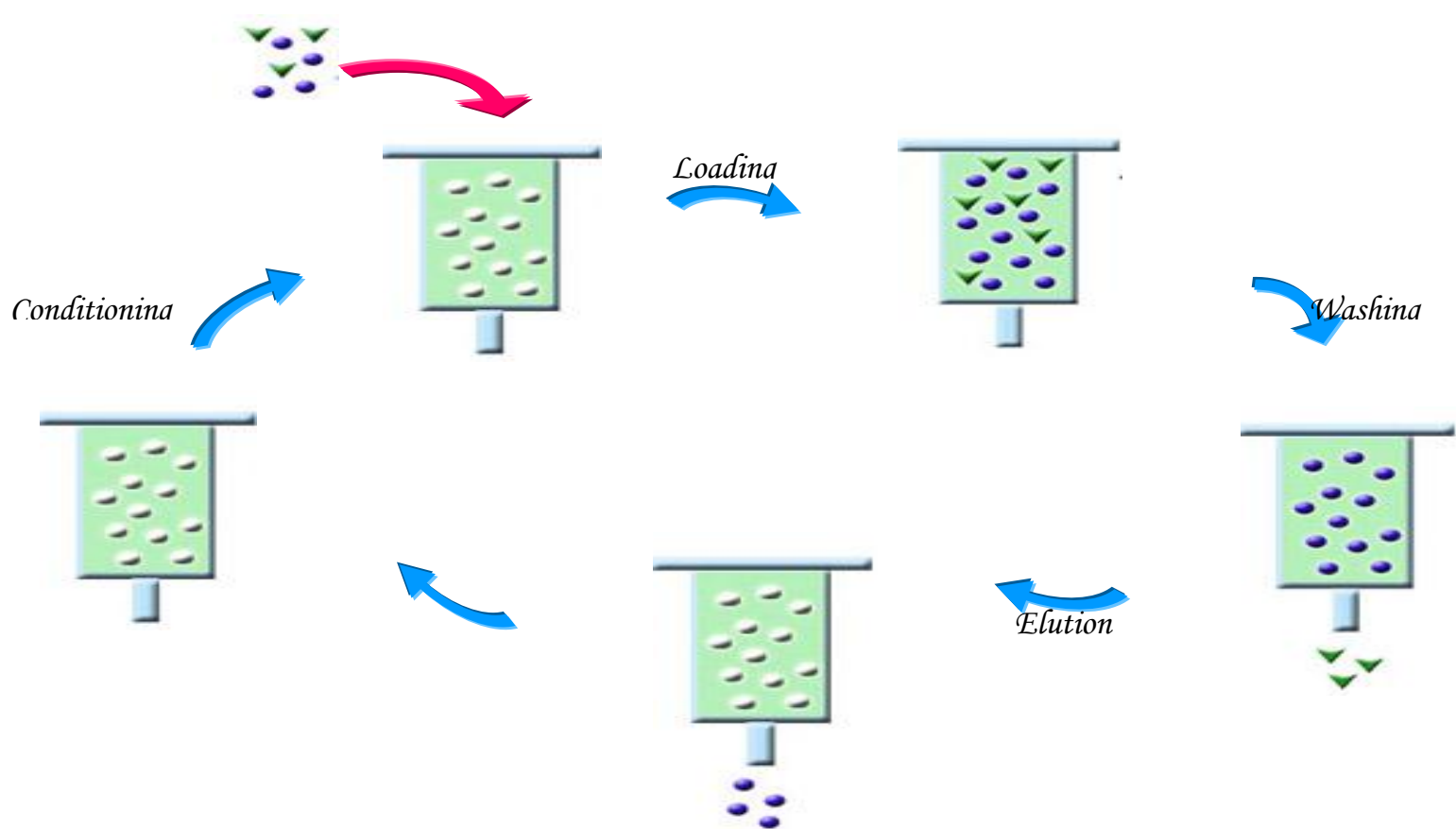


Fig. 1.1 Principle of solid phase extraction

The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 ml to 1 l. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation) of the sample.

The third step (which is optional) is the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent without displacing the analytes. A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorbent. This will eliminate the presence of water in the final extract, which in some cases, may hinder the subsequent concentration of the extract and/or the analysis.

The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. In addition, the flow rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots and before the elution to let the solvent soak the liquid sorbent.

1.3.7.2 Sorbent formats

Different types of sorbent formats such as filled micro columns, syringe barrels, cartridges and discs are developed for solid phase extraction (Figure 1.2).

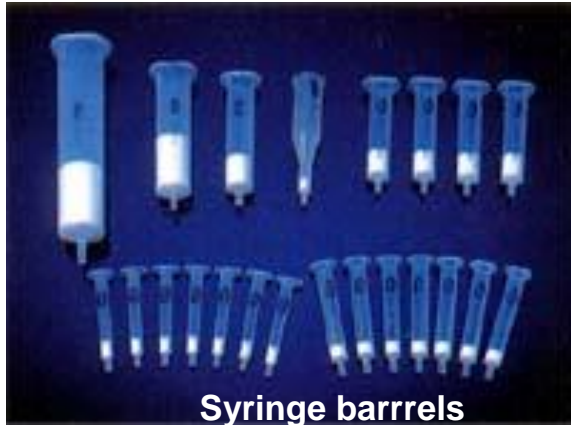


Fig. 1.2: Disposable sorbent containers

(a) Microcolumn

The use of microcolumn is a common procedure for extraction of trace elements from various samples. It affords the opportunity of packing the column with the desired sorbent so that the broader choice than the commercial disposable containers is available. In addition, the size of the column (ie. the sorbent weight) may be adopted depending on the sample volume. In particular, it allows larger volumes thus enabling the preconcentration of metal ions at very low concentration levels. However, such columns must be reused, so that careful blank washings should be conducted to avoid cross contamination. In addition, columns with narrow internal diameter limit usable flow rates to a range 1-10 ml/min that necessitates long trace enrichment times for large sample volumes [18]. Microcolumns are frequently used in systems affording the online coupling of SPE to analytical techniques. However, in that case, the size of the column is limited to achieve acceptable analytical performance.

(b) Disposable cartridges and syringe barrels

Now-a-days, the most frequently used design in off-line SPE is the cartridge or the syringe barrel. They are usually made of polypropylene or polyethylene and filled with packing material having different functional groups. The solid sorbent is contained between two 20 μm polypropylene frits (in some cases they may be made of glass). They afford great selectivity due to the broad types of sorbent contained in commercially available systems with different column volumes available. In addition, their disposable character prevents possible cross contamination.

The major disadvantages of cartridges and syringe barrels are slow sampling processing rates and a low tolerance to blockage by particles and adsorbed matrix components, due to their small cross-sectional area. Channeling reduces the capacity of cartridge to retain analytes and results in contamination of the isolated analytes with impurities originating from the manufacturing and

packing process. Such contaminants were prominent for C₁₈ silica cartridges while less in case of C₁₈-silica disks [19,20].

(c) **Disks**

The use of flat disks with high cross-sectional area may largely prevent all the problems encountered with column, cartridges and tubes. The packing material is usually embedded in an inert matrix of polytetrafluoroethylene (PTFE) microfibrils, with a typical composition of 90% w/w sorbent and 10% w/w PTFE fibres [21]. Other types of disks use a glass-fibre matrix to hold the sorbent particles, in order to enable a higher flow rate. The disks are available in different diameter from 4 to 90 mm, the size most frequently used in conjunction with a filtration apparatus connected to water aspirator. In order to remove the potential interferences and to ensure optimal extraction of analyte of interest, disk cleaning and conditioning should be done before its use. One of the drawbacks of using disks is the decrease in the breakthrough volume (which is the volume that can be percolated without analyte losses). In addition, disks have lower capacity than cartridges so that for real samples [eg. high content of natural organic matter in river water) incomplete retention of the target metal species may result. As a consequence, disks are recommended when there is a strong interaction between the analyte and the sorbent.

1.3.7.3 Sorbents used in solid phase extraction

Solid sorbents may be hydrophobic or polar. It is common to call reversed-phase sorbents i.e., the packing materials that are more hydrophobic than the sample and are frequently used with aqueous samples. On the other hand, normal phase sorbents refer to materials more polar than the sample and they are used when the sample is an organic solvent containing the target compounds. When hydrophobic supports are used, retention of ionic metal species will require the formation of hydrophobic complexes. This can be achieved through addition of the proper reagent to the sample or through immobilization of the reagent on the

hydrophobic solid sorbent. Immobilization may also provide a significant development in trace analysis, because metal equilibrium in the sample may not be affected by reaction on the cartridge. The important sorbents are given in Figure 1.3.

Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for a solid sorbents are (i) the possibility to extract a large number of trace elements over a wide pH range, (ii) the fast and quantitative sorption and elution, (iii) high capacity, (iv) regenerability and (v) accessibility. In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacities. The broad variety of sorbents available explains one of the most powerful aspects of SPE, viz. selectivity. Sorbents can be mainly categorized as organic based ones (natural polymers, as well as synthetic polymers) and inorganic based ones [silica gel (SiO_2), alumina (Al_2O_3), magnesia (MgO) and other oxide species]. Immobilisation of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of extraction. The selectivity of the modified phases towards certain metal ions is attributed to several well known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups, and the type of interacting functional groups. However, the selective extraction of a single trace element from other interfering ion(s) represents a direct challenge for finding a suitable phase capable of exhibiting a sufficient affinity to selectively bind that metal ion. For particular applications, the combinations of two sorbents may thus be advisable.

(a) Inorganic solid supports

Inorganic based sorbents are mainly made of silica gel even though other inorganic oxides may be used. Silica gel can be used as a very successful adsorbing agent, as it does not swell or strain, has good mechanical strength and can undergo heat treatment. In addition, chelating agents can be loaded easily on

silica gel with high stability, or be bound chemically to the support, affording a higher stability. The surface of silica gel is characterized by the presence of silanoyl groups, which are known to be weak ion exchanger causing low interaction, binding and extraction of ionic species [22]. In particular, silica gel presents high sorption capacity for metal ions, such as Cu, Ni, Co, Zn or Fe [23]. Retention is highly dependent on sample pH with quantitative retention requiring pH values over 7.5-8.0. Under acidic conditions, silanoyl groups are protonated and the ion exchange capacity of the silica gel is greatly reduced or even reduced

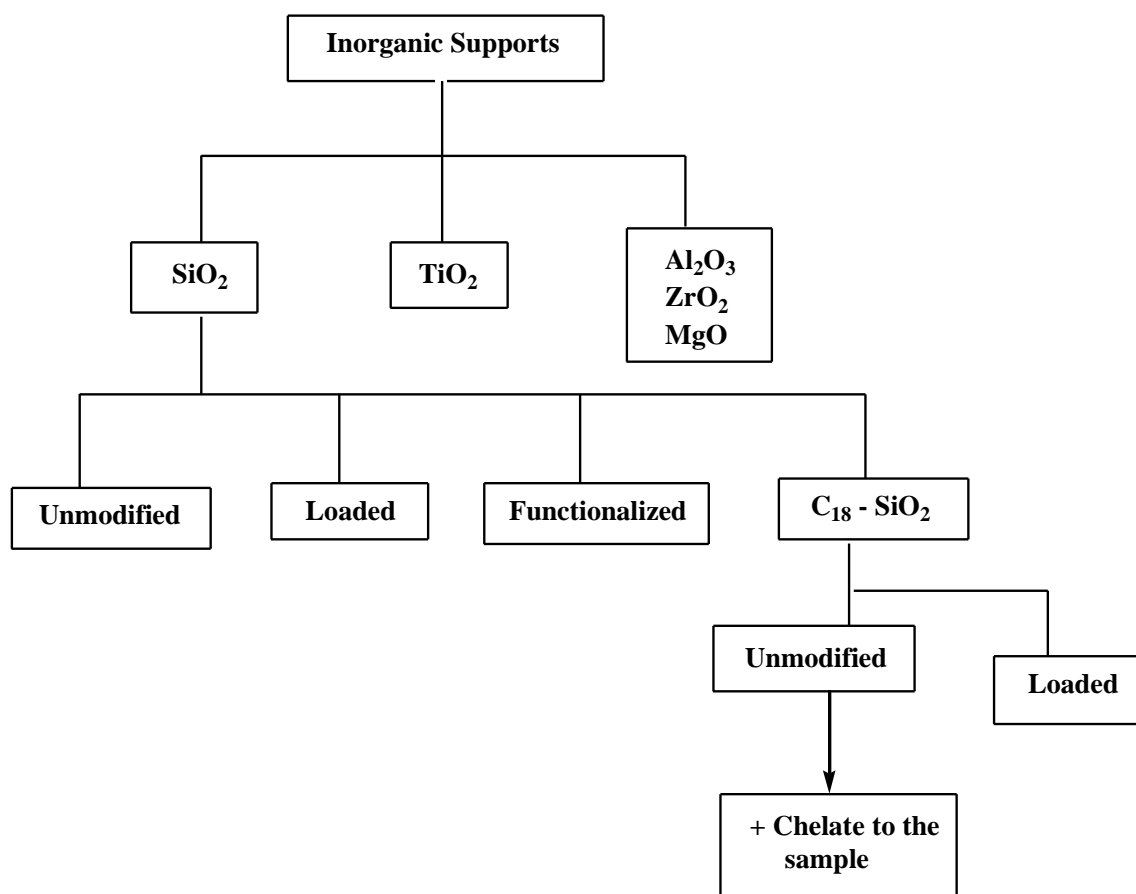


Figure 1.3: Sorbents used in solid phase extraction

to zero at low pHs. In addition, this sorbent has a very low selectivity, and is prone to hydrolysis at basic pH. Consequently, modification of the silica gel surface has been performed to obtain solid sorbents with greater selectivity. Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first case, a chemical

bond is formed between silica gel surface groups and those of organic compound (functionalized sorbent). In the second approach, the organic compound is directly adsorbed on the silanol groups of the silica gel surface (impregnated or loaded sorbent), either by passing the reagent solution through a column packed with the adsorbent or by soaking the adsorbent in the reagent solution. Increased stability of the sorbents is obtained by the chemical binding of chelating functional groups on silica gel [24]. It should be clear in mind that despite chemical bonding of functional groups on the silica gel surface, free silanol groups still remain [25]. Their number can be minimized by end-capping the sorbent, but some will still be present. As a consequence, they will participate in the retention of trace elements somewhat, especially at pHs above their pKa (ionized form).

(b) Other inorganic oxides

Apart from silica, other inorganic oxides have been tested for the adsorption of trace elements. Whereas SiO_2 , due to its acidic properties, is expected to adsorb only cations, basic oxides such as magnesia – MgO should adsorb only anions. As a matter of fact, adsorption of ions on oxide surfaces is believed to proceed with participation of hydroxyl groups. These groups are negatively charged (deprotonated) under basic conditions, thereby retaining anions. Consequently, amphoteric oxides (namely titania TiO_2 , alumina Al_2O_3 , zirconia ZrO_2), cations are adsorbed under acidic conditions (pH above the isoelectric point of the oxide which was reported to be 6.2 for TiO_2 [27] while anions are adsorbed under basic conditions (pH > 9) below the isoelectric point of the oxide).

(c) Organic-inorganic hybrids

Despite the large variety of bonded phases available, octadecyl bonded silica has currently become the most popular phase used. Bare C_{18} -silica can also retain a fraction of inorganic trace elements, probably due to the presence of

silanoyl groups on its surface [26]. Retention on C₁₈-silica may improve by the addition of a ligand reagent to the sample before its percolation through the sorbent. Despite their broad application to trace element preconcentration, bonded silica phases (either C₁₈-silica or functionalized-silica gel) present the drawback of a limited range of pH that can be used, as in acidic (below 2 to 4) and basic (above 8). Hydrolysis may occur, which changes the interactions that occur between the sorbent and the trace elements. As a consequence, polymeric sorbents are preferred.

(d) Organic based sorbents

Organic based sorbents may be divided into polymeric and non-polymeric sorbents. Polymeric sorbents have been, by far, the most used for trace element preconcentration having the advantage over bonded silica in that they are used over the entire pH range. Their disadvantage is that the conditioning step is more time consuming as they require extensive cleaning before use. For this purpose of this, organic sorbents are used for the preconcentration of trace elements.

In most applications, new sorbents have been synthesized by chemically bonding chelating groups to polymeric crosslinked chains and characterizing their ability to selectively adsorb trace elements. Most of the chelating groups reported have low water solubility to avoid their leaching from the sorbent, as most applications deal with aqueous samples. At the same time, a too hydrophobic group will hinder wettability of the sorbent by the aqueous sample, resulting in poor retention efficiency. In addition to the functional group, the efficiency of polymeric sorbents depends on various physiochemical parameters such as particle size, surface area, pore diameter, pore volume, degree of crosslinking and particle size distribution.

(i) Polystyrene-divinyl benzene

Macroporus hydrophobic resins of the Amberlite XAD series are good supports for developing chelating matrices. Amerblite XAD-1, XAD-2, XAD-4, and XAD-16 are polystyrene divinyl benzene (PS – DVB) resins with a hydrophobic character and no ion-exchange capacity. In addition to the hydrophobic interaction that also occurs with C₁₈ silica, such sorbents allow $\Pi - \Pi$ interactions with aromatic analytes.

Due to the hydrophobic character of PS – DVB, retention of trace elements on such sorbents requires the addition of a ligand to the sample. Inorganic ligands may be used [28] but organic ligands are preferred. Alternatively, ligands may be attached to the PS-DVB by physical adsorption such as dithizone [29] etc. However, in practice, the resins prepared by impregnation of the ligand are difficult to reuse, due to partial leaching of the ligand (thus resulting in poor repeatability). To overcome this problem, the resin may be chemically functionalized. The ligands are generally coupled to a methylene or an azo spacer on the matrix. Of great interest are also the sulfonated PS-DVB resins, as they show excellent hydrophilicity and high extraction coefficients for polar organic compounds [30].

(ii) Divinyl benzene – vinyl pyrrolidone copolymers

Sorbents made of divinyl benzene – vinyl pyrrolidone (DVB-VP) copolymers have recently been developed, such as Oasis HLB [30]. The hydrophilic N-vinyl pyrrolidone affords good wettability of the resin, while the hydrophobic divinyl benzene provides reversed phase retention of analytes. The use of Oasis MCX, a sulphonated divinyl benzene – vinyl pyrrolidine copolymer may be useful for the retention of trace element species, as this sorbent combines with the properties of the previous sorbents with those of a strong cation – exchanger.

(iii) Polyacrylate polymer

Amberlite XAD-7 and XAD-8 are ethylene-dimethacrylate resins. They are non-aromatic in character and possess very low ion exchange capacity. Due to the polarity of acrylates, such resin enables the recovery of polar compounds. However, this polarity is quite moderate so that most of the time reagents are added to increase retention. Direct addition to the sample is sometimes performed. As an example, Cu(II) forms a complex with 8-hydroxyquinoline-5-sulfonic acid, which can be further retained on Amberlite XAD-8 as an ion pair with cetyltrimethyl ammonium (CTA) [31]. Yet, most of the time chelating ligands have been loaded on such resins, mainly Amberlite XAD-7 to increase their retention capacity for trace elements and/or their selectivity such as xylenol orange [32], Dimethyl glyoxal bis[4-phenyl-3-thiosemicarbazone)] [DMBS] [33] etc. Such loaded sorbents are stable for several months and can be reused. For a higher stability, chemical binding of the chelating group may be performed, as reported on poly(ethylene glycol dimethacrylate-hydroxyethyl-methacrylate) microbeads [34].

(iv) Polyurethane polymers

Due to its sorption capacity for several trace elements polyurethane foam has been tested for use in SPE. Most of the time, complexing reagents are added to enhance the sorption capacity. Hence, polyurethane foam coated with DMG, NaDDTC or hexamethylenedithiocarbamate (HMDC) was found in retaining trace elements [35-37]. Chelating reagent can also be directly added to the sample, and the metal chelates further retained on polyurethane foam, as observed with thiocyanate complexes [38,39] and Diethyldithiophosphate (DDTP) complexes [40].

(v) Polyethylene polymers

Polyethylene is also attractive for SPE of trace elements as this supports adsorbs several metals complexed with hydrophobic ligands. Additionally, the

adsorbed complexes can be eluted with a small volume of organic solvents permitting high enrichment factors. Polyethylene can also be used in strongly acidic and basic media and for that reason it has been used as a sorbent for the retention of chromium in an acidic medium after the addition of diphenyl carbazide [41].

(vi) Polytetrafluoroethylene polymers

PTFE can retain trace elements after addition of a chelating reagent to the sample such as ammonium pyrrolidine dithiocarbamate (APDC), NaDDTC, or dithizone [42-44]. The sorbent can be used as PTFE turnings [45,46], PTFE beads [47], or as a PTFE tubing in a knotted reactor.

(vii) Polystyrene polymers

Polystyrene polymers may be an interesting alternative to common sorbents (namely Amberlites XAD-2 and XAD-8, C₁₈ silica), as they have a hyper crosslink structure. The addition of reagent to the sample is required to form complexes that are further retained on the hydrophobic sorbent.

(viii) Polyamide polymers

Polyamide polymers have been used for the retention of rare earth elements [48]. A chelating reagent was added to the sample for complexing the trace elements. This reagent thorin[o-(disulfo-2-hydroxy-1-naphthyl azo)benzene arsenic acid] was chosen to enable interaction with the sorbent through electrostatic forces and non-hydrophobic interaction.

(ix) Iminodiacetate – type chelating resins

Polymeric resins containing iminodiacetate groups (- CH₂ – N (CH₂COO)₂) as active sites (IDA resins) have been widely used for the retention of trace elements. They have been synthesized by bonding the iminodiacetate functional

groups to several polymeric sorbents, such as polystyrene[chelex-100] or a highly crosslinked agarose gel (IDA- Nova rose) [49]. The spacer arm length was found to have an effect on the formation of metal complex species in the chelating resin. A major drawback of such sorbents is that, due to the weak acid character of the functional groups, the degree of protonation will critically affect the ability of the resin to retain metal cations. Hence, for chelex-100, protonation of the carboxylates and the donor N atom are reported to be complete at pH 2.21 while a completely deprotonated form is reached at pH 12.30. Also such sorbents are non-selective, so that trace element retention may be reduced due to retention of major ions. Besides, the presence of ligands in the sample may prevent trace element retention on the sorbent due to their complexation as observed in real waters due to the presence of organic matter [50].

(x) Propylene diamine tetraacetate – type chelating resins

The synthesis of a fine particle macroporus polymer based propylene diaminetetra acetic acid (PDATA) type resin has been recently reported [51]. The structure of this sorbent is very similar to that of ethylene diamine tetraacetic acid (EDTA) with a spacer arm enabling the retention of several trace elements upon chelation.

(xi) Polyacrylonitrile based resins

Polyacrylonitrile fibers have been functionalized to obtain ion exchange chelating sorbents with amino phosphonic dithiocarbamate or amino thiourea groups. However, as such synthesis is time consuming, an alternative is to coat the polyacrylonitrile fibre with a proper reagent for further trace element retention such as Quinoline-8-ol [52].

(xii) Ring-opening metathesis polymerization based polymers

A high capacity carboxylic acid functionalized resin has been prepared using the ring opening metathesis polymerization (ROMP) [53]. Electron

microscopy revealed that the obtained material consists of irregularly shaped, agglomerated particles having a nonporous structure with diameter and specific surface area dependent on the polymerization sequence and stoichiometry. This material was pH stable and could be reused. The presence of carboxylic group confers an excellent hydrophilic character to the sorbent (ensuring a high wettability of the sorbent by water). While the polyunsaturation of the carrier chain as well as the entire backbone provides for a significant reversed phase character. The carboxylic acid groups provide weak coordination sites enabling the retention of rare earth elements. Similarly, dipyridylamide functionalized resins have been reported to allow the extraction of “Soft” metals such as Palladium(II) and mercury(II) [54].

(xiii) Cellulose sorbents

Cellulose was found effective in retaining trace elements in water samples either directly or upon addition of a chelating agent to the sample [55]. In particular, the selective retention of Cr(III) was reported thereby enabling chromium speciation. This sorbent may also be functionalized to increase the SPE selectively. Thus the selenium speciation has been reported on cellulose functionalized with quarternary amine due to selective elution of the retained Se(IV) and Se(VI) species using nitric acid at two different concentrations [56].

(xiv) Naphthalene based sorbents

Retention of trace elements on microcrystalline naphthalene is also feasible either after addition of a ligand to the sample [57] or after modification of naphthalene by coprecipitation to ensure better adsorption characteristics towards trace elements [58,59]. In addition, until now it has been reserved to batch experiments.

(xv) Carbon sorbents

Activated carbon is prepared by low-temperature oxidation of charcoals. Due to their large surface areas (300-1000 cm²/g), these sorbents are well reorganized for their very strong sorption both for trace organic compounds and trace elements. There is evidence of two types of adsorption sites on activated carbons. (1) graphite-like basal planes that enable adsorption through Vander waals forces especially Π -electron interactions, and (2) polar groups like carbonyls, hydroxyls and carboxyls that may interact via ionic interaction of hydrogen bonding [60]. Consequently, trace elements may be directly adsorbed on activated carbon [61]. Metal chelates may also be retained on this sorbent after the addition of a proper chelating agent to the sample such as amino acids [62], dithizone [63] and APDC etc [64]. The ligand should be chosen to have a strong interaction with the activated carbon, otherwise complete dissociation of the metal chelate would be observed.

The main drawback when using activated carbon is their heterogenous surface with active functional groups that often led to low reproducibility. In addition, these sorbents are very reactive and can act as catalysts for oxidation and other chemical reactions. Fortunately, along with the development of a polymer materials and bonded phases, a new generation of carbon sorbents appeared in the 1970's and 1980's with the more homogeneous structure and more reproducible properties. Graphitized carbon blocks (GCB) are obtained from heating carbon blacks at 2700-3000°C in an inert atmosphere [65]. They are non-specific and non-porous sorbents (surface area approx. 100 m²/g), and are considered to be both reversed phase sorbents and anion exchangers due to the presence of positive charged chemical heterogeneities on their surface. Such sorbents have been extensively used in the past years for the SPE of polar organic pollutants from water samples, but their use for trace elements is still rare [66]. Their main drawbacks are possible irreversible retention of analytes, which may be over by elution in the back flush mode, and poor mechanical stability porous graphitized carbon (PGC) is a more stable carbon bases sorbent than GCB as the graphite is

immobilized on a silica substrate. So this sorbent should be suitable for trace element retention even though until now its applications have been limited to trace organic compounds. Recently, fullerenes and carbon nanotubes has been used for preconcentration of traces of inorganics.

1.2.7.4 Chelating groups

Several functional group atoms are capable of chelating trace elements. The atoms most frequently used are nitrogen (eg. N present in amines azo groups, amides, nitriles), oxygen (eg. O present in carboxylic, hydroxylic, phenolic, carbonyl, phosphoryl groups and sulfur (eg. S present in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards trace elements. In practice, inorganic cations may be divided into 3 groups.

(i) **Group I ‘Hard’ cations:** These preferentially react via electrostatic interactions (due to a gain in entropy caused by changes in orientation of hydration water molecules). This group includes alkaline and alkaline earth metals (Ca^{2+} , Mg^{2+} , Na^+) that form rather weak outersphere complexes with only hard oxygen ligands.

(ii) **Group II ‘Borderline cations:** These have an intermediate character, this group contains Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} and Mn^{2+} . They possess affinity for both hard and soft ligands.

(ii) **Group II ‘Soft cations’:** These tend to form covalent bonds. Hence Cd^{2+} and Hg^{2+} possess strong affinity for intermediates (N) and soft (S) ligands.

For soft metals, the following order of donor atoms affinity is observed, $\text{O} < \text{N} < \text{S}$. A reversed order is observed for hard cations. For a bidentate ligand, affinity for a soft metal increases with overall softness of the donor atoms. $(\text{O}, \text{O}) < (\text{O}, \text{N}) < (\text{N}, \text{N}), (\text{N}, \text{S})$. The order is reversed for hard metals. In general, the

competition for a given ligand essentially involves group (i) and (ii) metals for O sites, and metals of group (ii) and (iii) are weak.

Chelating agents may be directly added to the sample for chelating trace elements, the resulting metal chelate being further retained on an appropriate sorbent. An alternative which is gaining importance in the past 3 years is to introduce the functional chelating group into the sorbent by three different means: (i) the synthesis of new sorbents containing chelate group (new sorbents) (ii) the chemical bonding of such groups on existing sorbents (functionalized sorbents), and (iii) the physical binding of the groups on the sorbent by impregnating the solid matrix with a solution containing the chelating ligand (impregnated, coated or loaded sorbents). The latter remains the most simple to be used in practice. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the life time of the impregnated sorbent.

Binding of metal ions to the chelate functionality is dependent on several factors: (i) nature, charge, and size of the metal ion, (ii) nature of the donor atoms present in the ligand, (iv) buffering conditions which favour certain metal extraction and binding to active donor or groups and (iv) nature of the solid support (eg. degree of crosslinking of a polymer). In some cases, the behaviour of immobilized chelating sorbents towards metal preconcentration may be predicted using the known values of the stability constants of the metals with the investigated chelating agent [67]. However the presence of solid sorbent may also have an effect and lead to the formation of a complex with a different stoichiometry than the one observed in a homogenous reaction [68,69]. In fact several characteristics of the sorbent should be taken into account, namely the number of active groups available in the resin phase, the length of the spacer arm between the resin and the bound ligand [70], and the pore dimensions of the resin [71].

1.3 SCOPE OF THE SOLID-PHASE EXTRACTION

Classical liquid-liquid extractions of trace elements are usually time consuming, labor-intensive and beset with problems of emulsion and use of toxic solvents. In addition, they require strict control of extraction conditions such as temperature, pH and ionic strength. For all these reasons, several procedures tend to be replaced by SPE methods. The latter technique is attractive as it reduces consumption of and exposure to solvents, their disposal costs and extraction time [72]. It also allows the achievements of high recoveries [73], along with high enrichment factors. However, as different results between synthetic and real samples may be observed [74], recoveries should be estimated in both cases as far as possible. In addition, SPE can be interfaced online with analytical techniques such as liquid chromatography (LC) or atomic absorption spectrometry (AAS). 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. Finally SPE affords a broader range of applications than LLE due to large choice of solid sorbents.

1.4 Scope and objectives of the proposed 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 analysed directly. In trace analysis, liquid-liquid extractive concentration 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 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, new SPE's such as Quinoline-8-thiol, 1-(2-thiazolylazo)-2-naphthol, diarylazobisphenol and β -diketone modified sorbents were selected for the preparation of various chelate modified materials. Hence, the following are the prime goals of this investigation.

- (i) Synthesis and characterization of most suitable solid phase extractants for the selective preconcentration/separation of metal ions.
- (ii) Development of novel preconcentrative separation procedures in conjunction with UV-visible spectrometry/flame atomic absorption spectrometry.
- (iii) Testing the accuracy of the developed preconcentration procedures by analyzing certified reference materials.
- (iv) Application of the developed preconcentration procedures for the determination of trace elements from environmental and biological samples and removal of toxic traces from environmental samples.

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CHAPTER 2

QUINOLINE-8-THIOL MODIFIED NAPHTHALENE AS SOLID PHASE EXTRACTANT FOR THE PRECONCENTRATION OF MERCURY(II)

2.1 INTRODUCTION

Mercury has been extensively used in the production of electrical goods, pulp and paper products, paints, dental applications and pesticide formulations. About half of the anthropogenic input to the environment has come from manufacturing caustic soda and chlorine by the electrolysis of brine. Because of such a wide use and the volatility of some species, mercury is now a global pollutant which has been measured in the deep ocean, the atmosphere, Antarctica and Arctic.

Mercury is found at trace levels in many minerals, with continental rocks containing an average of 80 $\mu\text{g}/\text{kg}$ [1]. Soil mercury concentrations may vary dramatically depending on the local geology and industry. Typically soils are reported to contain 0.01-0.5 $\mu\text{g}/\text{g}$ [2]. Mercury is normally present in plant tissues in the range 30-700 $\mu\text{g}/\text{g}$ [3]. Mercury concentrations in water at various typical levels are reported as ranging from 0.0001 to 2.8 $\mu\text{g}/\text{l}$ in freshwater, and from 0.01 to 0.22 $\mu\text{g}/\text{l}$ in sea water [4].

The mercury poisoning in human is measured by the analysis of blood, tissues, urine, serum and hair samples. Mathews [5] has reported elevated levels of mercury in blood and hair as a result of consuming fish contaminated with mercury. In the 1950's and 1960's two major epidemics of methyl mercury poisoning through the fish consumption occurred in Minnamata Bay and Niigata (both in Japan) where thousands of people were affected [6]. Hair is a suitable indicator for monitoring of human exposure to mercury, which reflects organic mercury in hair when exposure is prolonged and relatively constant. The straight

line fitted to the data obtained on mercury(II) analysis of hair and blood samples are related by,

$$\text{Hair mercury} = 0.367 \times \text{blood mercury} + 0.694$$

where the mercury concentration is expressed in μg . However, it is easier to monitor the levels of mercury in hair rather than blood samples. In hair, mercury exists in the form of methyl mercury. Methyl mercury in hair is analysed through a three step procedure – digestion, extraction and determination. Digestion is an essential step for the release of methyl mercury bound to hair with cystine sulphur or the sulphhydryl (SH) group in amino acids [7]. The digestion step can break the existing bonds between hair and methyl mercury. Two kinds of heated digestions have been used, either acidic [8] or basic [9]. In view of the low levels of mercury, it is often followed by extraction with suitable solvents [10] or solid phase supports. However, the latter approach is preferred due to the advantages like low solvent consumption, absence of emulsion etc.

Various solid supports have been used for mercury (II) extraction. Among these silica gel [11-14], ion-exchange resins [15], natural clays [16] and naphthalene [17-19] are promising supports. The latter sorbent is preferred in view of the easy dissolution in acetone or dimethyl formamide for subsequent determination by spectrophotometry. This eliminates the tedious elution step.

Molten naphthalene was used as an extractant in the initial stages for the preconcentration of inorganics [20]. However, this technique is not suitable for preconcentrating metals which form thermally unstable complexes [21]. Subsequently, the solid-liquid separation after coprecipitative preconcentration of metal chelates onto microcrystalline naphthalene was widely used as it is rapid, economical and can be applied to many types of complexes. This technique is especially attractive for complexes that have poor solubility in organic solvents [22]. The only difficulty is in the filtrations of small amounts of naphthalene. Hence, column preconcentration using naphthalene is being recently employed for the preconcentration of trace and ultra trace amounts of inorganics [23]. These procedures are really time consuming as 6-8 h is required for preconcentration of

inorganics present in 1.0 l of sample solution. In view of this, batch preconcentration procedures still play significant role in preconcentration of inorganics from dilute aqueous solutions. Table 2.1 summarizes the salient features of preconcentration procedures developed for mercury(II) using naphthalene as collector.

Table 2.1 Summary of preconcentration procedures developed for mercury (II) using naphthalene as collector

Sl. No.	Detection method	Reagent	pH	Detection limit (µg/ml)	Linear range (µg/ml)	Application	Ref.
1	Anodic stripping – differential pulse voltammetry	Methyl trioctyl ammonium chloride	-	0.13	1.2-8.7	Natural waters, waste water, synthetic samples	24
2	CVAAS	Dithizone	-	-	-	Water samples	19

In all the above described procedures, metal complexes are coprecipitated onto microcrystalline naphthalene. In the present work, metal chelates were not adsorbed, instead chelate modified naphthalene was used for adsorbing metal ions. Taking into account the high affinity of mercury species to organic reagents with sulphur donor atoms, quinoline-8-thiol was selected for possible SPE preconcentration of mercury (II).

Thus, in the method described below, mercury(II) is selectively preconcentrated by using quinoline-8-thiol modified naphthalene as solid phase extractant (SPE). The SPE can be prepared simply by pouring an acetone solution of naphthalene and the reagent into water. The material prepared is used for the preconcentration of mercury (II). Further, mercury (II) preconcentrated on naphthalene is filtered and dissolved in acetone for determined subsequently by spectrophotometry using dithizone procedure [25]. Various parameters that

influence the preconcentration of mercury (II) by solid phase extraction were systematically optimized and the results obtained are discussed in the following pages.

2.2 PRELIMINARY INVESTIGATIONS

The solid phase extraction of 10 µg of mercury (II) present in 250 ml of aqueous solution was carried out by adjusting the pH to 6.0 in the presence of 10 ml of 1.0 M sodium acetate-acetic acid buffer onto 0.5 g of quinoline-8-thiol modified naphthalene. The mercury (II) preconcentrated onto quinoline-8-thiol modified naphthalene was dissolved in 2 ml of acetone. To the above acetone solution, 2.5 ml each of 5.0 M sulphuric acid and 6.0 M acetic acid were added, diluted to 15 ml with chloroform equilibrated water and shaken for 1 min with 5 ml of dithizone in chloroform. The chloroform layer was collected over anhydrous sodium sulphate and the absorbance of mercury - dithizone complex was measured at 500 nm. The mechanism of SPE of mercury(II) using quinoline-8-thiol modified naphthalene is given in Fig.2.1.

2.3 OPTIMIZATION OF MAIN EXPERIMENTAL VARIABLES

2.3.1 Effect of pH

The effect of pH on the preconcentration of 10 µg of mercury (II) present in 250 ml of aqueous phase onto 0.5 g of quinoline-8-thiol modified naphthalene was studied in the pH range 2.0-10.0 in steps of 1.0. The mercury (II) preconcentrated onto quinoline-8-thiol modified naphthalene was determined after the dissolution of SPE in acetone and determined by using dithizone procedure. The extraction of mercury(II) onto quinoline-8-thiol modified naphthalene is constant (Fig.2.2) and maximum in the pH range 5.0-7.0. In all subsequent experiments, the pH was adjusted to 6.0 ± 1.0 using ammonium acetate buffer.

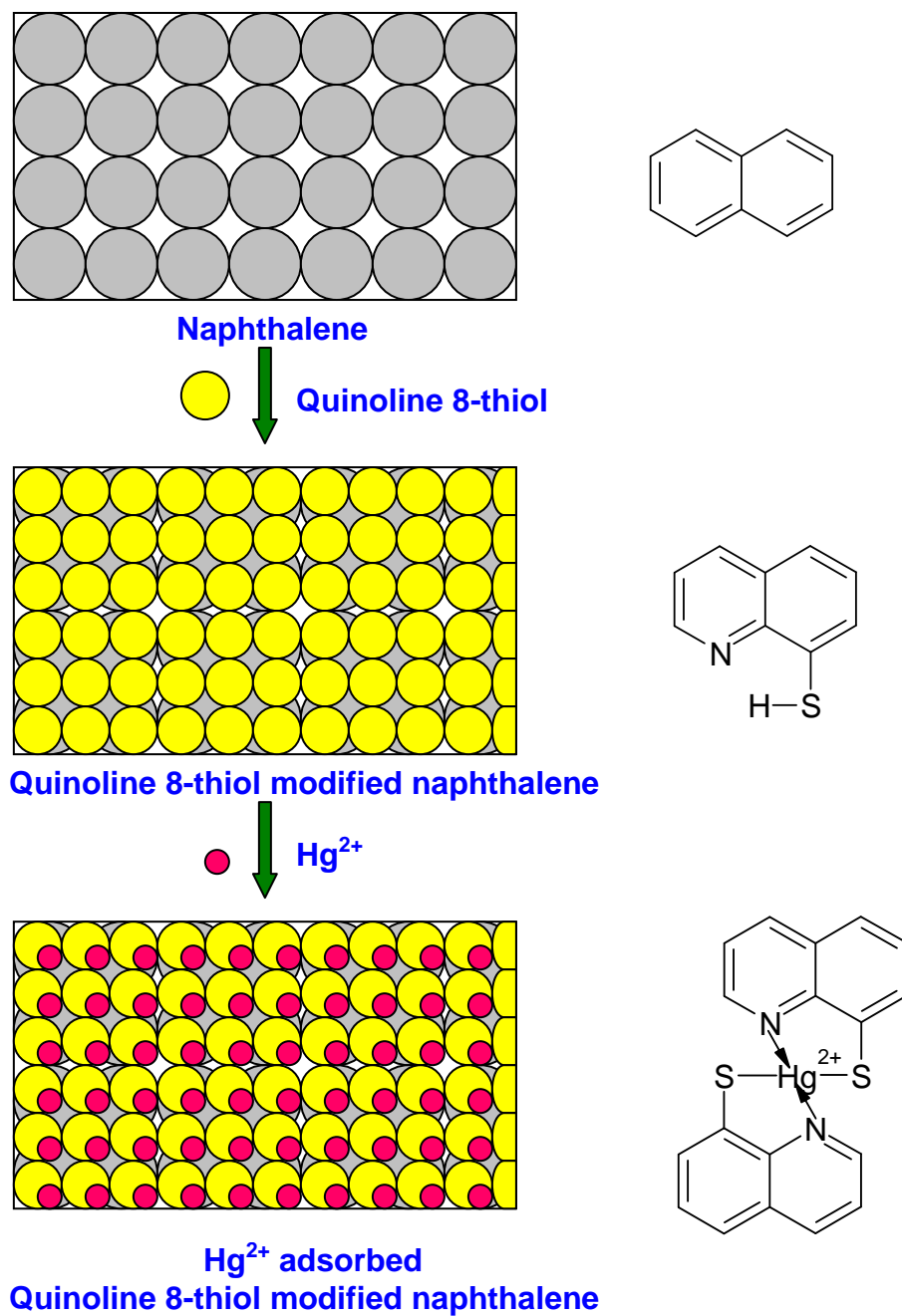


Fig. 2.1 Mechanism of SPE of mercury (II) using quinoline-8-thiol modified naphthalene.

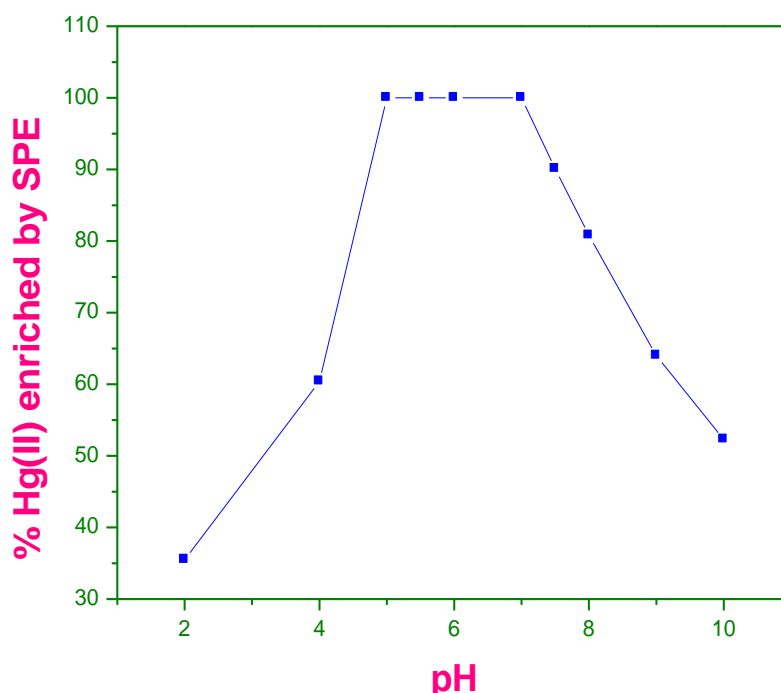


Fig 2.2 Effect of pH

2.3.2 Effect of Quinoline-8-thiol concentration in naphthalene

The quinoline-8-thiol concentration in naphthalene was varied from 0.1-10%. Mercury (II) enriched onto quinoline-8-thiol modified naphthalene was determined spectrophotometrically using dithizone as reagent. The results obtained are shown in Figure 2.3. The enrichment of mercury(II) onto quinoline-8-thiol modified naphthalene was quantitative when the concentration of quinoline-8-thiol is more than 1%. Hence, in all subsequent experiments, 1% quinoline-8-thiol modified naphthalene was used. Further, a minimum of 0.5g of 1% quinoline-8-thiol modified naphthalene is essential for quantitative enrichment of mercury(II).

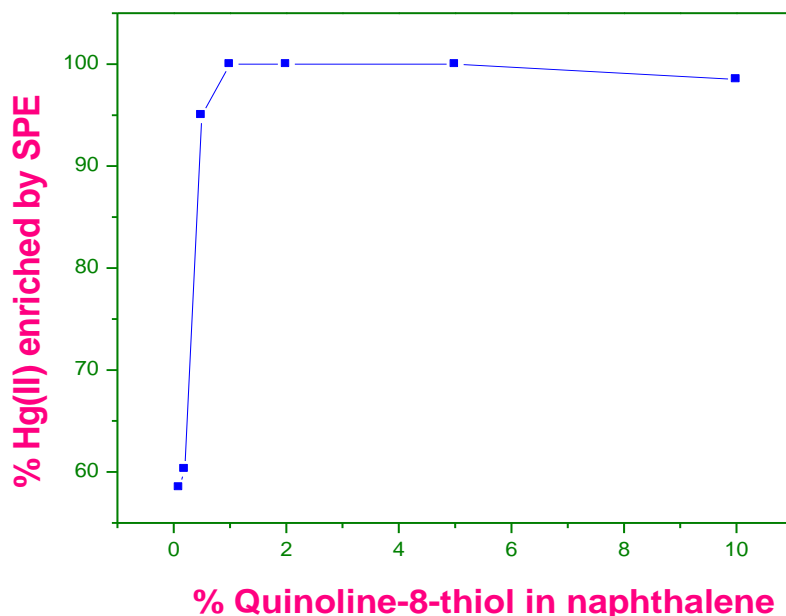


Fig. 2.3 Effect of quinoline-8-thiol concentration in naphthalene

2.3.3 Effect of time of stirring

The time of stirring was varied from 5 to 60 minutes during the preconcentration of mercury (II) onto quinoline-8-thiol modified naphthalene. The determination of mercury (II) enriched on to quinoline 8-thiol modified naphthalene was carried out as described in section 2.3.1. The results obtained are shown in figure 2.4. It is clear that a minimum of 15 minute of stirring time was enough for quantitative enrichment of mercury (II). In all subsequent experiments 15 minute stirring time was used.

2.3.4 Effect of aqueous phase volume

The effect of aqueous phase volume on the preconcentration of mercury (II) onto quinoline-8-thiol modified naphthalene in the range 10-250 ml was studied. The preconcentrated mercury (II) onto quinoline-8-thiol modified naphthalene was determined by dithizone procedure as described in Section 2.3.1. The results obtained (Table 2.2) indicate that quantitative preconcentration of mercury (II) was observed up to 250 ml and thus enabling enrichment factor of 50.

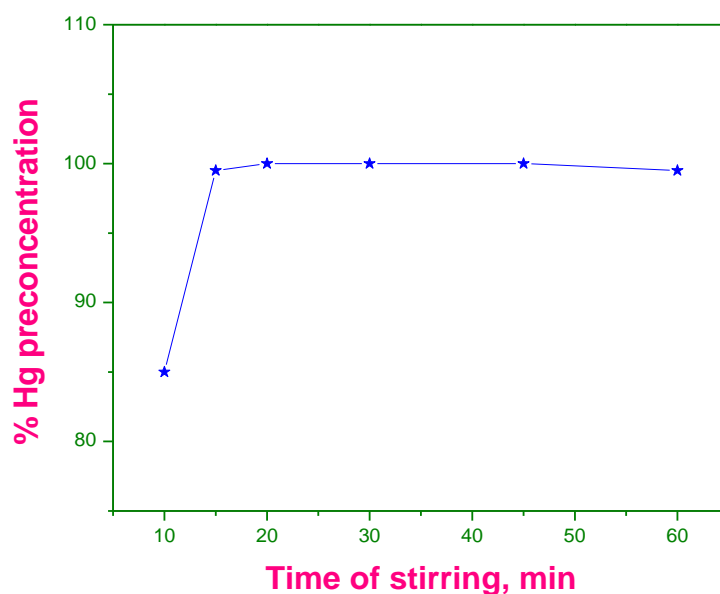


Fig. 2.4 Effect of time of stirring

Table 2.2 Effect of aqueous phase volume

Aqueous phase volume (ml)	% of Hg pre-concentrated
10	99.0 ± 1.0
25	99.0 ± 1.0
50	99.0 ± 1.0
100	99.0 ± 1.0
250	98.0 ± 2.0
500	94.5 ± 1.5
1000	90.5 ± 1.5

2.3.5 Choice of solvent

Various solvents were tested for the dissolution of the mercury chelate of quinoline-8-thiol together with naphthalene. This material was found to be insoluble in many non-aqueous solvents but dissolved easily in water miscible solvents like acetone, DMF, acetonitrile and DMSO. 2ml of acetone or DMF were enough for the dissolution of 0.5 g of mercury (II) adsorbed quinoline-8-thiol modified naphthalene. On the other hand, 2.5 and 5.0 ml of acetonitrile and DMSO were required for complete dissolution. Hence, acetone was chosen in further studies in view of high solubility and low cost.

2.4 CALIBRATION GRAPH, SENSITIVITY AND PRECISION

A series of solutions containing 0.5 to 50 μg of mercury (II) was diluted to 250ml and the pH was adjusted to 6.0 ± 1.0 by using ammonium acetate buffer. 0.5g of quinoline-8-thiol modified naphthalene was added to the above solution and stirred for 15 minutes. The solution was filtered and the residue obtained was dissolved in 2 ml of acetone and transferred in to separating funnel containing 10ml of chloroform equilibrated water, 2.5ml each of 5.0M sulphuric acid and acetic acid and 5ml dithizone in CHCl_3 . The mixture was shaken for about 1 min. The organic layer was separated and collected in the 10 ml dry standard flask and the absorbance was measured at 500nm [25]. Under the optimum conditions described above, the calibration curve (Fig.2.5) was linear over the concentration range 0.5-50 μg present in 250 ml of the sample solution.

Ten replicate determinations of 10 μg of mercury (II) present in 250 ml of the solution gave a mean absorbance of 0.206 with a relative standard deviation of 1.95% (cf. Table 2.3). The limit of detection (lowest concentration below which recoveries becomes non quantitative) corresponding to three times the standard deviation of the blank (3σ) was found to be $2\mu\text{g/l}$. All the statistical calculations are based on the average of triplicate readings for each standard solutions in the given range.

2.5 EFFECT OF DIVERSE IONS

Sample solutions containing 10 μg of mercury(II) and various amounts of different metal ions were subjected to preconcentration and determination by following the procedure described in Section 2.4. The tolerance limit (error < 3%) are given in Table 2.4. From the table, no interference was observed due to 100-fold amounts of Li(I), Na(I), K(I), Ca(II), Ba(II), Sr(II), Be(II), Pb(II), Co(II), Ni(II), Al(III), La(III), Zr(IV), Th(IV), U(VI), NO_2^- , Cl^- , NO_3^- , SO_4^{2-} , 50 fold amounts of Cd(II), Cu(II) and Cr(III) and 10 fold amounts of Mn(II), Fe(II),

Te(IV), V(V) and Mo(VI). Further, equal amounts of Sb(III) and Cr(VI) also did not interfere in the above developed preconcentration procedure.

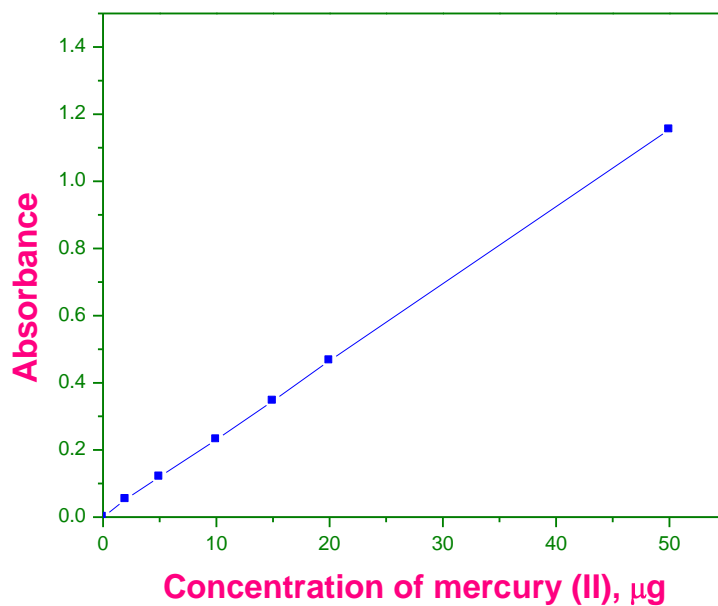


Fig.2.5 Calibration graph

Table 2.3 Precision studies

Sl.No.	Absorbance	Hg(II) found (μg) X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
1	0.202	9.80	- 0.20	0.0400
2	0.208	10.09	0.09	0.0081
3	0.205	9.95	- 0.05	0.0025
4	0.206	10.00	0.00	0.0000
5	0.210	10.19	0.19	0.0361
6	0.199	9.66	- 0.34	0.1156
7	0.210	10.24	0.24	0.0576
8	0.202	9.81	- 0.19	0.0361
9	0.208	10.10	0.10	0.0100
10	0.210	10.19	0.19	0.0361

$$\bar{X}_i = 10.00 \quad \Sigma (X_i - \bar{X})^2 = 0.3441$$

$$\sigma = \sqrt{\frac{\Sigma(X_i - X)^2}{n-1}}$$

$$\sigma = \sqrt{\frac{0.3441}{9}} = 0.1949$$

$$\text{Relative standard deviation} = \frac{0.1949}{10.00} \times 100 = 1.949\%$$

Table 2.4 Effect of diverse ions

Sl. No.	Ion	Compound taken	Tolerance limit*
1	Li	Li ₂ CO ₃	100
2	Na	NaCl	100
3	K	KCl	100
4	Ca	Ca(OH) ₂	100
5	Ba	BaCl ₂ .2H ₂ O	100
6	Sr	SrCl ₂ .6H ₂ O	100
7	Be	BeSO ₄ .4H ₂ O	100
8	Cd	3CdSO ₄ .8H ₂ O	50
9	Pb	Pb(NO ₃) ₂	100
10	Zn	ZnO	100
11	Co(II)	Co(NO ₃) ₂ .6H ₂ O	100
12	Mn(II)	MnCl ₂ .4H ₂ O	10
13	Cu(II)	CuSO ₄ .5H ₂ O	50
14	Fe(III)	FeCl ₃	-
15	Al(III)	Al ₂ O ₃	-
16	Sb(III)	Sb ₂ O ₃	1
17	La(III)	La(NO ₃) ₃ .6H ₂ O	-
18	Bi(III)	Bi(NO ₃) ₃ .5H ₂ O	-
19	Zr(IV)	ZrOCl ₂ .8H ₂ O	100
20	Th(IV)	Th(NO ₃) ₄ .6H ₂ O	10
21	U(VI)	UO ₂ (CH ₃ COO) ₂ .2H ₂ O	100
22	Te(IV)	TeCl ₄	10
23	Mo(VI)	Na ₂ MoO ₄ .H ₂ O	10
24	Cr(VI)	K ₂ Cr ₂ O ₇	1
25	Br ⁻	KBr	-
26	I ⁻	KI	-
27	NO ₂ ⁻	NaNO ₂	100
28	SCN ⁻	KSCN	-
29	AsO ₄ ³⁻	Na ₂ HAsO ₄ .7H ₂ O	100
30	VO ₄ ³⁻	Na ₃ VO ₄ .H ₂ O	-

*Maximum Interferent tested = 1000 µg

2.6 SPECTRAL STUDIES

Compounds	Spectral Data
A: Naphthalene	IR: 3040cm ⁻¹ , 1610 cm ⁻¹ ¹ H NMR: δ: 7.7 [4H,q], δ: 7.5 [4H,q].
B: Quinoline8-thiol modified naphthalene	Additional peaks IR: 3040cm ⁻¹ , 2585cm ⁻¹ 680cm ⁻¹ ¹ H NMR: δ: 2.99
C: Quinoline8-thiol modified naphthalene + Mercury (II)	Peaks disappeared IR 2585cm ⁻¹ , 680cm ⁻¹ ¹ H NMR: δ: 2.99 Additional peaks IR: 439 cm ⁻¹ 640cm ⁻¹

On comparing the IR spectra of A and B two additional peaks appeared in B at 2585cm⁻¹ and 680cm⁻¹ which are characteristic peaks of S-H and C-S bonds. In the proton NMR also, an additional peak appeared at δ: 2.99. From these spectral studies, it was found that Quinoline-8-thiol is coprecipitated with naphthalene and totally acts as collector. While comparing the IR spectra of B and C two additional peaks are seen in C at 439cm⁻¹ and 640cm⁻¹, but the peak present in the spectrum of B at 2585cm⁻¹ disappears in the case of C. The peak at δ 2.99 in the NMR spectrum of B, corresponding to the S-H proton disappears in the spectrum of C. These spectral studies indicate the formation of mercury (II)-quinoline-8-thiol complex. The extra peak in the IR spectrum of C at 439cm⁻¹ indicates the Hg-S bond and the disappearance of peak at 2585cm⁻¹ in the IR spectrum the peak at δ :2.99 in the NMR spectrum of C indicate the loss of proton while complex formation. The shift in IR frequency from 680cm⁻¹ (in B) to 640cm⁻¹ (in C) confirms the complex formation through C-S bond.

2.7 EQUILIBRIUM LOADING OF CHELATING AGENT MODIFIED NAPHTHALENE

This experiment was carried out by equilibrating 0.05 g of quinoline-8-thiol modified naphthalene with 0.5 mg of mercury and filtered through a filter paper. The equilibrium loading of quinoline-8-thiol modified naphthalene was calculated to be 875 µg per g of SPE.

2.8 APPLICATION

2.8.1 Analysis of standard reference materials

The accuracy of the developed preconcentration procedure was tested by analyzing standard hair sample supplied by International Atomic Energy Agency, Vienna, Austria. The hair sample was dissolved in HNO₃-H₂O₂ mixture (3:2) and heated for 30 min at 200°C on a hot plate. The dissolved hair material is cooled and diluted with water. The mercury (II) present in the sample was preconcentrated by using quinoline-8-thiol modified naphthalene by following the procedure described in Section 2.4 and determined by dithizone procedure. The results obtained are shown in Table 2.5, from which it is clear that the amount of mercury (II) obtained in hair sample by the developed method is comparable with the certified values. Furthermore, known amounts of mercury (II) were added to standard reference material before dissolution prior to preconcentration and determination procedure. The recoveries were found to be good, indicating the suitability of the developed procedure for the determination of mercury (II) in hair samples. The flow chart for the analysis of human hair samples is given in Fig.2.6.

**Table 2.5 Determination of mercury (II) in hair samples
[Hair (IAEA-086) Standard reference material]**

Mercury (II) added $\mu\text{g/g}$ of hair sample	Mercury found $\mu\text{g/g}$		% Recovery
	Present method*	Certified value	
None	0.57 ± 0.01	0.573	-
0.50	1.06 ± 0.02	-	98.0 ± 1.5
1.00	1.56 ± 0.01	-	99.0 ± 0.8

*Average of 3 determinations

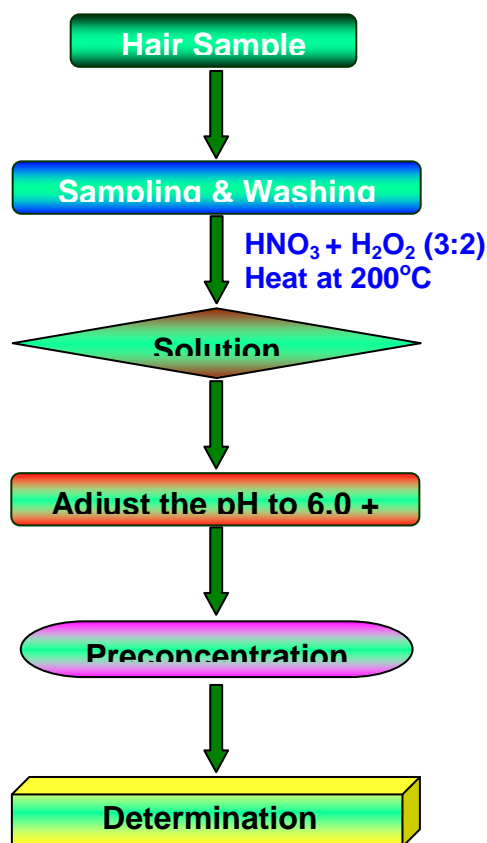


Fig. 2.6 Flow chart for the analysis of human hair samples

2.8.2 Analysis of human hair samples

Human hair samples of different age and sex, collected from different cities (Tirupati, Chennai, Madurai) were brought into solution, subjected to preconcentration by quinoline-8-thiol modified naphthalene and subsequent determination by dithizone procedure. The results obtained are shown in Table 2.6, along with the standard deviation for triplicate measurements. Furthermore, the results obtained by SPE enrichment followed by spectrophotometric procedure were compared with standard cold vapour mercury analyzer. The mercury(II) in human hair samples was in the range 0.25-1.60 $\mu\text{g/g}$ which are comparable to values reported in literature, viz. 1.8 (USA), 0.7 (Iraq) and 1.2 (Pakistan) $\mu\text{g/g}$ of mercury.

Table 2.6 Analysis of human hair samples

Sample	Mercury found ($\mu\text{g/g}$)	
	Present method*	Hg analyzer
1	0.40 \pm 0.01	0.60 \pm 0.01
2	0.65 \pm 0.01	0.60 \pm 0.01
3	0.27 \pm 0.01	0.25 \pm 0.01
4	< 0.1	< 0.1
5	0.27 \pm 0.01	0.25 \pm 0.01
6	1.50 \pm 0.03	1.60 \pm 0.03
7	1.30 \pm 0.01	1.40 \pm 0.03
8	1.30 \pm 0.01	1.40 \pm 0.02
9	1.08 \pm 0.01	1.00 \pm 0.02
10	2.50 \pm 0.04	2.60 \pm 0.04
11	0.54 \pm 0.01	0.50 \pm 0.02
12	0.40 \pm 0.01	0.40 \pm 0.01
13	0.75 \pm 0.01	0.80 \pm 0.01
14	0.27 \pm 0.01	0.80 \pm 0.01
15	1.54 \pm 0.02	1.40 \pm 0.02
16	1.00 \pm 0.02	1.00 \pm 0.02
17	< 0.1	< 0.1
18	< 0.1	< 0.1
19	< 0.1	< 0.1
20	0.41 \pm 0.01	0.41 \pm 0.01

*Average of three determinations

2.9 EXPERIMENTAL

2.9.1 Apparatus

Absorbance values were measured using Hitachi 220 microprocessor controlled double beam spectrophotometer (Hitachi, Japan). Magna IR-5560 spectrometer (Nicolet, USA) and DPX-300 NMR spectrometer (Brucker Avance, Switzerland) were used for taking IR & NMR spectra. LI-120 digital pH meter (ELICO, India) was used for pH measurements.

A pair of matched 10 mm quartz cuvettes which are cleaned with acid mixture thoroughly and washed with distilled water, was used for the study.

2.9.2 Reagents

- (1) Standard mercury(II) solution (1000 $\mu\text{g/ml}$): Prepared by dissolving 0.3385 g of mercury(II) chloride in water and diluted to 250 ml. This solution was standardized by titrating with EDTA. A suitable volume of this solution was diluted to get a 10 $\mu\text{g/ml}$ of working solution of mercury (II) as and when required.
- (2) Sulphuric acid solution (5.0M): 69.4 ml of AR grade concentrated sulphuric acid was added to 180 ml of distilled water.
- (3) Acetic acid solution (6.0M): 86.2 ml of glacial acetic acid was diluted to 250 ml.
- (4) Dithizone solution (0.001% w/v): 0.001 g of dithizone was dissolved in 100 ml of chloroform and stored in dark.
- (5) Other reagents like naphthalene, quinoline-8-thiol, acetone and other reagents were of analytical reagent grade. Double distilled water was used throughout.

2.9.3 Preparation of quinoline-8-thiol modified naphthalene

Quinoline-8-thiol and naphthalene in the weight ratio of 1:100 was dissolved in minimum amount of acetone. This 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 3 h and was allowed to settle for 10 min. It was filtered through a filter paper, placed in a Buchner funnel by suction, washed with water and dried in an oven at 40°C for several hours and then stored in amber coloured bottle and kept in desiccator.

2.10 GENERAL PROCEDURE

2.10.1 Solid phase extraction and determination of mercury(II)

A portion of mercury(II) solution (0.5-50 µg) was diluted to 250 ml and the pH was adjusted to 6.0±1.0 by using dil.HCl or NaOH after the addition of 10 ml of 1.0 M ammonium acetate buffer and transferred to 500 ml beaker. 0.5 g of quinoline-8-thiol modified naphthalene was added to the above solution and stirred for 15 min. The residue obtained after filtration was dissolved in 2 ml acetone and determined by dithizone procedure after adding 2.5 ml each of 5.0M sulphuric acid and 6.0M acetic acid, diluted to 15 ml with chloroform equilibrated water and shaken for 1 min with 5 ml of dithizone in chloroform. The chloroform layer was collected over anhydrous sodium sulphate and the absorbance of mercury-dithizone complex was measured at 500 nm.

2.10.2 Procedure for analysis of hair reference material

1 g of hair sample (IAEA-086) was dissolved in 25 ml of HNO₃-H₂O₂ mixture (3:2) and heated for 30 min at 200°C on hot plate. The solution was cooled and the pH of the solution was brought to 6.0±0.1 with sodium hydroxide after the addition of 10 ml of 1.0 M ammonium acetate buffer and transferred to 500 ml beaker. The preconcentration of mercury(II) on quinoline-8-thiol modified naphthalene and determination by dithizone were carried out as described in “General Procedure” given above. The mercury(II) content was

established by reference to calibration graph prepared by taking known amounts of mercury and determined by dithizone procedure.

2.10.3 Procedure for analysis of human hair samples

Hair samples were collected from males and females of different age, cities and states in India. The sampling protocol and washing procedures were carried out by Ryabukin [26], Assarian and Oberleas [27] and Rao et al [28]. One of the hair samples was dissolved in 25 ml of HNO₃-H₂O₂ mixture (3:2) and heated for 30 min at 200°C on hot plate. The solution was cooled and the pH was brought to 6.0±0.1 with sodium hydroxide after the addition of ammonium acetate buffer and transferred to 500 ml beaker. The preconcentration of mercury(II) onto quinoline-8-thiol modified naphthalene and determination by dithizone were carried out as described in “General Procedure” given above. The mercury(II) content was established by reference to calibration graph prepared by taking known amounts of mercury and determined by dithizone procedure.

2.11 CONCLUSION

The experiments reported in this study reveal the flexibility and reliability of preconcentration of mercury(II) by solid phase extraction in a batch mode and spectrophotometric determination. The limit of detection is lowered (0.001 µg/ml) when compared to methyltrioctyl ammonium chloride (D.L=0.13 µg/ml) modified naphthalene. The SPE procedure facilitates a 50 fold enrichment of mercury (II) from dilute solutions. Since the elution is not done here, more number of samples can be analyzed in a short time. The developed preconcentration procedure enables the reliable determination of mercury (II) in hair samples using a simple, low cost and readily available spectrophotometer.

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CHAPTER 3

REMOVAL OF TOXIC MERCURY(II) SPECIES FROM CHLOR-ALKALI INDUSTRIAL WASTES

3.1 INTRODUCTION

For many years, the chlor-alkali Industry all over the world has been a matter of concern because of the pollution due to the presence of mercury(II) in the wastage. In India, of recently, although the industries producing cast alkali have been switched over to more environmentally friendly membrane based process, still 50% of chlor-alkali industries are based on mercury cell process. Hence the contamination of mercury in brine sludge and effluents of chlor-alkali industry is more important compared to the waste from other industries such as paper and pulp, manufacture of vinyl chlorides, paints, pesticides, fungicides and cinnabar processing. Hence, the removal of mercury from these hazardous wastes assumes increasing importance.

Conventional mercury treatment technologies include precipitation [1-6], carbon adsorption [7-9], ion exchange [10-13], cementation [10-12] and roasting [13-15]. Hydrometallurgical routes [16-21] are also being considered as economic alternative for mercury(II) removal from waste streams. The above mentioned conventional mercury treatment processes are non-selective and roasting or retorting only removes mercury. However, ion exchange based methods are afford better removal of mercury. But these processes are time consuming and inherently expensive. Liquid-liquid extraction also emerged as an important technique for the removal of mercury(II) ions. Technicas Revnidas, SA, Spain [22] and Baba et al [23] have developed liquid-liquid extraction based processes for the removal of mercury(II) from waste streams of a chlor-alkali industry. But solid phase extraction now a days is emerging as a powerful

technique and in most instances replacing liquid-liquid extraction processes because of the following reasons.

- (1) Absence of emulsion
- (2) Minimal costs due to low consumption of reagents
- (3) Higher enrichment factors
- (4) Reusability of the adsorbent
- (5) Safety with respect to hazardous samples, and
- (6) More importantly environment friendly

Various SPE procedures described in the literature pertain to enrichment of traces of mercury(II) from dilute aqueous solutions prior to determination by suitable analytical techniques. However, none of these reports addresses the problem of removal of mercury from chlor-alkali industrial wastes. On the other hand, activated carbon (AC) is widely used all over the world for removal of mercury(II) from chlor-alkali wastes. However, the main problem lies in the storage and disposal of mercury(II) containing activated carbon. Chelate sorbed AC is thought to be a viable alternative to address the above disposable problem as it will reduce the amount of AC required for the removal of mercury(II). The disposal process may become an alternative if it can be recycled via several adsorption-desorption processes for the removal of mercury(II).

In the present work, selective SPE procedures were developed for the removal of mercury(II) from brine sludge and cell house effluents of a chlor-alkali industry with the use of one such extractant viz, 1(2-thiazolylazo)-2-naphthol sorbed activated carbon.

3.2 PREPARATION OF 1-(2-THIAZOLYLAZO) NAPHTHOL (TAN) SORBED AC

0.20g of TAN was dissolved in minimum amount of acetone and was poured as a fine stream into 500 ml of water containing 10 g of AC with constant stirring at room temperature. The resulting slurry was stirred for 1 h and was allowed to settle for 10 min. The bulk of the supernatant aqueous solution was

decanted and then filtered through a filter paper placed in a “Buchner funnel” by suction, washed with water and dried in a oven at 80°C for several hours and then stored in dessicator.

3.3 PRELIMINARY INVESTIGATIONS

The solid phase extraction of 5 µg of mercury(II) whose pH was adjusted to 6.0±0.2 after adding 10 ml of 1.0 M of ammonium acetate onto 0.2 g of 2% TAN sorbed AC. The mercury(II) adsorbed on TAN modified AC was eluted with 2x10 ml of 1.0 M HNO₃. The mercury(II) in the eluent was determined spectrophotometrically using Iodide - Rhodamine 6G procedure [24]. These studies gave encouraging results in the removal of mercury(II) from dilute aqueous solutions and detailed optimization studies were carried out for its removal.

3.4 OPTIMIZATION OF EXPERIMENTAL VARIABLES

3.4.1 Effect of pH

The effect of pH on the removal of 5 µg of mercury(II) present in 1.0 l of solution was studied by adding 0.2 g of 2% TAN sorbed AC as SPE in the pH range 5.0-9.0. Mercury(II) preconcentrated onto TAN sorbed AC was determined spectrophotometrically via Iodide - Rhodamine 6G procedure, after eluting with 2x10 ml of 1.0 M HNO₃. The percent removal of mercury(II) onto TAN sorbed AC is constant and maximum in the pH range 5.8-6.2 (Fig.3.1). In all subsequent work, the pH was adjusted to 6.0±0.2 after the addition of 10 ml of 1.0 M of ammonium acetate buffer.

3.4.2 Effect of TAN concentration in activated carbon

The concentration of TAN in AC was varied from 0.1 to 5.0%. Mercury(II) enriched onto TAN sorbed AC was determined spectrophotometrically as described in Section 3.4.1. The results obtained are shown in Fig.3.2. The removal

of 5 μ g of mercury(II) present in 1.0 l of solution was quantitative when the concentration of TAN in AC was greater than 2% (Fig.3.2). Hence, 2% TAN sorbed AC was used in the subsequent studies.

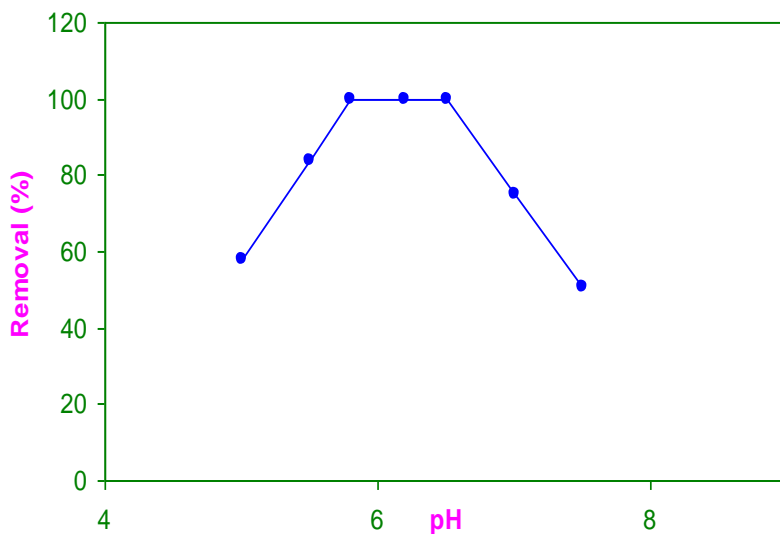


Fig.3.1 Effect of pH

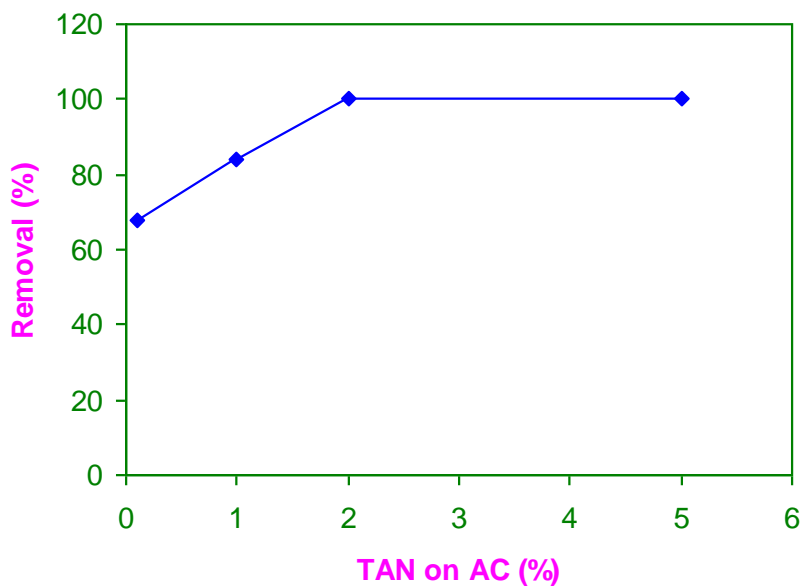


Fig.3.2 Effect of TAN concentration in AC

3.4.3 Effect of weight of chelate sorbed activated carbon

The weight of TAN sorbed AC was varied from 0.05 to 0.5 g. The removal of mercury(II) was quantitative when the amount of TAN sorbed AC was greater than 0.1 g (See Fig.3.3). Hence, 0.2 g of TAN sorbed AC was recommended for quantitative removal of mercury(II).

3.4.4 Effect of time of stirring

The time of stirring was varied from 5-60 min during the removal of 5 μg of mercury(II) present in 1.0 l of solution by using TAN sorbed AC. The results obtained are shown in Fig.3.4, from which it is clear that a minimum of 10 min of stirring was enough for the quantitative removal of mercury(II) by TAN modified AC. Ten minutes of stirring time was used in all subsequent experiments.

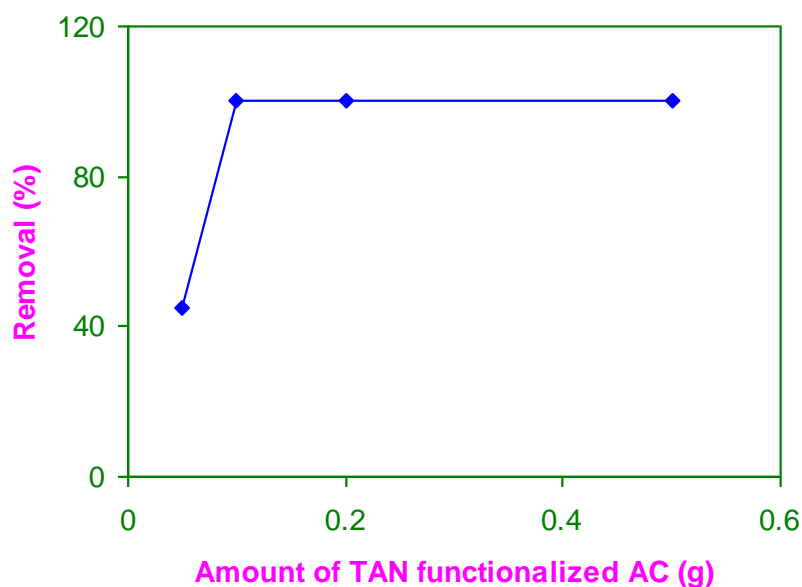


Fig.3.3 Effect of weight of TAN sorbed AC on removal of mercury(II)

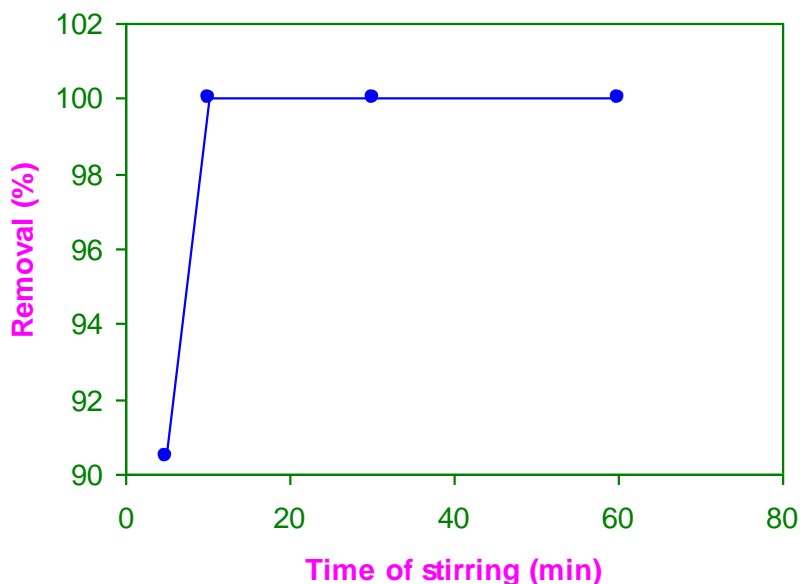


Fig.3.4 Effect of time of stirring on removal of mercury (II)

3.4.5 Effect of aqueous phase volume

The effect of aqueous phase volume on the removal of 5 µg of mercury(II) with TAN sorbed AC was studied in the range 25-1000 ml. The results obtained as shown in Table 3.1 indicate that quantitative removal of mercury(II) was possible even up to 1.0 l of sample solution.

Table 3.1 Effect of aqueous phase volume

Aqueous phase volume (ml)	% of Hg Removal
25	> 99.8
50	> 99.8
100	> 99.8
250	> 99.8
500	> 99.8
1000	> 99.5

3.4.6 Choice of eluting agent

The mercury(II) adsorbed on TAN sorbed AC was eluted with 1.0M of mineral acids such as hydrochloric acid, sulphuric acid and nitric acid. The results obtained are shown in Table 3.2. The quantitative removal was achieved with

sulphuric acid and nitric acid. Nitric acid eluent was used for all subsequent studies.

Table 3.2 Choice of eluent

Eluent (1.0M) used	% removal of mercury(II)
HCl	73.4
H ₂ SO ₄	> 99.8
HNO ₃	> 99.8

3.4.7 Reuse studies

TAN modified AC was recycled for several times. Even after ten cycles of sorption and desorption of mercury(II) from TAN sorbed AC, the removal of mercury(II) was >99%.

3.5 EFFECT OF DIVERSE IONS

Sample solutions containing 5µg of mercury(II) and various amount of different metal ions were subjected to removal of mercury(II) by following the procedure described in section 3.4.1. No deleterious effect was observed due to 100-fold amounts of Li(I), Na(I), Ca(II), Ba(II), Sr(II), Be(II), Co(II), Pb(II), Ni(II), Al(III), La(III), Zr(IV), Th(IV), U(VI), NO₂⁻, Cl⁻, SO₄²⁻, 50 fold amounts of Cd(II), Cu(II) and Cr(III), and 10 fold amounts of Mn(II), Fe(II), and Mo(VI) in removal of mercury(II). Thus, mercury(II) can be selectively removed when present along with above metal ions through the use of TAN modified AC as SPE material.

3.6 EQUILIBRIUM LOADING OF MERCURY(II) ONTO TAN

This experiment was carried out by taking a solution containing 0.5 mg of mercury(II) and 0.2 g of TAN modified AC and 10 ml of 1.0M ammonium acetate buffer was added. The pH was adjusted to 6.0±0.2 and was diluted to 25 ml and transferred to a 60 ml separating funnel. This solution was equilibrated for 30 min and filtered through a filter paper. The amount of mercury(II) left out in the filtrate was determined by Iodide - Rhodamine 6G procedure. The equilibrium loading of TAN sorbed AC SPE material was found to be 2.24 mg/g of the

adsorbent which is much higher when compared to AC alone (≈ 0.75 mg/g). Therefore TAN modified AC effectively removes mercury(II) approximately 3 times when compared to AC alone.

3.7 MERCURY(II) REMOVAL STUDIES

3.7.1 Aqueous solutions

Mercury(II) present at levels of $5\mu\text{g}$ in 1.0 l of aqueous solution was stirred with TAN sorbed AC. The filtrate was analysed by CVAAS. This result indicates the absence of mercury(II). This means that all the mercury(II) ions present in the aqueous solution has been removed completely. Furthermore, the amount of mercury(II) present in AC phase was also determined after the elution with HNO_3 . These CVAAS studies indicate quantitative removal of mercury(II) in all tested concentration levels confirming that TAN sorbed AC can reliably be used for the removal of mercury(II).

3.7.2 Synthetic chlor-alkali effluent

Synthetic samples containing other inorganic species corresponding to composition of chlor-alkali industrial waste of M/S Travancore-Cochin Chemicals Limited, Kerala, (Table 3.3) were prepared and tested for the removal of mercury(II) by using TAN sorbed AC. The removal of mercury(II) was unaffected in presence of various extraneous ions.

Table 3.3 Typical composition of chlor-alkali industrial waste of M/s. Travancore-Cochin Chemicals Limited, Kerala

Chemical composition	Concentration
Ca	38.6 mg/ml
Mg	5.8 mg/ml
Zn	21.6 $\mu\text{g/ml}$
Fe(III)	6.5 $\mu\text{g/ml}$
Hg(II)	2.75 $\mu\text{g/ml}$
Ba	45.4 $\mu\text{g/ml}$

3.7.3 Brine sludge

The developed solid phase extraction procedure for the extraction of mercury(II) using TAN sorbed AC was applied for the removal of mercury(II) from the brine sludge collected from M/s. Travancore-Cochin Chemicals Limited, Cochin, India. One gram of brine sludge sample was dissolved in 25 ml of 1:1 HNO₃ and heated until it is dissolved. The resulting solution was diluted to 100 ml with deionised water. The pH of this solution was adjusted to 6.0±0.2 and 0.2 g of 2% TAN modified AC was added. The resulting solution was stirred for 10 min and the mercury(II) adsorbed on TAN sorbed AC was eluted with 2x10 ml of 1.0M HNO₃. Suitable aliquots of this eluent was taken and removal of mercury(II) using TAN sorbed AC SPE was determined by Iodide - Rhodamine 6G and CVAAS procedures. The removal of mercury(II) by the developed preconcentration procedure was found to be > 99.8% (See Table 3.4) indicating the quantitative removal of mercury(II) from brine sludge sample.

Table 3.4 Removal of mercury(II) from brine sludge and cell house effluents of chlor-alkali industry*

Sl.No.	Description of sample	Mercury(II) added	Mercury(II) removed**	% Removal
			Present method (SPE-Spect.)	
1	Brine sludge (µg/g)	-	128.0±1.0	-
		60.0	188.0±2.0	>99.8
		120.0	250.0±3.0	>99.8
2	Cell house effluent (µg/l)	-	1.63±0.01	-
		0.8	2.42±0.02	>99.8
		1.60	3.23±0.03	>99.8

*collected from M/s. Travancore-Cochin Chemicals Limited, Cochin, India

**Average of 3 determinations

3.7.4 Removal of mercury(II) from cell house effluent

Suitable aliquots of cell house effluent collected from M/s. Travancore-Cochin Chemicals Limited, Cochin, India were taken and the pH was adjusted to

6.0±0.2. The preconcentration, elution, determination by Iodide-Rhodamine 6G and CVAAS procedures were carried out as described in Section 3.7.3. The mercury left out in the aqueous phase was < 0.2%.

The mercury(II) concentration in the brine sludge cell house effluent were found to be ~125 µg/g and ~1.60 µg/l as determined by CVAAS.

3.8 EXPERIMENTAL

3.8.1 Apparatus

A Hitachi-220 double beam spectrophotometer and an ECIL make cold vapour atomic absorption spectrometer were used for the estimation of mercury(II) and LI-120 digital pH meter (ELICO, India) was used for pH measurements.

3.8.2 Reagents

Activated carbon (AC), 1-(2-thiazolyl-2-naphthol(TAN) were obtained from Aldrich Chemical Company Inc., Milwaukee, WI, USA. All other chemicals used were of analytical reagent grade.

3.8.3 Preparation of TAN sorbed activated carbon

0.2g of TAN was dissolved in minimum amount of acetone and was poured as a fine stream into 500ml of water containing 10g of AC with constant stirring at room temperature. The resulting suspension was stirred for 1 hour and was allowed to settle for 10 min. Then, bulk of the supernatant solution was decanted and filtered through a filter paper placed in a Buchner funnel by suction, washed with water and dried in an oven at 80°C for several hours and then stored in desiccator.

3.9 REMOVAL STUDIES

The SPE of mercury from the brine sludge and cell house effluent of chlor-alkali industry is comprised of the following steps:

- (1) Dissolution of the brine sludge with 1:1 HNO₃.
- (2) The pH of the resultant brine sludge or cell house effluent solutions were adjusted to 6.0±0.2 and extracted with 0.2 g of 2% TAN modified AC SPE material, whereupon mercury(II) was selectively removed with TAN sorbed AC.
- (3) Elution of the mercury(II) bound on TAN sorbed AC SPE by using 2x10 ml of 1.0M HNO₃ to remove all the mercury(II) present in SPE.

This investigation reveals that > 99.8% mercury(II) can be decontaminated from brine sludge/cell house effluent. The flow chart for the removal of mercury(II) from brine sludge and cell house effluents of chlor-alkali industry is given in Fig. 3.5.

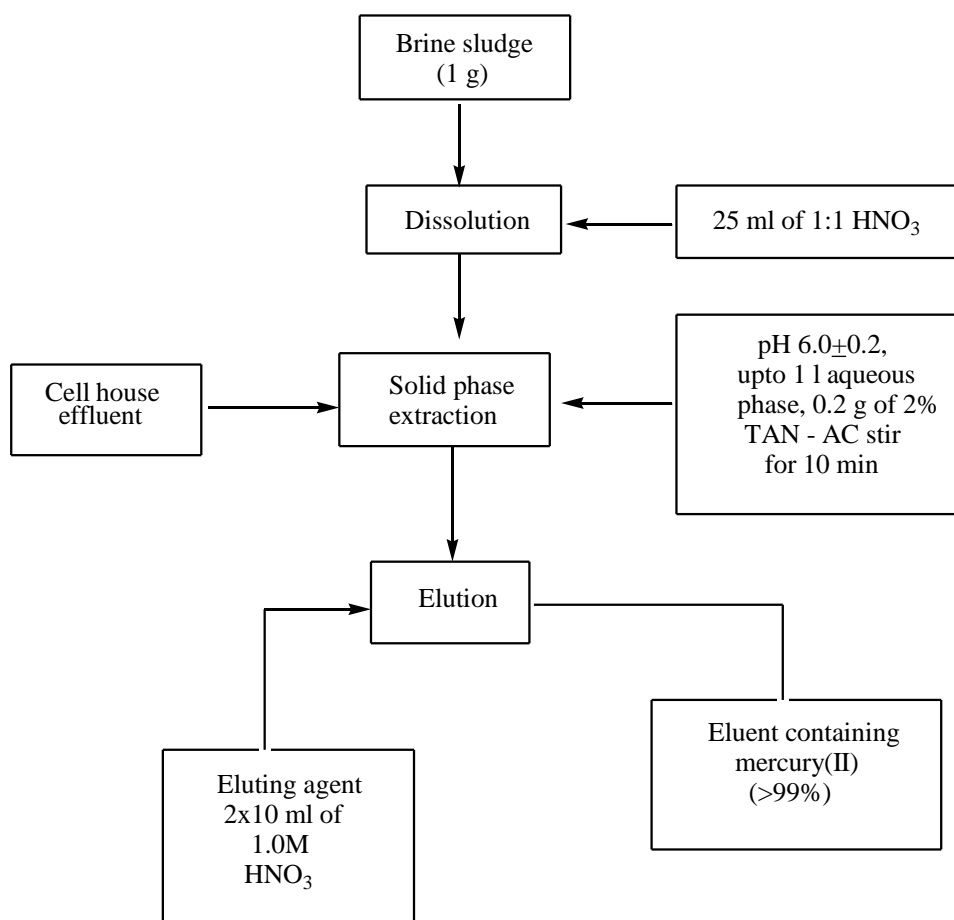


Fig 3.5 Flow chart for removal of mercury(II) from brine sludge and cell house effluents of chlor-alkali industry

3.10 CONCLUSION

This study clearly demonstrates the use of TAN functionalized AC solid phase extractant for selective removal of mercury(II) from dilute aqueous solutions containing Mg(II), Ca(II), Ba(II) and Fe(III) ions. In addition, the results clearly demonstrated the usefulness of TAN modified AC for selective removal of mercury(II) from hazardous materials like brine sludge and cell house effluents of chlor-alkali industry. Furthermore, the higher retention/sorption capacity of TAN sorbed AC compared to AC for mercury(II) enabled the minimization of subsequent waste disposal problems. In view of the reusability over 10 cycles makes this TAN sorbed AC as an attractive material for the removal of mercury(II) from chlor-alkali industry wastes.

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CHAPTER 4

SOLID PHASE EXTRACTIVE PRECONCENTRATION OF URANIUM(VI) USING DIARYLAZOBISPHENOL MODIFIED ACTIVATED CARBON

4.1 INTRODUCTION

Uranium is a natural and commonly occurring radioactive element. It is found in very small amounts in nature in the form of minerals but may be processed into a silver coloured metal. Rocks, soil, surface and ground water, air and plant, and animal cells contain varying amounts of uranium. Typical concentrations in most materials are a few parts per million (ppm). Some rocks and soils may also contain greater amounts of uranium. The concentration of uranium in phosphate rocks is in the range 0 – 0.12 mg/g. The total amount of natural uranium can be carried into rivers and lakes. The main civilian use of uranium is in nuclear power plants and on helicopters and air planes. It is also used by the armed forces as shielding to protect Army tanks, parts of bullets and missiles to help them go through enemy armored vehicles, as a source of power, and in nuclear weapons, very small amounts are used to make some ceramic ornament glazes, light bulbs, photographic chemicals, and household products. The low concentrations of uranium encountered in geological and environmental samples and the presence of high levels of interfering matrix constituents prevent its direct determination. Hence, the recovery of uranium from dissolved solutions of minerals and ores assumes importance prior to its determination.

Uranium possesses both chemical and radiological hazards, and is extremely toxic. The high toxicity of soluble compounds of uranium [(UF₆, UO₂(NO₃)₂, UO₂Cl₂, UO₂F₂, and uranyl acetates, sulphates and carbonates) is largely manifested in irreversible kidney damage. Insoluble compounds of uranium (UO₂, U₃O₈) are extremely poisonous and induce damage to liver. The

safe concentration of uranium in drinking water may be within the range of proposed guideline value of 2-30 µg/l. The most stable form of uranium(VI) in aqueous solution that probably exists in most of the body fluids is dioxouranium, commonly known as the uranyl ion. This is an ion of intermediate hardness with high affinity for hard bases like O & N, donor atoms. Because of this, various preconcentrative separation techniques are employed for selective removal of toxic uranium from environmental samples.

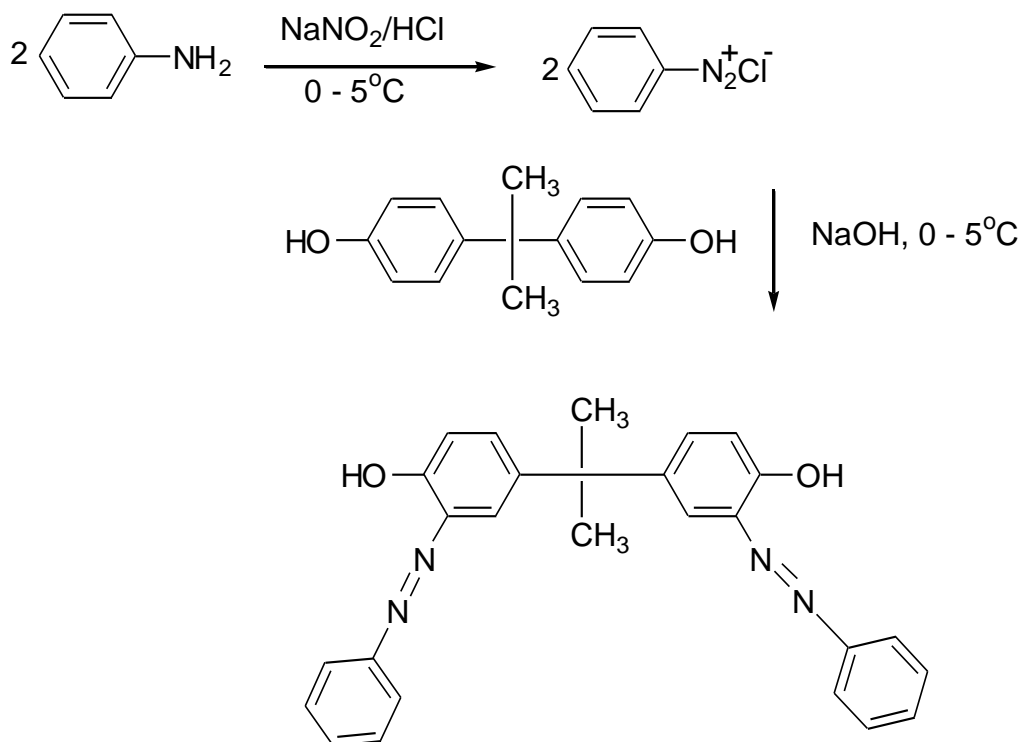
Activated carbon was one of the good solid support in view of high surface area, ease of elution, ready availability and high retention capacity. However, activated carbon alone does not adsorb inorganics quantitatively at trace and ultra trace levels. On the other hand, chelates of uranium(VI) with pyrocatechol violet [1], a quinoline-8-ol [2], 1,2-cyclohexane dioxime [3] and anthranilic acid [4] are adsorbed onto activated carbon for the enrichment of Cu, Mn, Co, Cd, Pb, Ni, Cr and lanthanides. To the best of our knowledge, there is no SPE procedures reported for uranyl ion using chelate modified activated carbon. It has been shown that azo group and phenolic OH was highly selective for uranium. Hence, the present work attempts on the synthesis of chelate having two such binding sites within the same molecules to achieve higher percent extraction and sorption capacity and its use as sorbent material by modifying AC to recover uranium from dilute solutions of geological materials and quantitative removal from environmental solutions.

Various parameters that influence the recovery/removal of uranium(VI) by solid phase extraction were systematically optimized and the results obtained are discussed in the following pages.

4.2 SYNTHESIS OF DIARYLAZOBISPHENOL

The synthesis of diarylazo bisphenol involves an aromatic electrophilic substitution reaction. Once aromatic primary amine is diazotized, the generated diazonium chloride undergoes coupling reaction with phenol. Since the para

position of phenolic group is blocked, normally it prefers the ortho position for the coupling.



4.3 CHARACTERIZATION OF DIARYLAZOBISPHENOL

4.3.1 IR spectra

The IR spectral data show the absorption peaks at $3200\text{-}3400\text{ cm}^{-1}$ (-OH frequency) and $1148, 1506\text{ cm}^{-1}$ (-N=N- stretching frequency) [5].

4.3.2 ^1H NMR

^1H NMR shows a methyl group (-CH₃) resonating at $\delta:1.68$ ppm (singlet), phenolic (-OH) group resonating at $\delta:12.92$ ppm (singlet) and aromatic protons resonating between $\delta:6.74$ and 7.88 ppm.

4.3.3 ¹³C NMR

¹³C NMR spectrum shows methyl carbon resonating at δ :30.922 ppm, quaternary aliphatic carbon resonating at δ :1.693 ppm, - OH group attached to carbon atom resonating at δ :153 ppm, azo group attached to carbon resonating carbon atom resonating at δ :142 ppm and aromatic carbon resonating between δ : 114.87 and 136.7 ppm.

4.3.4 Elemental analysis

The nitrogen content in the diarylazobisphenol confirmed the IR and NMR spectral data described above. The results of elemental analysis are given in Table 4.1.

Table 4.1 Elemental analysis of Diarylazobisphenol

Elements (%)	Carbon (C)	Hydrogen (H)	Nitrogen (N)
Calculated	74.31	5.50	12.88
Found	74.90	6.17	12.48

4.4 PREPARATION OF DIARYLAZOBISPHENOL MODIFIED ACTIVATED CARBON (AC)

Acetone solution of diarylazobisphenol (0.1 g in 5 ml) was added drop wise to a suspension of 10 g of activated carbon in 1.0 l of deionised water with constant stirring at room temperature. The resulting mixture was stirred for 3 h and was allowed to settle for 10 min. Then it was filtered through filter paper placed in a Buchner funnel by suction, washed with deionised water, dried in an oven at 60°C for several hours and then stored in an amber coloured bottle.

4.5 PRELIMINARY INVESTIGATIONS

The glass column was packed with 50 mg of diarylazobisphenol (1%) modified activated carbon. It was washed 3-4 times with deionised water. A portion of uranium(VI) solution (25 μ g) was diluted to 1.0 l and the pH was adjusted to 4.5 \pm 0.5 after adding 5 ml of 1.0 M sodium acetate – acetic acid buffer.

The above solution was passed through the column with a flow rate of 1.0 ml/min. The adsorbed uranium(VI) on diarylazobisphenol modified AC was eluted with 10 ml of 1.0 M HCl. Five ml of 1:1 HCl and 2.5 ml of 0.1% arsenazo(III) were added to the above solution and diluted to 25 ml with deionized water. The absorbance of uranium(VI) – arsenazo(III) complex was measured at 656 nm. The results show that uranium(VI) is quantitatively retained on diarylazobisphenol modified activated carbon.

4.6 OPTIMIZATION OF EXPERIMENTAL VARIABLES

4.6.1 Preparation of column

The glass column (Vensil, size 3.5mm diameter and 20cm length) was packed with 50mg of diarylazobisphenol modified activated carbon. It was first washed with 25ml of 1.0M HCl and then with deionized water until it is free from acid, after each cycle of preconcentration and elution experiments the glass column is regenerated by washing with 20ml of 1.0 M HCl and conditioned by passing acetate buffer of pH ~5. (Fig. 4.1).

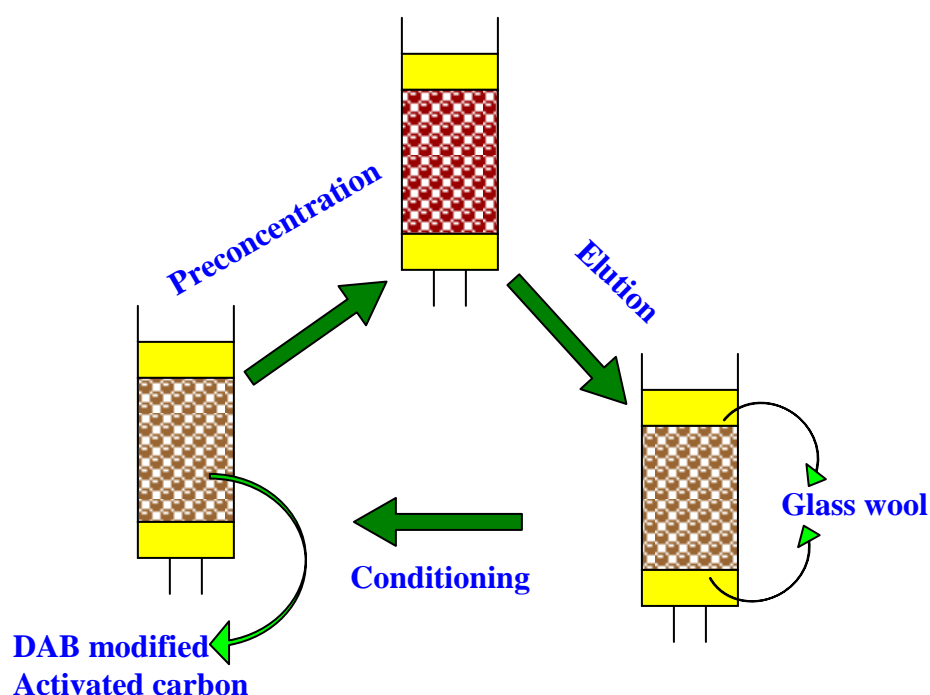


Fig.4.1: Schematic representation of off-line column preconcentration

4.6.2 Effect of pH

The glass column was packed with 50 mg of diarylazobisphenol modified activated carbon. It was washed with 3 to 4 times with deionised water. A set of solutions (volume = 1.0 l) containing 100 μg of uranium (VI) was taken and the pH was adjusted between 2.0 to 6.0 in steps of 1.0. The uranium (VI) solution was passed through the column with a flow rate of 1 ml/min. The adsorbed uranium (VI) onto diaryl azobisphenol modified AC was eluted with 10 ml of 1.0 M HCl. To the eluate 2.5 ml each of concentrated HCl and arsenazo(III) were added and made up to 25 ml, using deionised water and determined spectrophotometrically at a wavelength maximum of 656 nm. Blank was also done for each pH value. The blank corrected results obtained are shown in Fig.4.2. The enrichment of uranium(VI) onto diarylazobisphenol modified activated carbon was quantitative in the pH range 4 to 5. Hence, in further studies, the pH was kept at 4.5 ± 0.5 using dil. HCl or NaOH after the addition of 5 ml of 1.0 M sodium acetate-acetic acid buffer.

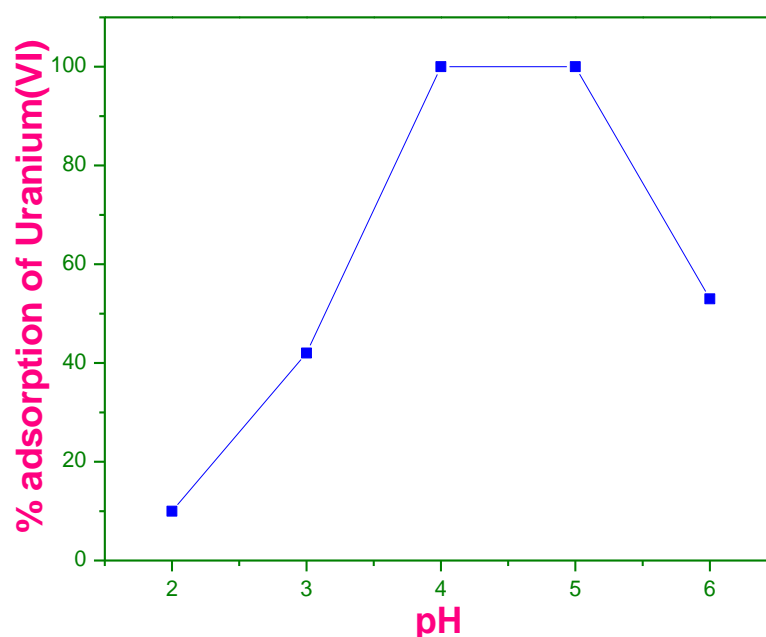


Fig.4.2 Effect of pH

4.6.3 Effect of diarylazobisphenol concentration

In the study on the effect of diarylazobisphenol concentration, a solution containing 100 µg of uranium in 1.0 l of aqueous phase was adjusted to the pH 4.5 ± 0.5 using pH meter. Different concentrations of diarylazobisphenol on activated carbon were prepared in the range 0.1 – 10%. The adsorption of uranium (VI) on diarylazobisphenol modified activated carbon and determination by arsenazo(III) procedure was carried out as described in section 4.6.2. The results obtained are shown in Fig.4.3. From the figure, it is clear that the enrichment of uranium (VI) on diarylazobisphenol modified activated carbon was quantitative in the diarylazobisphenol concentration of $> 0.2\%$. Hence, 1% diarylazobisphenol modified activated carbon was used in the subsequent experiments.

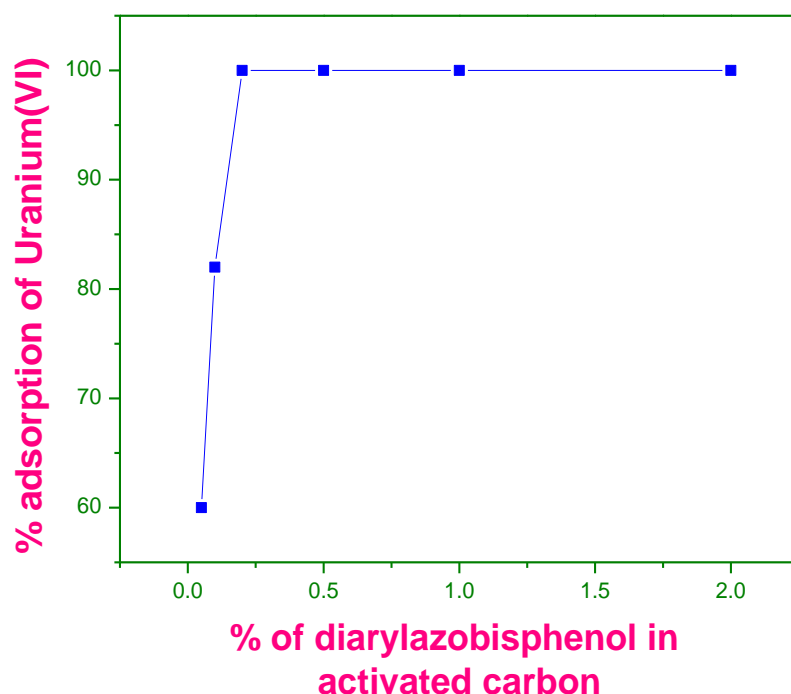


Fig.4.3 Effect of diarylazobisphenol concentration

4.6.4 Effects of amounts of diarylazobisphenol modified activated carbon

The amount of diarylazobisphenol (1%) modified activated carbon was varied from 0.01-0.5 g in a volume of 1.0 l. The adsorption of uranium on

diarylazobisphenol modified activated carbon and determination by arsenazo(III) was carried out as described in pH studies. The results obtained are shown in Fig.4.4 from which it is clear that as low as 0.02 g of 1% diarylazobisphenol activated carbon is required for quantitative enrichment of uranium.

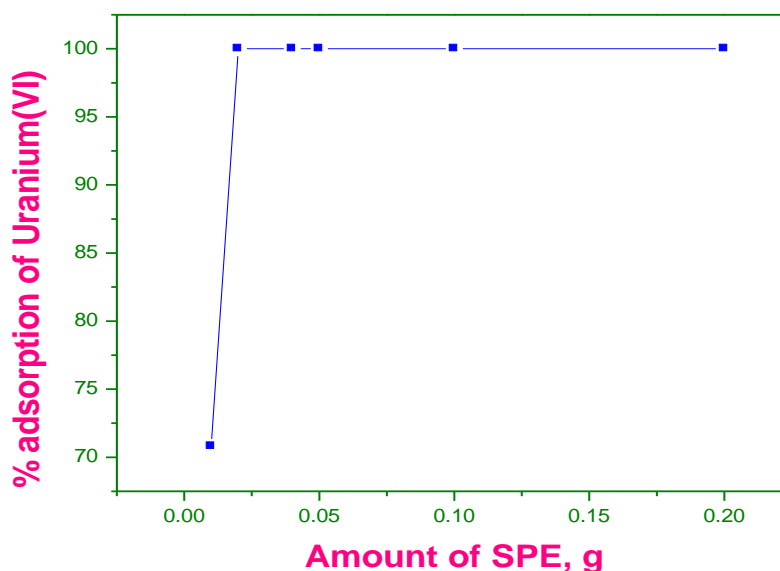


Fig.4.4 Effect of amount of DAB modified SPE

4.6.5 Effect of preconcentration flow rate

For the sorption of uranium(VI) on to diarylazobisphenol modified activated carbon, a flow rates in the range 0.5 to 2 ml/min was studied. To 100 μg of uranium present in 1.0 l deionized water, the pH was adjusted to 4.5 ± 0.5 using dilute HCl or NaOH and passed through the diarylazobisphenol modified activated carbon. The results obtained are shown in Fig.4.5 from which it is clear that only up to 1 ml/min of flow rate allows for quantitative enrichment of uranium (VI) on diarylazobisphenol modified activated carbon. At flow rates higher than 1.0 ml/min uranium (VI) does not equilibrate adequately with the diarylazobisphenol modified activated carbon.

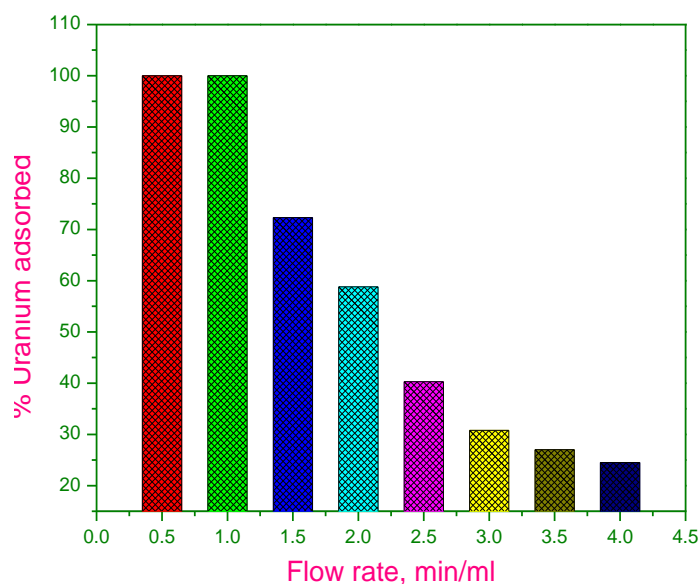


Fig.4.5 Effect of preconcentration flow rate

4.6.6 Effect of elution flow rate

The flow rate on the elution of previously sorbed uranium(VI) on diarylazobisphenol modified activated carbon was varied from 0.5 to 3 ml/min. The results obtained are shown in Fig.4.6, from which it is clear that the elution is independent of flow rate up to 3 ml/min. The flow rates higher than 3 ml/min could not be obtained in the present column studies.

4.6.7 Effect of aqueous phase volume

The effect of aqueous phase volume on the adsorption of uranium (VI) onto diarylazobisphenol modified activated carbon in the range 25 ml to 1.0 l was studied. In these studies, 100 μ g of uranium(VI) was present in deionised water and the pH of aqueous phase was adjusted to 4.5 ± 0.5 using dil. HCl or NaOH. The adsorbed uranium onto 0.05 g of diarylazobisphenol modified activated carbon after elution was determined by arsenazo(III) procedure as described in pH studies. The results obtained are shown in Fig.4.6, from which it is clear that uranium(VI) was quantitatively adsorbed upto 1.0 l of aqueous phase.

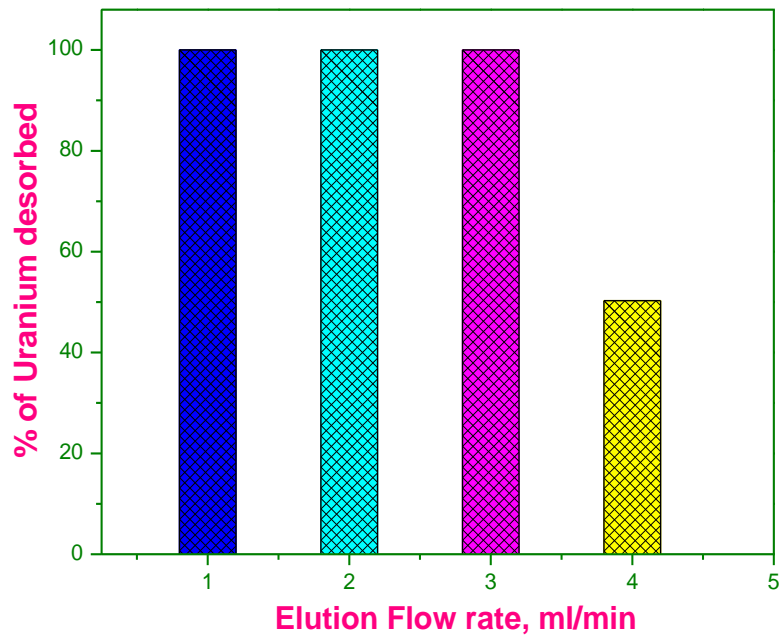


Fig.4.6 Effect of elution flow rate

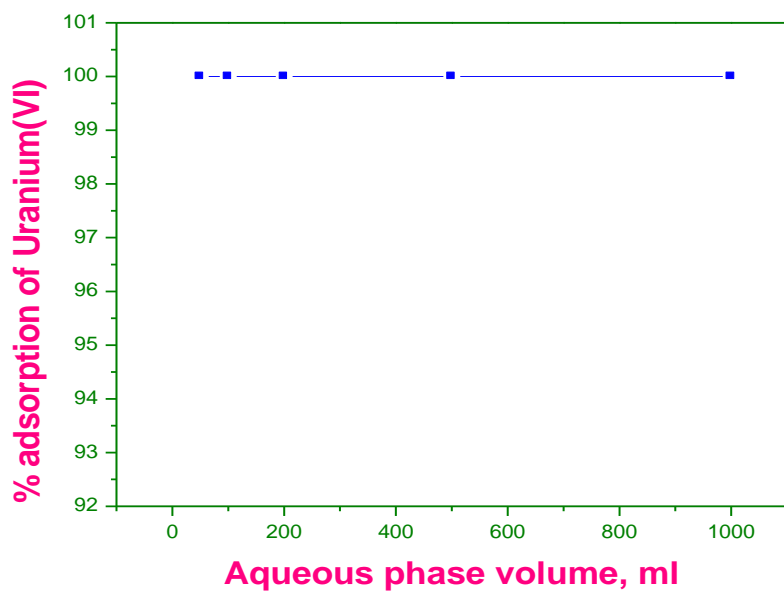


Fig.4.7 Effect of aqueous phase volume

4.6.8 Effect of diverse ions

Sample solutions containing 100 µg of uranium and various amounts of neutral electrolytes and metal ions were examined by the general procedure described in pH studies. The tolerance limits corresponding to an error of less than 3% given in Table 4.2.

Table 4.2 Effect of diverse ions

Sl. No.	Electrolyte/metal ion	Compounds taken	Tolerance limit
1	None	-	1g
2	NaCl	NaCl	1g
3	NaNO ₃	NaNO ₃	1g
4	Na ₂ SO ₄	Na ₂ SO ₄	1g
5	KCl	KCl	1g
6	CaCl ₂	CaCl ₂	1g
7	NH ₄ Cl	NH ₄ Cl	1g
8	MgCl ₂	MgCl ₂	1g
9	KSCN	KSCN	1g
10	KH ₂ PO ₄	KH ₂ PO ₄	10 mg
11	EDTA	EDTA	50 µg
12	NaSCN	NaSCN	1g
13	Citrate	C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O	10 mg
14	Thiourea	Thiourea	1000 µg
15	Zn(II)	ZnCl ₂	1000 µg
16	Hg(II)	HgCl ₂	1000 µg
17	Cd(II)	Cd(NO ₃) ₂ ·4H ₂ O	1000 µg
18	Mg(II)	MgCl ₂	1000 µg
19	Sr(II)	SrCl ₂	1000 µg
20	Pb(II)	Pb(NO ₃) ₂	1000 µg
21	Co(II)	CoSO ₄ ·7H ₂ O	1000 µg
22	Mn(II)	MnSO ₄ ·H ₂ O	1000 µg
23	Ni(II)	NiCl ₂ ·H ₂ O	1000 µg
24	Fe(III)	FeCl ₃	1000 µg
25	Al(III)	Al(NO ₃) ₃ ·9H ₂ O	1000 µg
26	Sn(II)	SnCl ₂ ·2HO	1000 µg
27	As(V)	Na ₂ HAsO ₄ ·7H ₂ O	1000 µg
28	Sb(III)	Sb ₂ O ₃	1000 µg
29	Mo(VI)	(NH ₄) ₂ MoO ₄	1000 µg
30	V(V)	NH ₄ VO ₃	1000 µg
31	Th(IV)	Th(NO ₃) ₄ ·6H ₂ O	50 µg

From the Table 4.2, it is clear that none of the species tested interfere in the developed preconcentration procedure in conjunction with spectrophotometric determination using Arsenazo-III reagent. On the otherhand, thorium interferes and has to be separated while analysing thorium containing samples.

4.6.9 Choice of eluting agent

The uranium(VI) adsorbed as diarylazobisphenol modified AC was eluted with 10 ml of 1.0 M of mineral acids such as hydrochloric acid, sulphuric acid and nitric acid. The results obtained are shown in Table 4.3. The quantitative removal of uranium(VI) was achieved with all the mineral acids tested. Hydrochloric acid (1.0 M) was used in all subsequent studies.

Table 4.3 Influence of eluting agents

Eluent used (1.0 M)	Recovery of uranium
HCl	> 99.8
H ₂ SO ₄	> 99.8
HNO ₃	> 99.8

4.7 CALIBRATION GRAPH, SENSITIVITY AND PRECISION

A series of solutions containing 5 to 100 µg of uranium(VI) was diluted to 1.0 l and the pH was adjusted to 4.5±0.5 using dil. HCl and dil. NaOH after adding sodium acetate-acetic acid and passed through the column packed with 50 mg diarylazobisphenol modified activated carbon. The adsorbed uranium(VI) was eluted with 10ml of 1.0 M HCl and determined spectrophotometrically after adding 5.0ml of 1:1 HCl and 2.5ml of 0.1% Arsenazo(III) solution in a total volume of 25ml. The absorbance of uranium(VI)-arsenazo(III) complex was measured at 656nm.

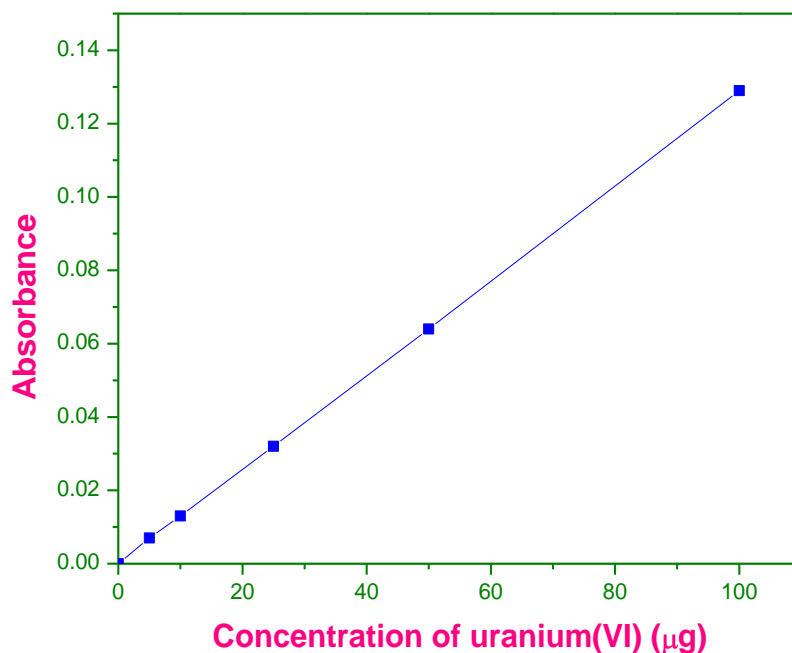


Fig 4.8: Calibration graph

Under the optimum condition described above (Fig. 4.8) the calibration curve was linear over the concentration range 0-100µg of Uranium(VI) present in 1.0 l of sample solution.

The linear equation with regression is:

$$Y = 0.00129 X + 0.00008$$

where, Y is the peak absorbance, X is the concentration in µg/l

The regression coefficient R is 0.9998

Ten replicate determinations of 25µg of uranium(VI) present in 1.0 l of a solution gave a mean absorbance of 0.032 with a coefficient of variation or relative standard deviation of 2%. (Table 4.4). The limit of detection (lowest concentration below which recoveries becomes non-quantitative) corresponding to three times the standard deviation of the blank (3σ) was found to be 5µg/l. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

Table 4.4 Precision studies

Sl. No.	Absorbance	U(VI) found (μg), X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
1	0.033	25.70	0.70	0.0049
2	0.032	24.92	-0.08	0.0064
3	0.031	24.14	-0.86	0.7396
4	0.032	24.92	-0.08	0.0064
5	0.031	24.14	-0.86	0.7396
6	0.033	25.70	0.70	0.0049
7	0.032	24.92	-0.08	0.0064
8	0.033	25.70	0.70	0.0049
9	0.031	24.14	-0.86	0.7396
10	0.033	25.70	0.70	0.0049

$$\bar{X} = 25.0$$

$$\Sigma(X_i - \bar{X})^2 = 2.2673$$

$$\sigma = 0.5018$$

$$\text{Coefficient of variation (C.V)} = 2\%$$

4.8 RETENTION CAPACITY OF DIARYLAZOBISPHENOL SUPPORTED ON ACTIVATED CARBON

To determine retention capacity or maximum amount of uranium(VI) sorbed per gram of diarylazobisphenol activated carbon, 50 mg of the diarylazobisphenol modified activated carbon was saturated with 2.0 mg of uranium(VI) present in 20 ml of solution under optimum conditions described above. The amount of uranium(VI) ion needed for saturation was determined spectrophotometrically after eluting with 10 ml of 1.0 M HCl. The retention capacity of uranium(VI) was found to be 18.35 mg/g of SPE which is higher than the chelate modified SPEs described in the literature (Table 4.5).

Table 4.5 Comparison of retention capacities of various SPE materials for uranium (VI)

SPE material	Retention/binding capacity ($\mu\text{g/g}$)	Reference
DCQ-naphthalene	1.88 \pm 0.02	[6]
PAN-Benzophenone	2.34 \pm 0.02	[7]
Q-Amberlite XAD-4	2.74 \pm 0.02	[8]
Azo-oxine ion exchanger	8.14 \pm 0.01	[9]
DAB-AC	18.35 \pm 0.02	Present method

4.9 ANALYSIS OF STANDARD REFERENCE MATERIAL (SUPPLIED BY NATIONAL RESEARCH COUNCIL, CANADA)

The accuracy of the developed preconcentration procedure was carried out by analyzing a standard marine sediment reference material (MESS-3) supplied by the National Research Council, Canada. The sample was brought into solution by fusing with KHSO_4 after fuming with HF and H_2SO_4 to remove silica. The uranium(VI) present in the sample was preconcentrated by diarylazobisphenol modified activated carbon by following the procedure described in section 4.6.2 and determined by arsenazo(III) procedure. The flow chart for the analysis of uranium in the soil and sediment samples is given in the Fig. 4.9. The results obtained are shown in Table 4.6, from which it is clear that the amount of uranium(VI) present in marine sediment sample by the developed method is comparable to information value given by NRC, Canada. Further, on adding known amounts of uranium(VI) to standard reference material before dissolution prior to preconcentration and determination, the recoveries were found to be good indicating the suitability of the developed procedure for the determination of uranium(VI) in sediment samples.

Table 4.6 Analysis of marine sediment standard reference material (MESS-3) (supplied by National Research Council, Canada)

Sl. No.	Uranium added ($\mu\text{g/g}$)	Uranium found ($\mu\text{g/g}$ of sample)	Recovery (%)
1	None	3.98 \pm 0.02	4
2	5.0	8.92 \pm 0.02	-
3	10.0	13.88 \pm 0.03	-

4.10 ANALYSIS OF SOIL AND MARINE SEDIMENT SAMPLES

Soil samples collected from two stations in Trivandrum and sediments of Karamana river, Trivandrum and Arabian Sea, Trivandrum were mineralized as described in section 4.9 and subjected to analysis for uranium(VI) using the general procedure described in experimental part. The results obtained by the present method agree well with ICP-MS values. From Table 4.7, it is clear that the developed preconcentration procedures enable the reliable determination of uranium(VI) in soils and sediments using simple technique like spectrophotometer.

Table 4.7 Analysis of soil and sediment samples

Sl. No.	Description of the sample	Uranium(VI) ($\mu\text{g/g}$)			Recovery (%)
		Present method	ICP-MS		
1	Soil sample from Station 1	-	6.72 \pm 0.02	6.96 \pm 0.01	-
		6.00	12.70 \pm 0.02	-	99.7 \pm 0.02
		12.00	18.60 \pm 0.03	-	99.7 \pm 0.02
2	Soil sample from Station 2	-	7.85 \pm 0.02	7.96 \pm 0.01	-
		8.00	15.77 \pm 0.03	-	99.0 \pm 0.8
		16.00	23.64 \pm 0.04	-	98.7 \pm 1.1
3	Karamana river sediment, Trivandrum	-	8.13 \pm 0.02	8.22 \pm 0.01	-
		8.00	16.04 \pm 0.03	-	98.9 \pm 1.0
		16.00	24.01 \pm 0.04	-	99.3 \pm 0.5
4	Marine sediment from Arabian sea, Trivandrum	-	4.85 \pm 0.02	4.96 \pm 0.01	-
		5.00	9.78 \pm 0.02	-	98.6 \pm 1.2
		10.00	14.80 \pm 0.03	-	99.5 \pm 0.3

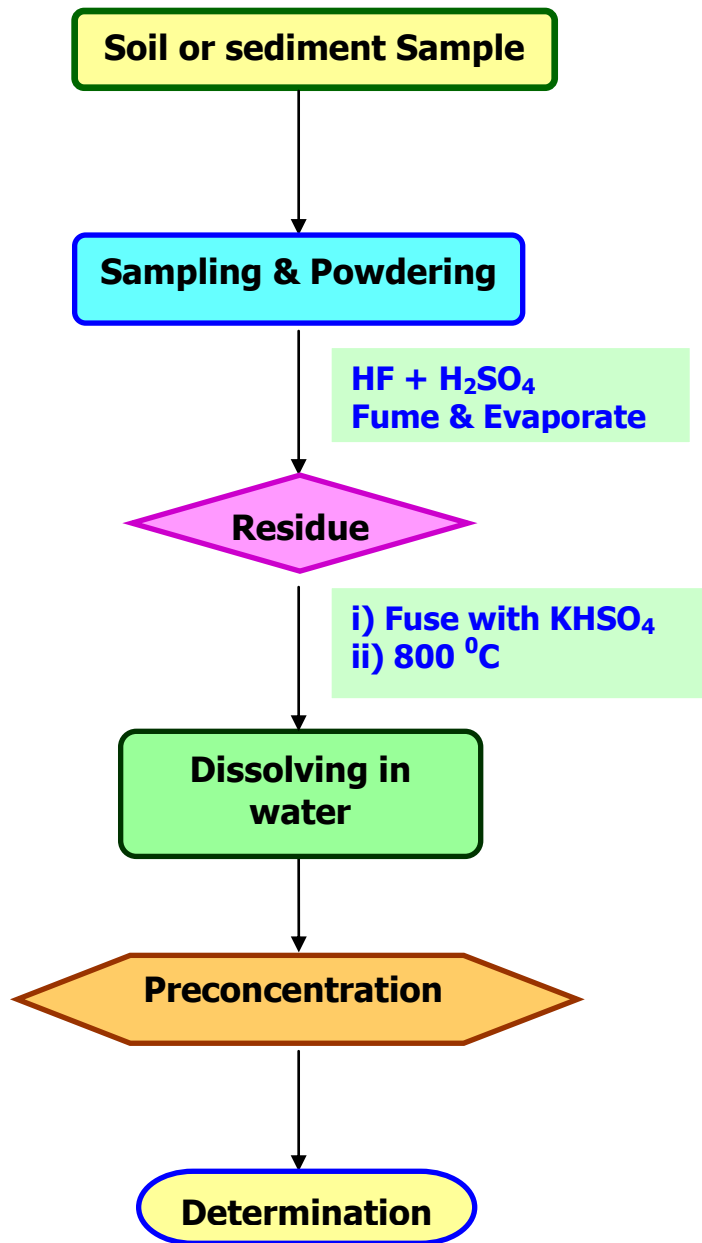


Fig. 4.9 Flow chart for the analysis of soils and sediments

4.11 REUSABILITY OF THE DIARYLAZOBISPHENOL MODIFIED ACTIVATED CARBON

The preconcentration and elution of uranyl ion onto/from the diarylazo-bisphenol modified activated carbon was tested under optimal conditions. The retention capacity of the diarylazo-bisphenol modified activated carbon remains unaltered even after 35 cycles of equilibration indicating the possible repeated use of the diarylazo-bisphenol modified activated carbon.

4.12 ADSORPTION KINETICS

The rate of loading of uranium(VI) on to DAB modified AC was determined by agitating 40 and 60 mg (Curves A & B in Fig.4.10) of uranium(VI) in a refrigerated incubation shaker at room temperature for 0.5, 1.5, 2.0, 4.0, 6.0, 10.0, 30 and 60 min. The amount of uranium(VI) loaded on to diarylazo-bisphenol modified activated carbon was determined by the general procedure described above. The equilibrium time in which DAB modified AC attains 50% saturation with uranium(VI) (i.e. when the amount of metal ion sorbed on the SPE is a half of its maximum sorption capacity) is called loading half-time ($t_{1/2}$). From the Curves A and B in Fig. 4.11, it is clear that the loading half time was < 30 s.

The kinetics of uranium(VI) adsorption on DAB modified activated carbon followed the first order rate expression given by Lagergren [10]

$$\text{Log}(q_e - q) = \log q_c - K_{ad} \frac{t}{2.303}$$

where ' q ' and ' q_c ' are the amounts of uranium(VI) adsorbed [mg/g of diarylazo-bisphenol modified activated carbon) at time, t (min)] and equilibrium time (60 min) respectively and K_{ad} is the rate constant of adsorption. Linear plots of $\log (q_e - q)$ versus ' t '. (Figs.4.10 & 4.11) shows the applicability of the above equation for diarylazo-bisphenol modified activated carbon. The correlation coefficients of linear plots obtained for Lagergren plots are 0.9991 and 0.99992 respectively for 40 and 60 mg/l of uranium(VI) solution. The K_{ad} calculated from

the slopes of Fig.4.11 are 0.1605 and 0.2222 l/min for 40 and 60 mg/l of uranium(VI) solution.

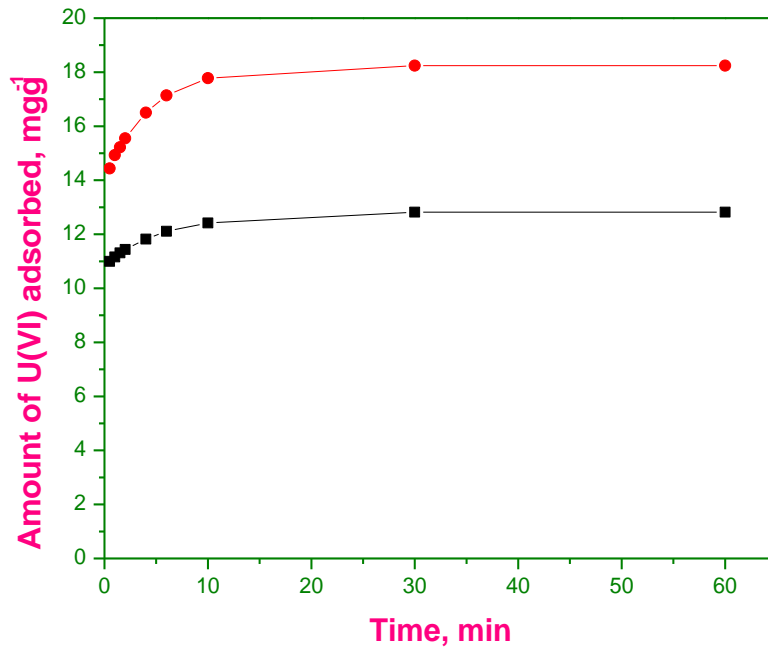


Fig. 4.10 Effect of agitation time on the adsorption of uranium(VI), Uranium (VI) concentration: (A) 40 mg/l (B) 60 mg/l Adsorbent dose ~250 mg/100ml

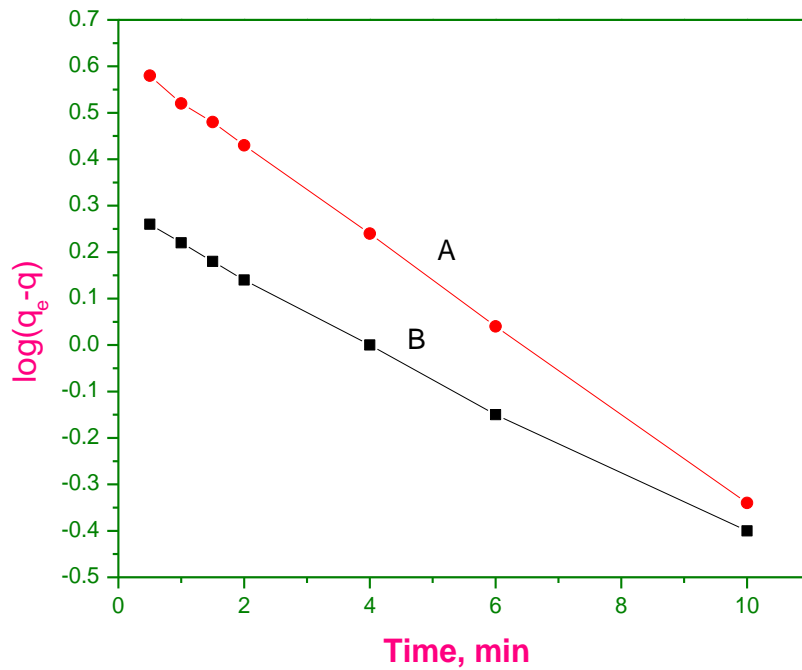


Fig. 4.11 Lagergren plots for the adsorption of Uranium (VI), Uranium (VI) concentration: (A) 40 mg/l (B) 60 mg/l

4.13 ADSORPTION ISOTHERMS

The adsorption of uranium(VI) as a function of diarylazobisphenol modified activated carbon was studied by equilibrating for 60 min in a refrigerated incubator shaker and the results obtained are shown in Fig.4.10. The amount of uranium(VI) loaded on to diarylazobisphenol modified activated carbon was determined by following the general procedure described above. The Langmuir treatment [11] is based on the assumption that (i) maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the energy of adsorption is constant and (iii) there is no transmigration of adsorbate in the plane of the surface

$$\frac{C_e}{q_e} = \frac{1}{(q_{ob})} + \frac{C_e}{q_o}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium and q_o and 'b' are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e versus C_e shows that adsorption obeys Langmuir adsorption model (Fig.4.12).

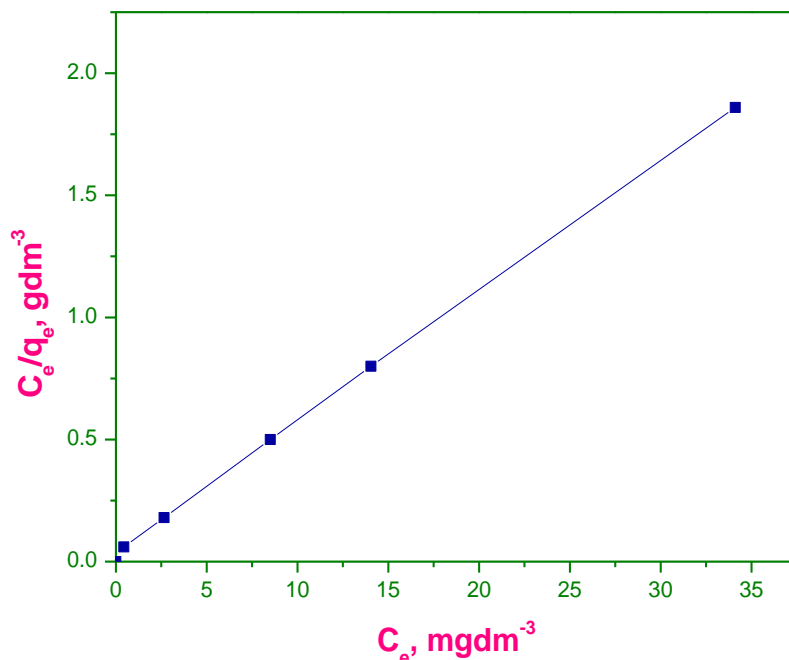


Fig.4.12 Langmuir plot for the adsorption of Uranium (VI), Uranium(VI) concentration: 20-100 mg/l, Equilibrium time: 60 min, Adsorbent dose: 250 mg/l

The correlation coefficient for the linear regression fits of the Langmuir plot was found to be 0.99997. q_0 and b determined from the Langmuir plot were found to be 18.72 mg/g and 1.2869 dm³ mg⁻¹.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_1 which is defined by $\frac{1}{1+bC_0}$, where 'b' is a Langmuir constant and C_0 is the initial concentration of uranium(VI) [13]. R_1 values observed between 0 and 1 indicate favourable adsorption of uranium(VI) on to DAB modified AC (Table 4.8).

Table 4.8 Equilibrium parameters (R_1)

Initial uranium(VI) concentrations, C_0 (mg/l)	R_1 value
20	0.037
30	0.025
40	0.019
60	0.013
80	0.010
100	0.008

The Freundlich equation was also applied to the adsorption. The Freundlich equation is basically empirical but is often useful as a means of data description. It generally agrees quite well with Langmuir equation and experimental data over a moderate range of adsorbate concentrations. The Freundlich isotherm is represented by the equation [12].

$$\text{Log}\left(\frac{x}{m}\right) = \log K_f + \left(\frac{1}{n}\right)\log C_e$$

where C_e is the equilibrium concentration (mg/l) and x/m is the amount adsorbed per unit mass of diarylazobisphenol modified activated carbon. A plot of $\log x/m$ vs $\log C_e$ (Fig.4.13) is linear and the constants K_f and n were found to be 2.0672 and 5.093 respectively. The value of $1 < n < 10$ shows a favourable adsorption of

uranium(VI) on to diarylazobisphenol modified activated carbon. The correlation coefficient for the Freundlich plot was found to be 0.99924.

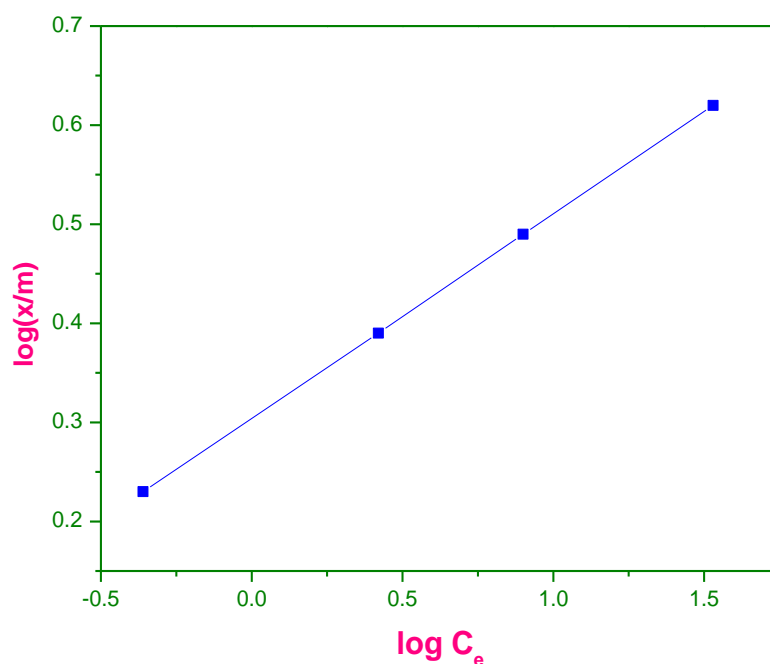


Fig. 4.13 Freundlich plots for the adsorption of uranium(VI), Uranium (VI) concentration: 20 – 100 mg/l, Equilibratin time: 60 min, Adsorbent dose: 250 mg/100ml

4.14 EXPERIMENTAL

4.14.1 Chemicals

A stock solution of uranium(VI) was prepared by dissolving 0.5047 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, USA) in deionised water. Conc. HNO_3 (5.0 ml) was added to 250 ml of solution to suppress hydrolysis. Activated carbon (Aldrich, USA), Arsenazo-III (Fluka, Buchs, Switzerland) and bisphenol (Aldrich, USA) were used. 0.1% of Arsenazo-III solution was prepared by dissolving 0.1 g of the reagent in 100 ml of deionised water. Sodium acetate – acetic acid buffer (1.0 M) was prepared to maintain the pH of the aqueous phase. Aniline was purchased from Glaxo (India). All other chemicals including electrolytes and other metal ions

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.

4.14.2 Apparatus

A Hitachi 220 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 FT-IR spectra. A DPX 300 MHz NMR spectrophotometer (Bruker Avance, Switzerland) was used to obtain the ^1H and ^{13}C NMR spectra. Perkin Elmer series 11 CHNS/U analyzer 2400 was used for carrying out CHN analysis. Imeva 433 Refrigerated Incubation Shaker (USA) was used for adsorption kinetic and adsorption isotherm studies. A Varian Ultra mass 700 Inductively Coupled Mass Spectrometer (ICP-MS) was used for analysis of soil and sediment samples.

4.14.3 Procedure for the synthesis of diarylazobisphenol

The diarylazobisphenol was synthesized by coupling a sodium salt of bisphenol with benzene diazonium chloride in a 1:2 molar ratio. Aniline (19.5 ml, 0.02 mol) was dissolved in 20 ml of 50% (v/v) HCl taken in a small conical flask. It was kept cool by immersing in an ice bath and diazotized by the addition of 1.66 g (0.024 mol) of sodium nitrite solution in 20 ml of water. Bisphenol (2.21 g, 0.01 mol) was dissolved in 10 ml sodium hydroxide solution (0.8 g sodium hydroxide in 10 ml of water) and the solution was cooled to 5°C by immersing in an ice bath, assisted by the direct addition of about 25 g of crushed ice. The cold solution of diazonium salt solution was added drop wise to above bisphenol solution. While stirring, a highly viscous semi-solid dye which is red in colour was separated. This mixture was allowed to stand in an ice bath for about 30 min with occasional stirring when all the diazonium salt has been added. The solution

was filtered through a Buchner funnel with gentle suction. The resulting dye was purified by colour and recrystallised in acetic acid.

4.14.4 General procedure

The glass column was packed with 50 mg of diarylazobisphenol (1% modified activated carbon. It was washed 3-4 times with deionised water. A portion of uranium(VI) solution (5-100 μg) was diluted to 1.0 l and the pH was adjusted to 4.5 ± 0.5 after adding 5 ml of 1.0 M sodium acetate –acetic acid buffer. The above solution was passed through the column with a flow rate of 1.0 ml/min. Uranium(VI) adsorbed on diarylazobisphenol modified activated carbon was eluted with 10 ml of 1.0 M HCl. 2.5 ml each of 1:1 HCl and 0.1% arsenazo(III) were added to the above solution and diluted to 25 ml with deionised water. The absorbance of uranium(VI) – arsenazo(III) complex was measured at 656 nm. The linear range of concentration of uranium using arsenazo(III) spectrophotometric procedure was 5-100 μg in a total volume of 25 ml.

4.14.5 Analysis of standard reference material (MESS-3) and soil or marine sediment

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°C on hot plate. The process was repeated twice. The residue was cooled and fused with 2.0 g of KHSO_4 at 800°C in electric Bunsen for 30 min. Then the melt was cooled, dissolved in 50 ml of water and diluted to 100 ml. Preconcentration of uranium(VI) on to diarylazobisphenol modified activated carbon and determination by arsenazo(III) was carried out as described in General Procedure given above.

4.15 CONCLUSION

The wide availability and good exchange properties of activated carbon have stimulated its use as solid supports for enrichment of trace ions. Since the surface area of activated carbon is greater, it retains the bigger organic molecules. Diarylazobisphenol a bigger chelating ligand is easily adsorbed on to activated

carbon. Thus, the preparation of SPE sorbent is easier than that of other solid sorbents used for similar purpose. The retention capacity of uranium(VI) on to diarylazobisphenol modified activated carbon (18.35 mg/g of SPE) is much higher than 1-(2-pyridylazo)naphthol modified benzophenone (2.39 mg/g of SPE) and 5,7-dichloroquinoline-8-ol modified naphthalene (1.88 mg/g of SPE). The SPE column preconcentration procedure developed using diarylazobisphenol modified AC facilitates a 100-fold enrichment of uranium(VI) from dilute aqueous solution. Diarylazobisphenol modified activated carbon have high mechanical strength as it is unaffected even after 35 cycles of preconcentration and elution. Equilibrium is fast as 80-90% of uranium(VI) is sorbed within 5 sec. The accuracy of the developed method was established by successfully analyzing the standard reference material (MESS-3) supplied by National Research Council, Canada. The developed preconcentration procedure enables the reliable determination of uranium(VI) in soil and marine sediment samples, using a simple low cost and readily available spectrometer. Even though not tested in view of the noninterference of diverse ions and neutral electrolytes on the recovery of uranium(VI), the developed SPE preconcentration procedure is also expected to find application in the selective removal of toxic uranium(VI) from various environmental samples including nuclear wastes.

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CHAPTER 5

SOLID PHASE EXTRACTIVE PRECONCENTRATION OF THORIUM(IV) BY USING β -DIKETONE FUNCTIONALIZED AMBERLITE XAD-4

5.1 INTRODUCTION

Thorium occurs rather widely in nature. Its abundance in the earth's crust is 8×10^{-4} percent by weight. Thorium is a lithophilic element, scattered throughout the terrestrial crust; a comparatively small number of its ores are known, the major useful source being monazite-bearing sand, which is a complex phosphate of thorium and rare earth elements with a variable amount of silicon-containing compounds of iron, aluminium and other elements. When igneous and metamorphic rocks undergo weathering, thorium is retained in the crystal lattice of thorium minerals, and therefore its content in sea water is low, i.e. 4×10^{-8} percent.

Thorium and its compounds and alloys find widespread use. Thus, thorium can be used as an alternative nuclear fuel by converting into ^{233}U . Thorium oxide finds application as catalyst, high temperature ceramic and high quality lenses. Furthermore, the alloy of thorium with magnesium is used in air craft engines and in air frame construction and with tungsten, is used in electric filaments.

However, the handling of thorium results in two types of hazards (i) a hazard from ingestion of an X-ray emitting member of thorium which can be fatal in case of a large scale permanent damage of bones, kidney and liver, (ii) hazard from proximity to X-ray emitters during working hours. The extent of danger depends on history of thorium, especially upon time elapsed from its last purification. Regarding the occupational hazard, the persons engaged in the manufacture of mantles using thorium has been known to get affected by a form

of diffuse dermatitis. This, with the additional swelling of the hand causes the formation of deep skin cracks.

The amount of thorium present in some of the environmental samples of sea water, igneous rocks, sedimentary rocks, earth and lunar soil are 9×10^{-3} , 9.6, 11.0, 6×10^{-2} and 2.5-4.8 ppm, respectively. The maximum permissible body burden for emitters is extremely low of the order of 0.03 Ci, also maximum permissible concentration in air is 0.027 mg/l for thorium(IV).

Monazite sand contains thorium in addition to rare earths. While processing for rare earth oxides from monazite sand, thorium is a valuable byproduct. After separation of thorium from rare earths by precipitation, rare earth chlorides contain trace and ultra trace amounts of thorium. The scheme for processing of rare earths is given in flow charts 5.1 and 5.2.

Chart 5.1 Mineral separation from beach sands

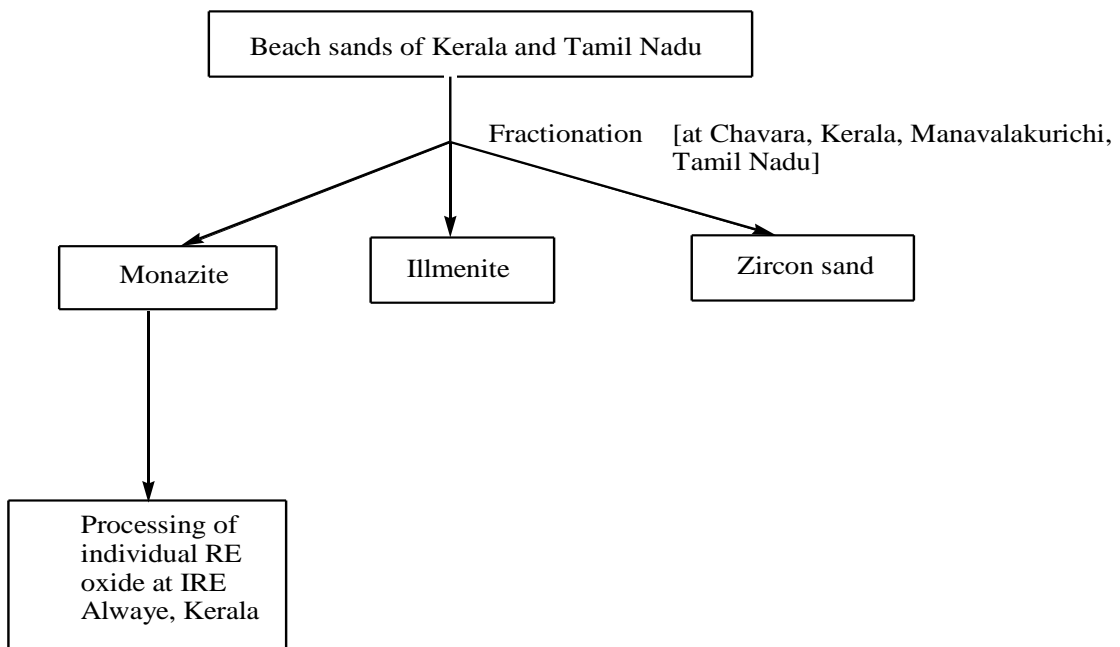
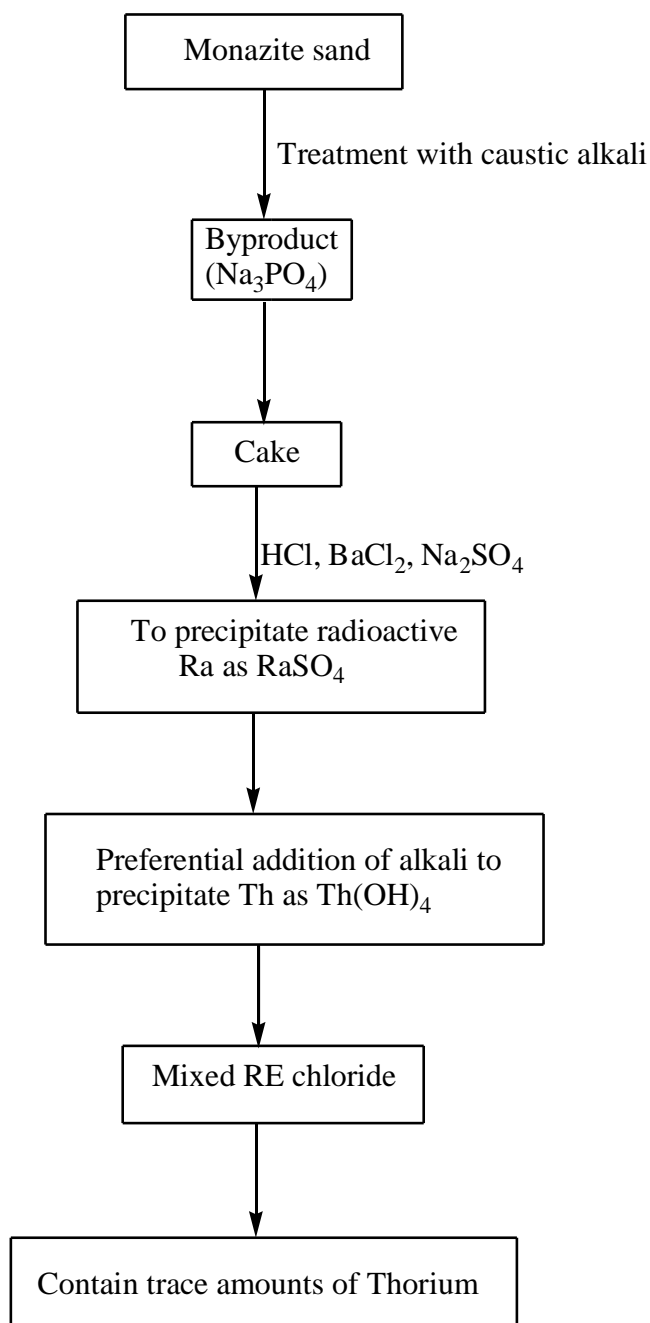


Chart 5.2 RE recovery from monazite sand



As thorium is present at trace levels in RE chloride concentrate, the preconcentration of thorium becomes essential prior to its determination. Preconcentrative separation of metal ions by solid phase extraction at trace/ultratrace level from complex matrices before their determination is a necessity at many times. The lack of selectivity of conventional ion exchange

resins has led to the development of a new class of polymers which are known as specific and selective ion exchange resins.

Skogseid [2,3] described the first such resin, a polystyrene derivative containing dipicrylamine groups, specific for potassium ion. A high selectivity of chelating ion exchangers lies in their ability to form stable, often covalent, complexes of varying strength with metal ions. Kennedy and Davier [3], observed that thorium(IV) and iron(III) and uranyl(VI) form strong complexes with phosphates and sulphonates. Gregore et al [4] postulated that a suitable chelating group for incorporation into a polymeric matrix should have the following properties.

- (i) It should be capable of resin formation or be capable of substitution into a polymeric matrix.
- (ii) It should be sufficiently stable so as to withstand the polymerization or resinification process.
- (iii) It should be strongly bounded so that its chelating ability is not hindered by the polymeric matrix.

The commercially available Amberlite series [5-8] because of its low crosslinking and the porous nature, have been found to be very promising supports for designing chelating resins. Amberlite XAD-2 functionalized with 1-pyrrolidine diethyl dithiocarbamate [9] o-vanillinthiosemicarbazone [10], pyrocatechol violet [11], o-aminophenol [12], 1-(2-pyridylazo)-2-naphthol [5], alizarin Red – S [6], Alamine 336 [7], salicylic acid [13], tyron [14], chromotropic acid [15], pyrocatechol [15], thiosalicylic acid [16], and quinalizarin [17], Amberlite XAD-4 functionalized with N-hydroxy ethylene diamine [8], 2-[5-bromo-2-pyridylazo)-5-diethylaminophenol [18], bicine [19], o-amino benzoic acid [20], and maleic acid [21] and Amberlite XAD-7 loaded/functionalized with dimethyl glyoxal [21], bis-(4-phenyl-3-thiosemicarbazone) [22], glyoxal dithiosemicarbazone [22] xylenol orange [23] and 8-(benzene sulfamido)-quinoline [24] are some of the recently developed ion recognition polymers using neutral polymer supports described in literature.

Amberlite XAD-4, a nonionic crosslinked polymer material which derives its absorptive properties from its macroreticular aromatic polymeric structure (See Fig.5.1) has both a continuous polymer phase and a continuous pore phase and high surface area ($\geq 750 \text{ m}^2/\text{g}$). This structure gives Amberlite XAD-4 polymeric adsorbent excellent physical, chemical and thermal stability. Further, these adsorbents can be used through repeated cycles in column or batch modes to preconcentratively separate inorganics from dilute solutions. β -diketones selectively binds thorium from other actinides. It is worthwhile to immobilize a β -diketone on Amberlite XAD-4 support.

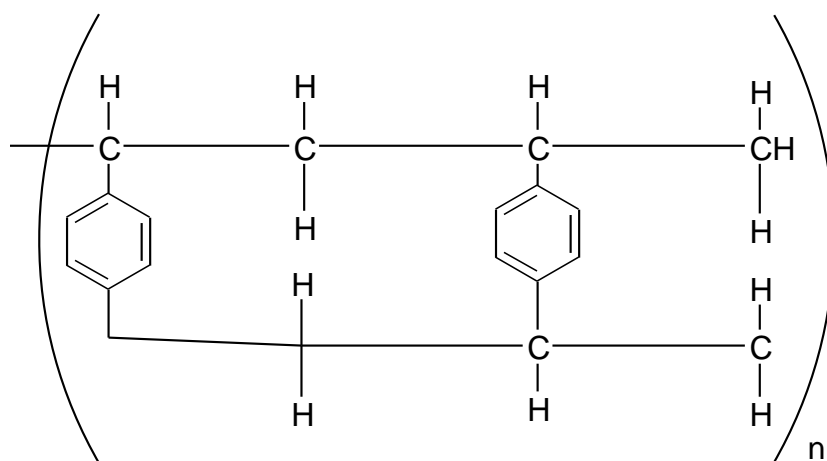
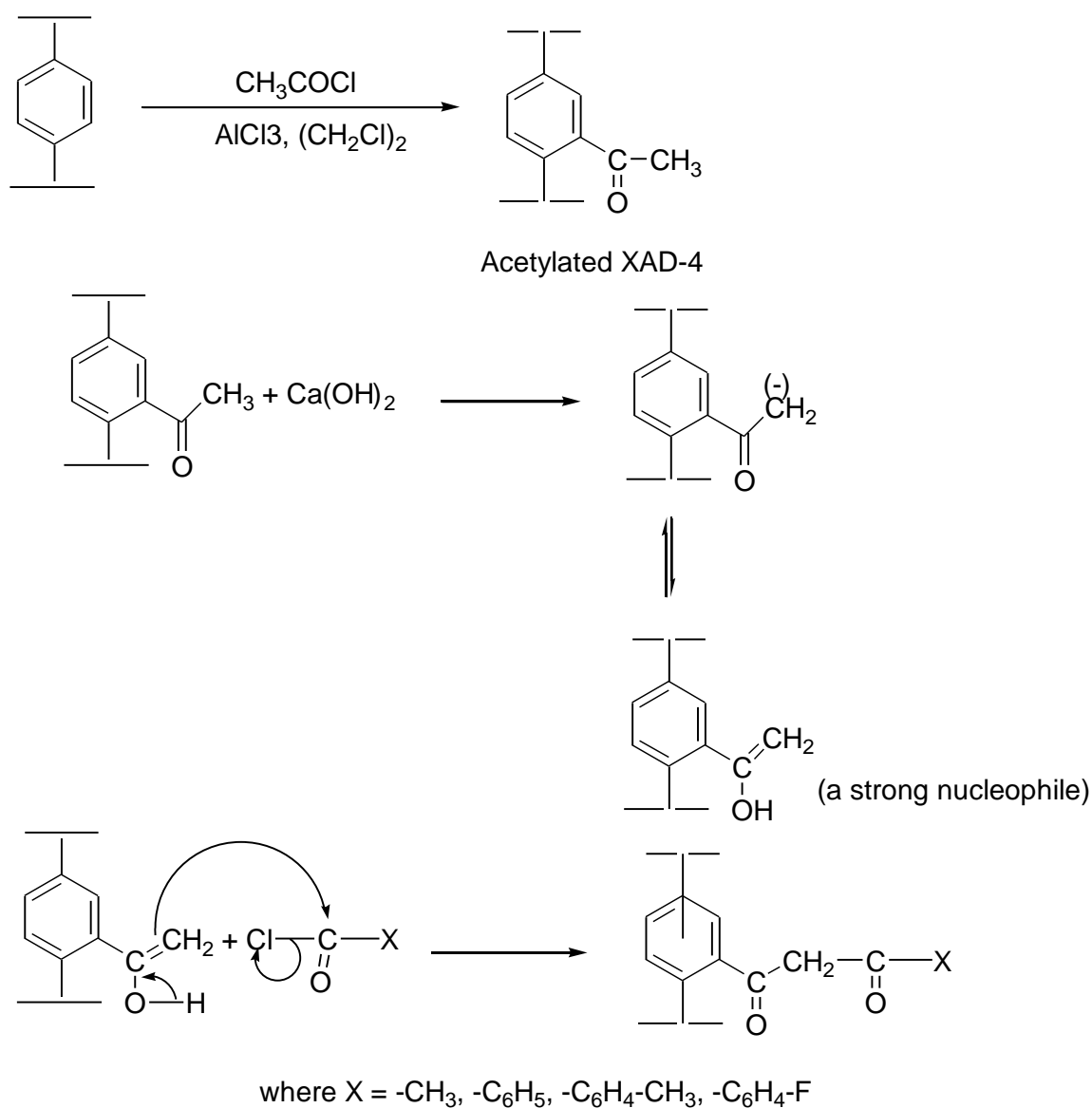


Fig.5.1 Chemical structure of Amberlite XAD-4

This chapter deals with the synthesis of a new ion recognition polymer, i.e. β -diketone functionalized Amberlite XAD-4 (a polystyrene-divinyl benzene resin) and its application for the preconcentrative separation of thorium(IV) from a large number of alkali, alkaline earth, transition and lanthanide metal ions.

5.2 SYNTHESIS OF β -DIKETONE FUNCTIONALIZED AMBERLITE XAD-4

The β -diketone can be immobilized through a Friedal-Crafts acylation followed by generation of enolate ion with calcium hydroxide and the subsequent reaction with acylhalides (Scheme 5.1).



Scheme 5.1 Synthesis of β -diketone immobilized Amberlite XAD-4

5.3 CHARACTERIZATION

5.3.1 IR spectra

The IR spectra of β -diketone functionalized Amberlite XAD-4 exhibits a broad peak at 3446.55 cm^{-1} and a sharp peak at 1689.93 cm^{-1} . This indicates that one of the keto group in β -diketone exists in enol form and other exists in keto form.

5.4 PRELIMINARY INVESTIGATIONS

The glass column (Vensil, size 7 mm diameter and 10 cm length) was packed with 0.5 g of β -diketone immobilized Amberlite XAD-4. It was first washed with 25 ml of 1.0 M 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 M HCl and conditioned by passing acetate buffer of pH ~5.

The solid phase extraction of 50 μ g of thorium(IV) present in 1 litre of the aqueous solution was carried out by adjusting the pH to 4.5 in presence of 10 ml of 1.0 M sodium acetate-acetic acid buffer and then passing through the column. The preconcentrated thorium(IV) was eluted with 10 ml of 1.0 M HCl. Thorium(IV) content in the eluent was determined spectrophotometrically after the addition of 5.0 ml of 1:1 HCl, 2.5 ml of 0.1% arsenazo(III) solution. The absorbance of thorium(IV)-arsenazo(III) complex was measured at 650 nm [25]. Chelating resins prepared are given in Table 5.1, from which it is clear that the β -diketone formed by fluoro-substituted benzoyl chloride alone extract thorium(IV) quantitatively. Hence, this chelating resin was selected for the preconcentration of thorium(IV) in subsequent studies.

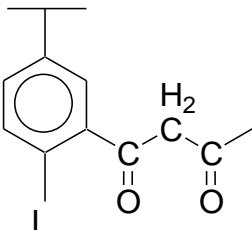
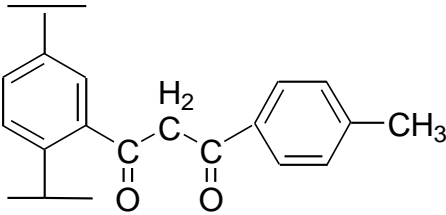
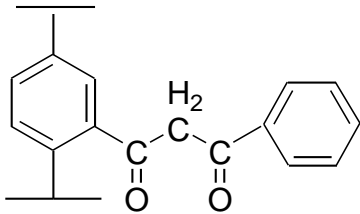
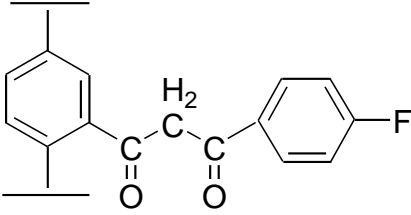
5.5 OPTIMIZATION OF MAIN EXPERIMENTAL VARIABLES

5.5.1 Effect of pH

A set of solutions (volume 1.0 l) containing 50 μ g of thorium(IV) was taken. The pH of the solutions was adjusted between 2.0 and 7.0 in steps of 1.0 with dilute HCl/NaOH, after the addition of 10 ml of 1.0 M acetate buffer solution. Then each set of the solutions was passed through the resin in the column at the rate of 2 ml/min and the preconcentrated thorium(IV) was eluted using 10 ml of 1.0 M HCl. Thorium(IV) ion solution was determined spectrophotometrically after the addition of 5.0 ml of 1:1 HCl 2.5 ml of 0.1%

arsenazo(III) and making upto a final volume of 25 ml. The absorbance of thorium(IV) – arsenazo(III) complex was measured at 650 nm. The variation of thorium(IV) enrichment with pH is shown in the Fig.5.2. The enrichment of thorium(IV) is constant and maximum in the pH range 4.5 to 5.5. In all subsequent works, the pH was adjusted to 5.0 ± 0.5 after the addition of 10 ml of 1.0 M sodium acetate-acetic acid buffer.

Table 5.1 Various β -diketone functionalized Amberlite XAD-4 resin

S.No.	Chelating Resin	Enrichment of Th(IV)
1	 <p>The structure shows a benzene ring with two vertical lines representing attachment points to a resin backbone. At the 1 and 3 positions of the ring, there are carbonyl groups (C=O) connected to a central methylene group (CH₂), which is in turn connected to another carbonyl group (C=O).</p>	55.5 ± 1.0
2	 <p>The structure shows a benzene ring with two vertical lines representing attachment points to a resin backbone. At the 1 and 3 positions of the ring, there are carbonyl groups (C=O) connected to a central methylene group (CH₂), which is in turn connected to another carbonyl group (C=O). This second carbonyl group is attached to a benzene ring with a methyl group (CH₃) at the para position.</p>	62.4 ± 1.2
3	 <p>The structure shows a benzene ring with two vertical lines representing attachment points to a resin backbone. At the 1 and 3 positions of the ring, there are carbonyl groups (C=O) connected to a central methylene group (CH₂), which is in turn connected to another carbonyl group (C=O). This second carbonyl group is attached to a phenyl ring.</p>	70.2 ± 1.4
4	 <p>The structure shows a benzene ring with two vertical lines representing attachment points to a resin backbone. At the 1 and 3 positions of the ring, there are carbonyl groups (C=O) connected to a central methylene group (CH₂), which is in turn connected to another carbonyl group (C=O). This second carbonyl group is attached to a benzene ring with a fluorine atom (F) at the para position.</p>	> 99.5

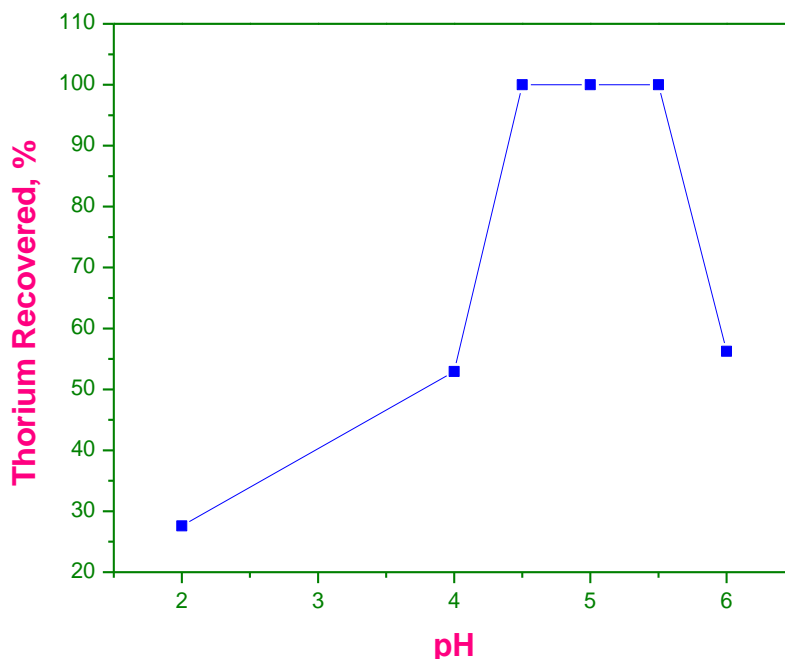


Figure 5.2 Effect of pH

5.5.2 Effect of preconcentration flow rate

The efficiency of preconcentration of thorium(IV) on to β -diketone functionalized Amberlite XAD-4 resin was studied at different flow rates. A set of solutions (1.0 l) containing 50 μg was adjusted to pH 5 ± 0.5 . These solutions were passed through the β -diketone functionalized Amberlite XAD-4 column at a flow rate varying between 1.0 to 4.0 ml/min. The preconcentrated thorium(IV) was eluted with 10.0 ml of 1.0 M HCl. The metal content of the eluate was determined as mentioned in “Section 5.5.1”. It was found that 1.0 – 3.0 ml/min flow rate was suitable for optimum loading of thorium(IV) on to resin (See Fig.5.3). The flow rates slower than 1.0 ml/min were not studied to avoid long analysis times. At flow rates higher than 3.0 ml/min, thorium(IV) does not equilibrate quantitatively with the resin bed. Hence 3.0 ml/min was used as the optimum flow rate in all subsequent studies.

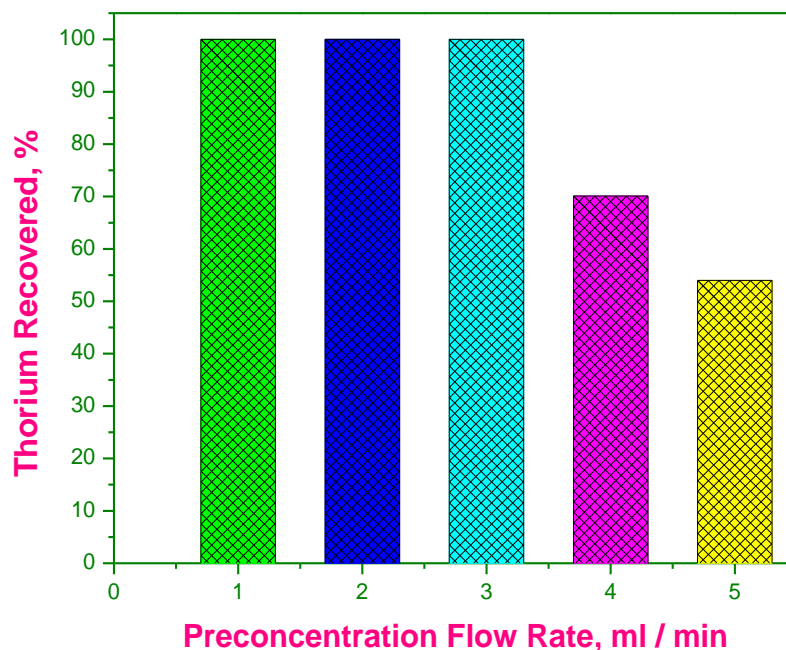


Figure 5.3 Effect of preconcentration flow rate

5.5.3 Effect of eluent concentration

A series of solutions (volume of each 1.0 l) containing 50 μg of thorium at optimum pH of 5.0 ± 0.5 was taken. Each of them was passed through the column of β -diketone functionalized Amberlite XAD-4 at an optimum flow rate of 2.0 ml/min. The preconcentrated thorium(IV) ion was eluted with 0.5 – 2.0 M of HCl and was determined spectrophotometrically as described in “Section 5.5.1”. The minimum HCl concentration for quantitative recovery of thorium is 1.0 M (See Table 5.2).

Table 5.2 Effect of eluent concentration

Concentration of hydrochloric acid (M)	Recovery (%)
0.1	42.4
0.5	66.6
1	> 99.5
2	> 99.5

5.5.4 Effect of elution flow rate

The preconcentrated thorium(IV) ion present in the β -diketone modified Amberlite XAD-4 was eluted with 10 ml of 1.0 M HCl by varying the flow rates in the range 1-5 ml/min. As seen from Table 5.3, it was found that upto 3.0 ml/min of flow rate do not affect the recovery of thorium(IV) and was used as the eluent flow rate in all subsequent studies.

Table 5.3 Effect of elution flow rate

Elution flow rate (ml/min)	Recovery (%)
1	> 99.5
2	> 99.5
3	> 99.5
4	85.6
5	54.3

5.5.5 Effect of eluent volume

Solution containing thorium(IV) was preconcentrated at optimum condition as explained in Section 5.5.1. The efficiency of the eluent (1.0 M HCl) was studied by taking its different volumes (1.0-10.0 ml). The thorium(IV) ion content in eluted HCl of various volumes (1.0-10.0 ml) was determined spectrophotometrically as given in Section 5.5.1. The results obtained are given in Fig.5.4. It was found that 5.0 ml of 1.0 M HCl was sufficient for quantitative recovery of thorium(IV). Therefore, for complete desorption, 10 ml of 1.0 M HCl was used.

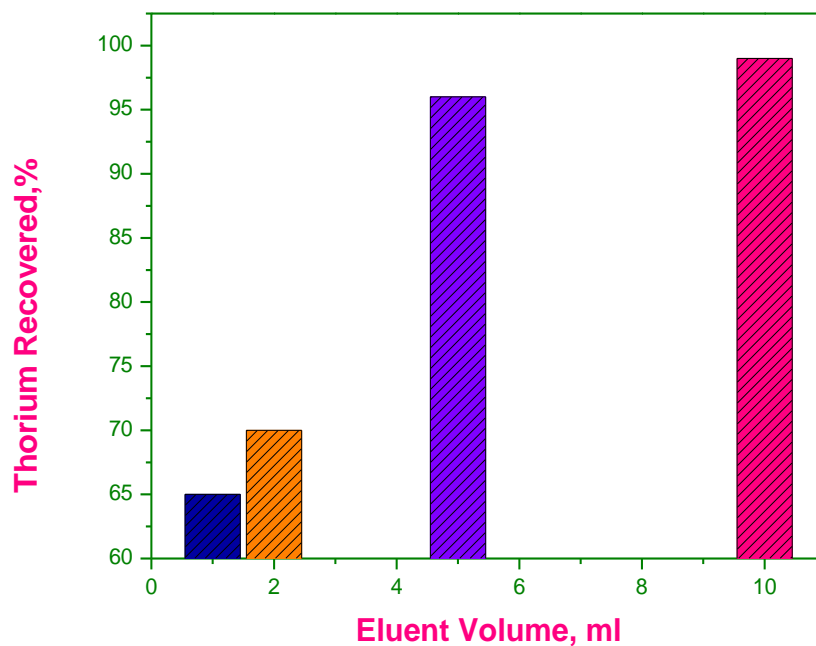


Figure 5.4 Effect of eluent volume

5.5.6 Effect of nature of eluent

A series of solutions (volume of each 1.0 l) containing 100 μg of thorium at optimum pH of 5.0 ± 0.5 was taken. These solutions were passed through the column of β -diketone functionalized Amberlite XAD-4 at an optimum flow rate. The thorium(IV) ion was eluted with different eluting agents such as hydrochloric acid (1.0 M), sulphuric acid (1.0 M) and nitric acid (1.0 M). The results obtained are shown in Table 5.4.

Table 5.4 Effect of nature of eluent

Eluent (1 M)	% desorption
HCl	> 99.5
H ₂ SO ₄	> 99.5
HNO ₃	64.8

From the table, it is clear that quantitative desorption is obtained with hydrochloric acid and sulphuric acid only. HCl was used in all subsequent studies.

5.5.7 Effect of sample volume

The preconcentration and elution of thorium(IV) on β -diketone functionalized Amberlite XAD-4 was studied by varying the volume of thorium solution from 25 to 1.0 l and keeping the total amount of loaded metal ion constant at 100 μg under optimum conditions. The enriched thorium ion was eluted with HCl, and measured spectrophotometrically by following the procedure given in section 5.5.1. Quantitative recoveries of thorium were obtained up to 1.0 l (Fig.5.5) resulting in an enrichment factor of ~ 100 .

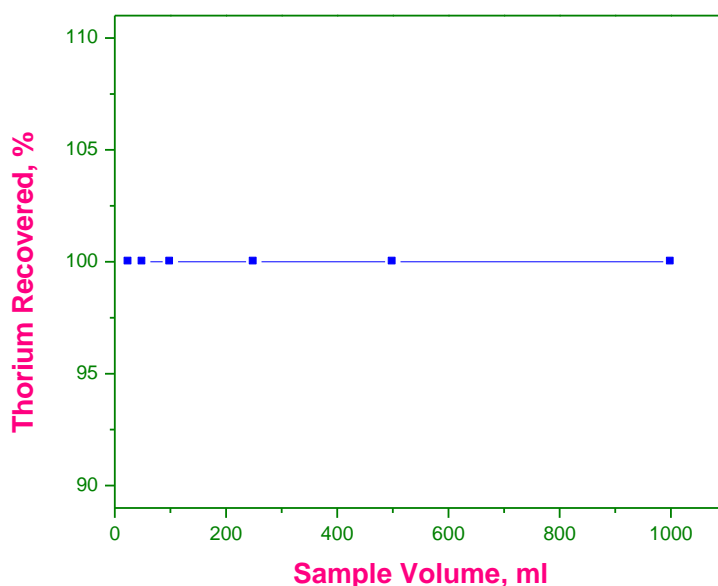


Figure 5.5 Effect of sample volume

5.6 CALIBRATION GRAPH, SENSITIVITY AND PRECISION STUDIES

A set of solution (volume 1.0 l) containing thorium(IV) ion concentration in the range 5-100 μg was taken. The pH of these solutions was adjusted to 5.0 ± 0.5 after the addition of 10 ml of 1.0 M sodium acetate-acetic acid buffer. These solutions were passed through a column packed with 0.5 g of β -diketone

functionalized Amberlite XAD-4 at a flow rate of 2.0 ml/min. The thorium(IV) ions pre-concentrated on the resin at the optimal conditions were eluted with 10.0 ml of 1.0 M HCl and determined spectrophotometrically after adding 5.0 ml of 1:1 HCl and 2.5 ml of 0.1% arsenazo(III) solution in a total volume of 25 ml. The absorbance of thorium(IV)-arsenazo(III) complex was measured at 650 nm.

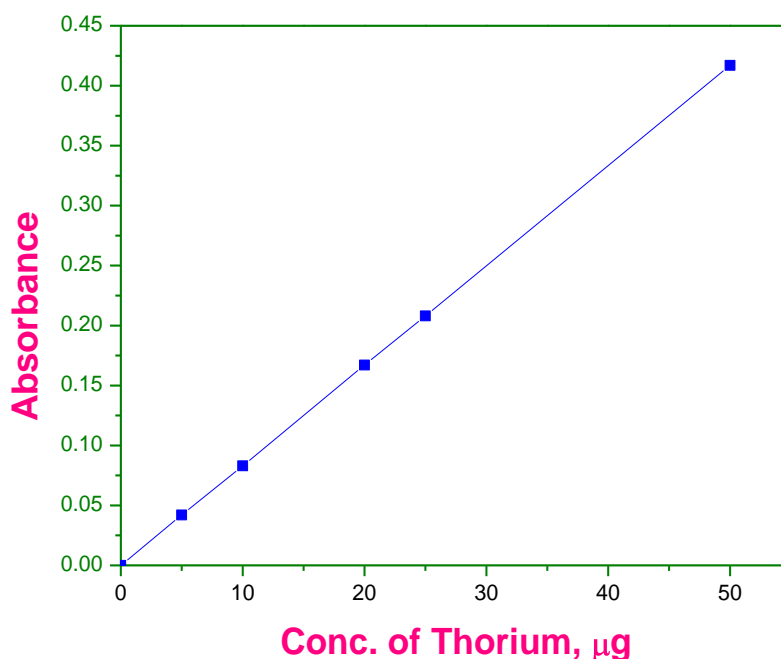


Figure 5.6 Calibration graph

The linear equation with regression (R) is as follows:

$$Y = 0.00813X - 5 \times 10^{-4}$$

$$R = 1$$

Ten replicate determinations of 10 µg of thorium present in 1.0 l of solution gave a mean absorbance of 0.083 with a relative standard deviation of 2.16. The limit of detection (lowest concentration below which recoveries becomes non-quantitative) corresponding to 3 times the standard deviation of blank was found

to be 0.5 μ g/l. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

Table 5.5 Precision studies

Sl.No.	Absorbance	Th(IV) found (μ g)	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
1	0.084	10.12	- 0.121	0.015
2	0.083	10.00	- 0.001	0.000
3	0.084	10.12	- 0.121	0.015
4	0.082	9.88	0.119	0.014
5	0.083	10.00	- 0.001	0.000
6	0.080	9.64	0.359	0.129
7	0.086	10.36	- 0.361	0.130
8	0.081	9.76	0.239	0.057
9	0.082	9.87	0.129	0.016
10	0.085	10.24	0.241	0.058

$$\bar{X}_i = 10.00$$

$$\Sigma (X_i - \bar{X})^2 = 0.424$$

$$SD = 0.218$$

$$\text{Coefficient of variation} = 2.16\%$$

5.7 RETENTION CAPACITY OF β -DIKETONE FUNCTIONALIZED AMBERLITE XAD-4

To determine the retention capacity (maximum amount of thorium(IV) preconcentrated per g of resin), 1g of the resin was saturated with thorium(IV) ion in batch mode under optimum conditions. The amount of thorium ion needed for saturation was determined spectrophotometrically after eluting it with minimum volume of 1.0 M HCl. The retention capacities with β -diketone functionalized Amberlite XAD-4 were calculated to be 8.39 mg/g of resin. Table 5.6 compares the retention capacity of the present resin with various SPE sorbents reported in literature.

Table 5.6 Comparison of retention/sorption capacities of various SPE's prepared during offline enrichment of thorium(IV)

Sl. No.	Sorbent	Chelating agent	Retention/sorption capacity (mg/g) of SPE	Ref.
1	Benzophenone	5,7-dichloroquinoline-8-ol	1.10	[26]
2	Cellulose	Quinoline-8-ol	20.00	[27]
3	Merrifield chloromethylated resin	Thenoyl trifluoroacetone	27.84	[28]
4	Merrifield chloromethylated resin	Di-bis(1,2-ethylhexyl)malonamide	38.2	[29]
5	Poly(styrene- β -hydroxylamine)	37,38,39,40,41,42-hexahydroxy-1,8,13,19,25,31-hexacarboxy Calix[6]arene	108.34	[30]
6	Merrifield peptide resin	11,23-disemicabazeno-26,28-n-dipropoxy-25,27-hydroxy Calix[4]arene	2.78	[31]
7	Amberlite XAD-16	1,2-dihydroxy arsinoyl phenylamino methyl]phosphoric acid	109.04	[32]
8	Amberlite XAD-4	Malonic acid	19.28	[33]
9	Amberlite XAD-4	Octacarboxymethyl-C-methylCalix[4]resorcin arene	62.64	[34]
10	Amberlite XAD-4	o-Vannilin semicarbazone	3.23	[35]
11	Amberlite XAD-4	Bicine	58	[36]
12	Amberlite XAD-4	β -diketone	8.39	[Present method]

As seen from Table, the retention capacity for the newly synthesized β -diketone modified Amberlite XAD-4 resin better than over a few chelate modified SPE sorbents only.

5.8 STABILITY AND REUSABILITY OF THE RESIN

The preconcentration and elution of thorium(IV) ion onto/from the resin were tested under optimal conditions. The retention capacity of resin remains unaltered even after 25 cycles of equilibration. Therefore, the repeated use of the resin is feasible. The retention capacity of the resin, stored for more than 3 months under ambient conditions has been found to be practically unchanged.

5.9 TOLERANCE LIMITS OF ELECTROLYTES AND CATIONS

Sample solution containing 10 µg of thorium(IV) and various amounts of different electrolytes and other cations were passed through the column under optimal conditions and the preconcentrated thorium(IV) in the presence of other species was determined by the procedure described in Section 5.5.1. The tolerance limits (error < 3%) are given in Table 5.6. From this Table it is clear that none of the species tested interfere in the developed preconcentration procedure using arsenazo(III) as reagent. On the other hand, uranium interferes even at almost equal concentrations and has to be separated while analyzing uranium containing samples.

5.10 APPLICATIONS

5.10.1 Analysis of rare earth chloride

Rare earth chloride sample collected from Indian Rare Earths (IRE) Limited, Alwaye, India was dissolved in 10 ml of 1:1 HCl and thorium(IV) present in the sample was preconcentrated by using β-diketone functionalized Amberlite XAD-4 and subjected to determination by arsenazo(III) procedure as described in Experimental. The results obtained are shown in Table 5.7 from which it is clear that the developed method compares favourably with the standard ICP-MS procedure.

Table 5.6. Tolerance limits of electrolytes and cations

Sl.No.	Electrolyte/metal ion	Tolerance limits
1	NaF	1 g
2	NaNO ₃	1 g
3	Na ₂ SO ₄	1 g
4	KCl	1 g
5	CaCl ₂	1 g
6	MgCl ₂	1 g
7	NH ₄ Cl	1 g
8	KSCN	50 mg
9	Thiourea	50 mg
10	NaSCN	1 g
11	NaF	1 g
12	Sodium oxalate	50 mg
13	Trisodium citrate	10 mg
14	Potassium hydrogen phosphate	1 g
15	EDTA	50 mg
16	Zn(II)	1000 µg
17	Cd(II)	1000 µg
18	Hg(II)	1000 µg
19	Mg(II)	1000 µg
20	Sr(II)	1000 µg
21	Pb(II)	1000 µg
22	Co(II)	1000 µg
23	Mn(II)	1000 µg
24	Ni(II)	1000 µg
25	Fe(III)	1000 µg
26	Al(III) + KH ₂ PO ₄	500 µg
27	Sn(II)	1000 µg
28	Sb(III)	1000 µg
29	Mo(VI)	500 µg
30	V(V)	500 µg
31	Cu(II) + NaSCN	500 µg

Table 5.7 Analysis of lighter rare earth chloride

Sample	Thorium found ($\mu\text{g/ml}$)			Recovery
	Added	Present method	Standard ICP-AES	
Rare earth chloride	-	9.35	9.38	-
	5	15.32	-	> 99.5
	10	19.33	-	> 99.4

5.11 EXPERIMENTAL

5.11.1 Reagents

A stock solution of thorium(IV) solution was prepared by dissolving appropriate amount of thorium nitrate (Aldrich, USA) in deionised water. Arsenazo(III) (Fluka, Buchi, Switzerland) (0.1%) solution was prepared by dissolving 0.1 g of the reagent in 100 ml of deionised water. Sodium acetate-acetic acid buffer (1.0 M) was prepared to maintain the pH of the aqueous phase. Amberlite XAD-4 (surface area $725 \text{ m}^2/\text{g}$; pore diameter 5 mm and bead size 20-60 mesh) and p-toloyl chloride, 4-fluoro benzoyl chloride were obtained from Aldrich (Milwaukee, USA). Acetyl chloride, anhydrous AlCl_3 , benzoyl chloride, dichloroethane, and toluene were obtained from M/s. E-Merck, India. All other chemicals including electrolytes and other metal ions were of analytical reagent grade.

5.11.2 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. IR spectra ($4000\text{-}400 \text{ cm}^{-1}$) in KBr were recorded using MAGNA IR-560 spectrometer (Nicolet, USA).

5.11.3 Procedure for the synthesis of β -diketone functionalized Amberlite XAD-4

(i) Acetylation of Amberlite XAD-4

2.0g of Amberlite XAD-4 resin (20-60 mesh) was taken after drying at 110°C for an hour. 5.0g of anhydrous AlCl_3 in 10 ml of 1,2-dichloroethane, 4.0 ml

of acetyl chloride were added in small increments to the mixture. The sides of the flask were washed down with an additional 2.0 ml of 1,2-dichloroethane. A drying tube was attached and kept for 8 hours with stirring. Then the reaction mixture was poured into an ice and conc. HCl mixture. The acetylated resin was filtered, washed repeatedly with methanol, water and conc. HCl.

(ii) Immobilization of 4-fluorobenzoyl chloride

About 2-3 g of $\text{Ca}(\text{OH})_2$ and 20 ml of dried dioxan were taken in a round bottom flask. 2g of acetylated resin was added into it. The entire mixture was stirred very slowly for 30-45 minutes. 3 ml of 4-fluorobenzoyl chloride was added dropwise to the mixture. Again, it was stirred for 1 hour and kept for 8-9 hours.

The mixture was initially washed with conc. HCl to remove all the excess $\text{Ca}(\text{OH})_2$ present in it. Then it was washed with dried toluene. The resulting β -diketone Amberlite XAD-4 resin was repeatedly washed with dil. acid and distilled water. Finally it was washed with ether and air dried.

5.11.4 General procedure

5.11.4.1 Preconcentration and determination of thorium(IV)

0.5g of β -diketone functionalized Amberlite XAD-4 was packed in a glass column (Vensil, size 7 mm diameter and 10 cm length). The column was treated with 1.0 M HCl (50 ml) and washed with deionised water until free from acid. A portion of solution containing 2-50 μg of thorium was diluted to 1.0 l and the pH was adjusted to 5.0 ± 0.5 after the addition of 1.0 M sodium acetate-acetic acid buffer and passed through the above column at a flow rate of 3.0 ml/min. The metal ions were eluted from the resin bed using 10.0 ml of 1.0 M HCl and determined spectrophotometrically after the addition of 5 ml of 1:1 HCl, 2.5 ml of 0.1% arsenazo(III) in a total volume of 25 ml. The absorbance of thorium(IV) - arsenazo(III) complex was measured at 650 nm. The linear range of

concentration using arsenazo(III) spectrophotometric procedure was 2-50 μg in a total volume of 25 ml.

5.11.4.2 Analysis of rare earth chlorides

Rare earth chloride sample was obtained from Indian Rare Earths Limited, Alwaye, India which processes monazite sand collected from the beach sands of South Western and South Eastern parts of India. Suitable aliquots of the sample was subjected to preconcentration and determination procedure described above after adjusting the pH to 5.0 ± 0.5 using sodium hydroxide after the addition of 10 ml of 1.0 M of acetate buffer. The thorium content of mixed rare earth chloride sample was established by reference to a calibration curve prepared by following the general procedure described above and compared with standard ICP-AES values.

5.12 CONCLUSION

β -diketone immobilized onto acetylated Amberlite XAD-4 resin with 4-fluorobenzoyl chloride is an insoluble functionalized polymer, which provides good stability and selectivity towards thorium(IV) ions. The synthesis of this material is very simple. β -diketone derived from 4-fluorobenzoyl chloride exists in the enol form which was confirmed by IR spectra. Thorium(IV) replaces the hydrogen and gets coordinated to carbonyl oxygen and OH oxygen. The complex contains a six membered chelated delocalized structure that provide much stability.

The above investigations clearly indicate that β -diketone functionalized Amberlite XAD-4 resin has potential for the enrichment of thorium(IV) and its separation from alkali, alkaline earths, lanthanides and several transition metal ions. The retention capacity of the resin is moderate i.e. 8.39 mg/g. β -diketone modified Amberlite XAD-4 resin has high mechanical and chemical strength as it is unaffected even after 30-40 cycles of preconcentration and elution. The thorium content in rare earth chloride sample was established unequivocally by

using low cost, precise and readily available instrument like colorimeter in conjunction with the developed preconcentration procedure utilizing β -diketone immobilized Amberlite XAD-4 resin.

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CHAPTER 6

FLOW INJECTION ON-LINE SOLID PHASE EXTRACTIVE PRECONCENTRATION OF TRACE AMOUNTS OF COBALT AND NICKEL IN SOILS AND HUMAN HAIR SAMPLES AND DETERMINATION BY FLAME AAS

6.1 INTRODUCTION

Nickel is a siderophile element; its average abundance in crystal rocks is 75 $\mu\text{g/g}$. Nickel is present in trace amounts in natural water samples in the order of 1.5 $\mu\text{g/l}$. The safety value of nickel in drinking water is 20.0 $\mu\text{g/l}$. Nickel is a moderately toxic element as compared with other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer [1,2]. Moreover, nickel can cause a skin disorder known as nickel-eczema [3]. Such a disease [4,5] is very usual in workers who handle great amounts of this element and has been the subject of many studies. The skin disorder can also appear in people who have great sensitivity to nickel, and can be caused by wearing jewels made of nickel alloys, like rings, chains and bracelets. Studies have proved that women are more liable to this disease. Medical diagnosis is currently established through nickel determination in blood and urine. Other studies show that disease incidence increased in patients who consume foods rich in nickel such as oats, nuts, beans and chocolate.

Cobalt is an essential micronutrient for man, animals and plants for a range of metabolic processes [6,7]. Cobalt is found in vitamin B₁₂, but a methyl or methylene group replaces CN in native enzymes. Vitamin B₁₂ deficiency causes the severe disease – pernicious anaemia in humans, which indicates the critical role of cobalt. Though cobalt is a micronutrient, when present in concentrations

above the normal cellular levels it is toxic. Cobalt poisoning leads to gastro intestinal distress and heart failure.

The determination of nickel and cobalt are usually carried out by flame and graphite furnace atomic absorption spectrometry as well as spectrophotometric methods. However the determination of nickel and cobalt in biological and environmental samples is difficult due to various factors, the important of which are very low concentrations, contamination and loss of elements from samples during sampling, preservation and pretreatment. Due to the presence of nickel and cobalt in soils and human hair samples at low levels, the use of a preconcentration step prior to nickel and cobalt determination is necessary.

Conventional preconcentration/separation techniques such as coprecipitation [8,9], or liquid-liquid extraction [10,11], cloud point [12] or solid phase [13,14] extraction have been developed to overcome interferences from matrix elements as well as to improve detection limits during the determination of nickel and cobalt. Processes involving solid phase extraction show several advantages like availability and easy recovery of sorbent, attainability of high preconcentration factors [15,16], and safe handling. Therefore, these procedures avoid or minimize the use of organic solvents that are generally toxic.

On-line preconcentration systems using solid phase extraction are opportune for metal determination due to their flexibility, high sample throughput and versatility. Flow injection analysis (FIA) can be used to speed up the preconcentration process, reduce sample consumption and remove contamination from air and various vessels used for the preconcentration. Also batch preconcentration systems have a risk of contamination, and require relatively large amount of sample volume and time consuming. However online column preconcentration system require only a small amount of the sample volume and contamination from various vessels and air borne particles can be easily eliminated. Since the invention of FIA, online preconcentration with sorbent packed columns coupled to FAAS by Ruzika and Arndal [17], several researchers highlighted the versatility of these FI coupled systems and their superiority over

LLE. FIA preconcentration methods are based on the use of micro column packed with sorbents [18-20] or chelating resin such as Amberlite XAD-2 [21] or chelex-100 [22,23] or activated alumina [24-26], depending on the elements to be considered and matrix to be separated. Alternatively, a knotted reactor which consists of long PTFE tube properly knotted can be applied as a sorbent surface [27-29]. In both the cases, the metal ion forms a complex with a chelating agent and gets sorbed on the column material or on the surface of PTFE tube during loading/preconcentration period. Then, the retained complex is eluted by using methanol or ethanol [30,31], ammonium acetate [32] in case of packed column reactor, or by using isobutylmethyl ketone (IBMK) [33] in case of knotted reactor. Finally the eluent is injected into the nebuliser of FAAS. Various features of online preconcentration and FIA-AS procedures hitherto developed for the determination of cobalt and nickel are summarized in Table 6.1 [34-55].

This chapter concerns with the development of online flow injection-FAAS procedure for nickel and cobalt based on the sorption of their chelates (nickel and cobalt-2,3-dihydroxynaphthalene) on to commercially available C₁₈ bonded silica gel micro column.

Table 6.1 Summary of FIA-FAAS procedures developed since 1998 for the determination of Co and Ni

Sl.No.	Analytes	Detection technique	Chelating agent	Detection limit (ng/ml)	Linear range (ng/ml)	Enrichment factor*	Application	Ref.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Cobalt								
1	Co	FAAS	2-nitroso-1-naphthol	0.02	5 – 100	125	Water & VitaminB12	34
2	Co	FAAS	Nitroso-R-salt	1.25	1.25-220	79	Natural waters	35
3	Co	FAAS & ETAAS	Quinoline-8-ol & its derivatives	-	10 – 34	-		36
4	Co, Cu, Cd & Zn	FAAS	Dithione	1.06	-	52	Biological CRM's	37
5	Co	Spectrophotometry	4-benzoyl piperidinedithiocarbamate	0.1	0.6-100	-	Waters	38
6	Co	FAAS	1-nitroso-2-naphthol	3.2	0 – 250	17.2	CRM's of steels	39
7	Co	ETAAS	Nitroso-R-salt	5	-	15	Biological materials	40
8	Co, Cd, Pb, Cu, Mn, Bi, In & Be	ICPMS	8-hydroxy quinoline	-	-	300	Seawater	41
9	Co	FAAS	1-nitroso-2-naphthol	3.2	-	17.2	CRM's of steels	42
10	Co	FAAS	2-(2-thiazolyl azo)-p-cresol	0.13	0.5-10	-	Natural waters	43
11	Co	ETAAS	Ammonium pyrrolidine dithio carbamate	4	0.01-0.25	87	CRM's of water & mussel tissue	44
12	Ni	ETAAS	SP Sephadex resin	9	0.01-0.5	72.1	Human urine	45
13	Ni	ETAAS	SP Sephadex resin	10.2	0.01-0.5	71.1	Human urine &	46

							industrial waste	
14	Ni	FAAS	2-(2-benzothiazolylazo)-2-p-cresol	1.1	5 – 250	30	Biological CRM's	47
15	Ni	FAAS	Dimethyl glyoxime	3	-	21	CRMs of steels & mussel	48
16	Ni	ICPAES	Activated carbon	0.08	-	80	Natural waters	49
17	Ni	Spectrophotometry	Bis(acetylaceton)ethylene diimine	-	Upto 25000	-	Ni-Cu alloys	50
18	Ni & Zn	Spectrophotometry	1-(2-thiazolyl-azo)-2-naphthol	-	-	-	Cu-based alloys	51
19	Ni & Bi	ICP-MS	SP Sephadex resin	15	0.05-2.4	35.2	River sediment CRM	52
20	Ni, Cd & Pb	ICPAES	Cationic exchange resin	2	-	10	Food stuffs & vegetable materials	53
21	Ni, Pb, Cd, Cu, Zn & Fe	IC	8-hydroxy quinoline	0.06	-	2	Natural waters	54
Cobalt and Nickel								
22	Co, Ni, Al, V, Mn, Cu, Zn, Mo, Cd, Pb & U	ICPMS	Muromac A-1	0.014 & 0.029	1 – 30	7.0 & 6.0	Seawater CRMs	55
23	Co & Ni	FAAS	2,3-dihydroxy naphthalene	0.1	0.5 – 20	725, 600	Human hair, soils	Present method

6.2 PRELIMINARY STUDIES

Preliminary experiments showed that no detectable amounts of cobalt and nickel could be retained on the C₁₈ bonded silica gel column in the absence of the chelating agent. Ortho dihydric phenols and its derivatives were tested for chelation with cobalt and nickel and subsequent online solid phase extraction followed by elution with acidified methanol. The results obtained are given in Table 6.2., from which it is clear that 2,3-dihydroxy naphthalene gave maximum absorbance [0.200 and 0.160 for cobalt and nickel respectively], compared to other derivatives. Hence 2, 3-dihydroxy naphthalene was selected as the on-line preconcentration reagent in subsequent studies.

Table 6.2 Effect of chelating agents

Chelating agent	Absorbance	
	Co	Ni
Catechol	0.100	0.027
2,3-dihydroxy naphthalane	0.200	0.160
4,5-dihydroxy-1,3-benzene disulphonic acid	0.017	0.014

6.3 OPTIMIZATION OF ANALYTICAL PARAMETERS

6.3.1 Effect of pH

The pH/acidity of the sample is one of the critical variables for the formation of 2,3-dihydroxy naphthalene complex and its adsorption on the sorbent (C₁₈ bonded silica gel) surface. Hence, the pH of the solution of 10 µg/l of cobalt and nickel were varied over the range 1.0 -10.0 in steps of 1.0 after the addition of sodium acetate-acetic acid buffer. Samples and ammonical 2,3-dihydroxy naphthalene were pumped simultaneously for 60 s and mixed online. The preconcentrated cobalt and nickel complexes adsorbed on C₁₈ bonded silica gel were eluted with acidified methanol and was injected into the nebulizer for their

determination. SPE of cobalt and nickel onto C₁₈ bonded silica gel was found to be quantitative in the pH range of 2.0-8.0 [Fig 6.1]. At pHs > 8.0, the formation of hydroxyl species results in decrease in absorbance. Again, at pHs < 2, the absorbances are lower due to insufficient formation of the metal DHN complexes rather than the stability of the column material, as it is sufficiently resistant to acidic solutions.

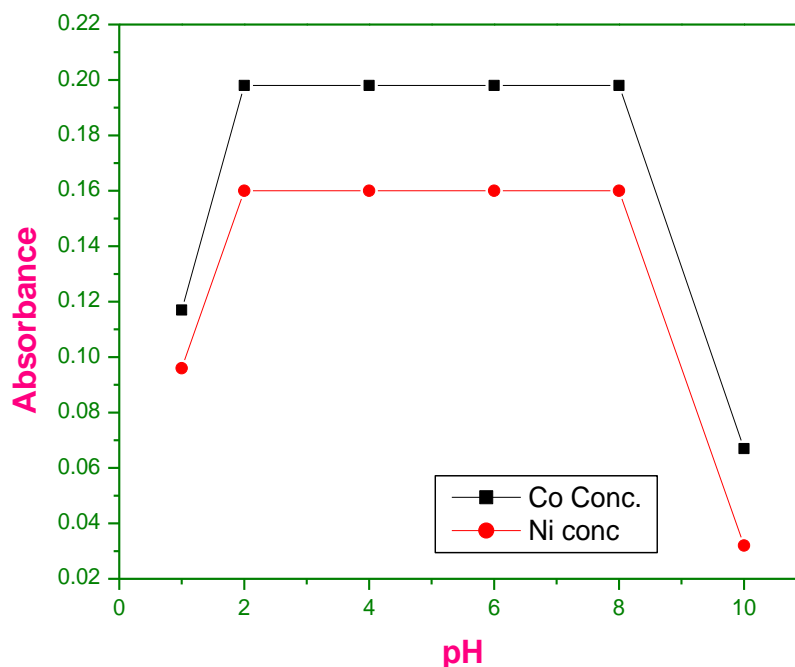


Figure 6.1 Effect of pH

6.3.2 Effect of NH₃ concentration

The preconcentration of 2,3-dihydroxy naphthalene complexes of 10 µg/l of cobalt and nickel onto C₁₈ bonded silica gel were studied at ammonical concentrations of 0.05 – 0.5 M in steps of 0.05. The sample and reagent were pumped simultaneously through the column during loading, eluted with acidified methanol and fed to the nebulizer of FAAS. The results obtained are shown in Table 6.3, from which it is clear that maximum analytical signals were obtained with 0.05 – 0.1 M and 0.05 – 0.08 M in the case of cobalt and nickel respectively. As the reagent is not soluble at ammonia concentrations less than 0.05 M, 2,3-dihydroxy naphthalene was prepared in 0.075 M ammonia in subsequent studies.

Table 6.3. Effect of ammonia concentration on FIA-FAAS analytical signals of Co and Ni (10 µg/l of Co and Ni)

Sl.No.	NH ₃ ,concentration(M)	Absorbance	
		Co	Ni
1	0.05	0.200	0.160
2	0.075	0.200	0.160
3	0.100	0.199	0.062
4	0.500	0.067	0.050

6.3.3 Effect of concentration of 2,3-dihydroxy naphthalene

A set of solutions of cobalt and nickel with 10 µg/l were adjusted to the pH 5.0±3.0 and the 2,3-dihydroxy naphthalene solutions in the concentration range 0.005-1.00% prepared in 0.075 M ammonia were pumped through the column. The preconcentrated cobalt and nickel was eluted with acidified methanol and introduced into the nebulizer for its determination. Variation of 2,3-dihydroxy naphthalene concentrations in the range 0.005-1% show that the sorption of cobalt and nickel (Fig. 6.2) was maximum when it is greater than 0.1%. Therefore 0.2% of 2,3-dihydroxy naphthalene was used for the subsequent studies.

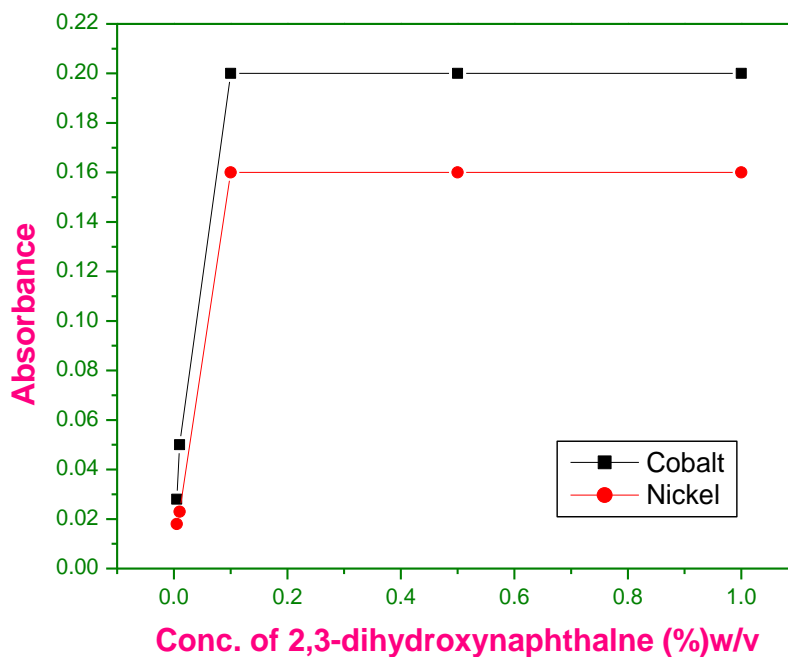


Figure 6.2 Effect of concentration of 2,3-dihydroxy naphthalene

6.3.4 Choice of eluent

Various water miscible solvents (acidified to pH ~2.0) such as methanol, dimethyl formamide, dimethyl sulphoxide and acetonitrile were tested for the elution of previously sorbed 2,3-dihydroxy naphthalene complexes of cobalt and nickel on C₁₈ bonded silica gel. Methanol gave the highest absorbance compared to other solvents and was selected for subsequent studies. It was found that nitric acid in the range 0.01-0.1 M quantitatively elute the cobalt or nickel – 2,3-dihydroxy naphthalene complexes (sorbed during the preconcentration step) on C₁₈ bonded silica gel.

6.4 OPTIMIZATION OF FLOW INJECTION CONDITIONS

6.4.1 Flow conditions

High sample loading flow rates are important for efficient preconcentration and high sample throughput. In general, FI sample flow rates are limited by the back pressure produced by the column and/or sorption efficiency, which decreases with the decreasing flow rate. No degradation of sorption efficiency was observed upto a loading flow rate of 15.6 ml/min of the cobalt and nickel, 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 adds to the total loading flow rate and hence calls for a proportional decrease in the sample flow rate. The reagent flow rate should not be too low so as to ensure good mixing of the reagent and sample solutions. An optimum sample and reagent flow rates of 11.6 and 4.0 ml/min respectively were used in subsequent studies.

An elution flow rate of 5.0 ml/min provided 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. The lower flow rate in the FI mode in comparison with conventional free uptake of the nebulizer is also beneficial for the droplet diameter distribution, which is shifted to smaller droplets and is therefore less prone to vaporization interference.

6.4.2 Loading time

The influence of sample loading time was studied in the range 30 to 240 seconds at the optimum conditions established above. The preconcentration efficiency was found to increase linearly upto 240 s (Fig.6.3). This fact proved that even at long loading times and prolonged sample flow, no negative effect is produced from partial leaching of the complex. Finally, a 60 s loading time was chosen as a compromise between high sensitivity and sufficient sampling frequency.

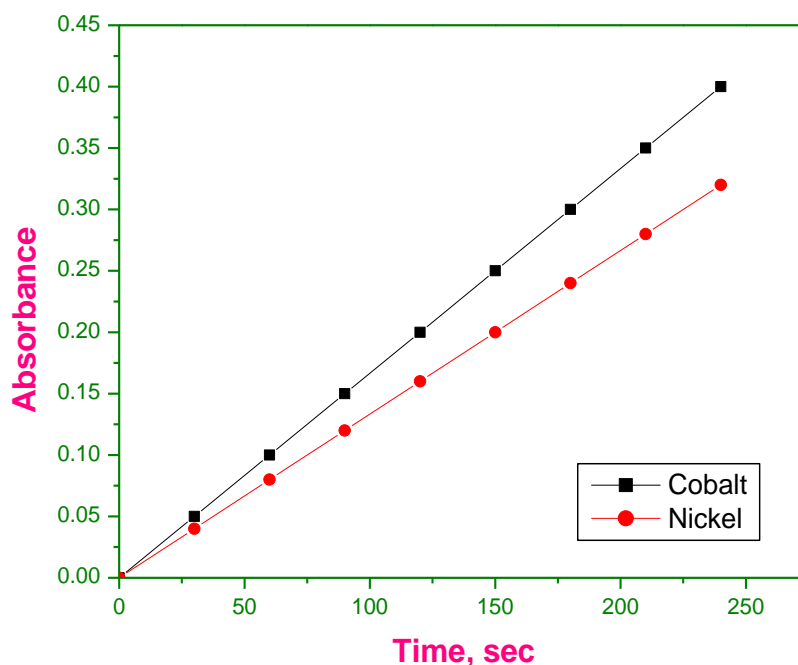


Fig 6.3 Effect of Loading Time

6.5 CALIBRATION GRAPH AND PRECISION

A set of solutions of cobalt and nickel containing 1 – 20 µg/l whose pH has been adjusted to 5.0±3.0 and 2,3-dihydroxy naphthalene solution of concentration 0.2% in 0.075 M ammonia were pumped through the column for 60 s. The sample and reagent flow rate were 11.6 ml/min and 4.0 ml/min respectively. The preconcentrated cobalt and nickel onto C₁₈ bonded silica gel was eluted with acidified methanol at a flow rate of 5 ml/min and introduced into the nebulizer of FAAS for determination. The calibration graph is linear upto 1-20 µg/l of cobalt and nickel. The linear equation with regression R is as follows.

$$Y = A + BX$$

Where B is the slope, A is intercept, Y is peak height absorbance and X is concentration in µg/l.

For cobalt

$$Y = 0.0006 + 0.01998X$$

$$R = 0.99999$$

For Nickel

$$Y = 0.0043 + 0.01538X$$

$$R = 0.99995$$

The detection limit (3σ) was calculated to be 0.087 and 0.1µg/l for cobalt and nickel respectively and the relative standard deviation for ten replicate measurements of 10 µg/l cobalt and nickel were 0.88 and 1.0% respectively (See Table 6.4 and 6.5).

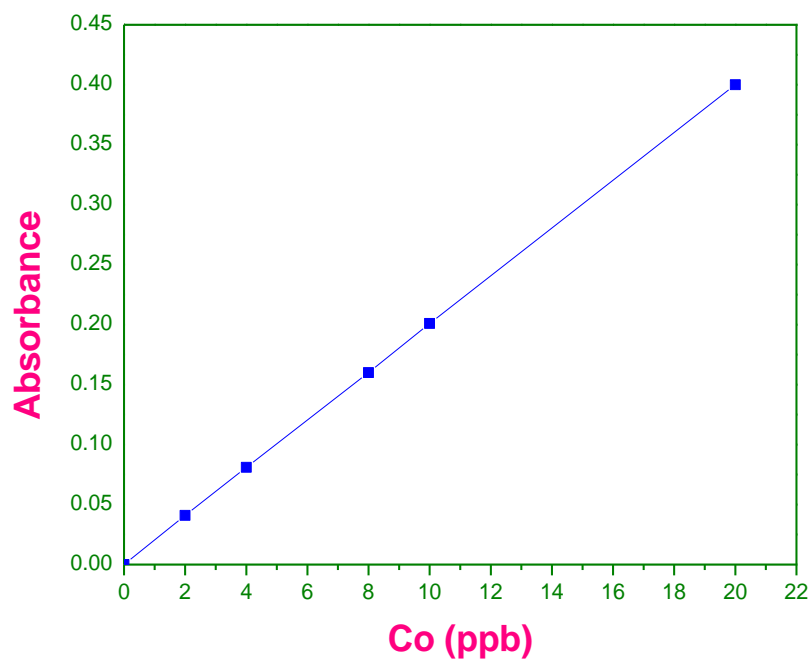


Figure 6.4 Calibration plot for Cobalt

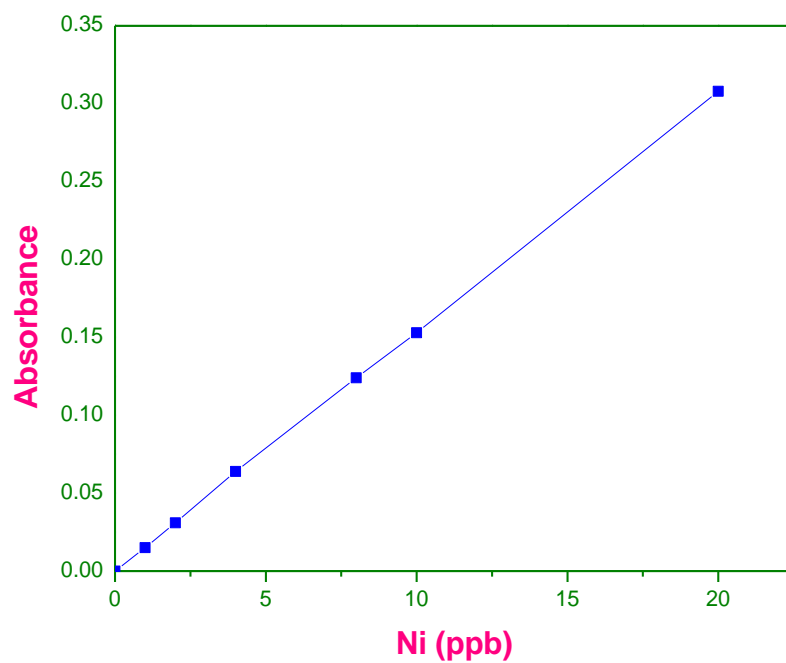


Figure 6.5 Calibration plot for Nickel

Table 6.4 Precision studies for cobalt

Sl.No.	Absorbance	Co found (μg) X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
1	0.200	10.00	-0.03	0.0009
2	0.198	9.90	-0.13	0.0169
3	0.197	9.85	-0.18	0.0324
4	0.201	10.05	0.02	0.0004
5	0.198	9.90	-0.013	0.0169
6	0.204	10.20	-0.01	0.0001
7	0.201	10.05	0.02	0.0004
8	0.201	10.05	0.02	0.0004
9	0.204	10.20	-0.01	0.0001
10	0.202	10.10	-0.02	0.0004

$$\bar{X} = 10.030$$

$$\Sigma(X_i - \bar{X})^2 = 0.0689$$

$$\sigma = 0.075.$$

$$\text{RSD} = 0.875\%.$$

Table 6.5 Precision studies for Nickel

Sl.No.	Absorbance	Ni found X_i (μg)	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
1	0.160	10.00	- 0.03	0.0009
2	0.162	10.13	0.10	0.0100
3	0.161	10.06	0.03	0.0009
4	0.159	9.94	- 0.09	0.0081
5	0.163	10.18	0.15	0.0225
6	0.159	9.94	- 0.09	0.0081
7	0.162	10.13	0.10	0.0100
8	0.161	10.06	0.03	0.0009
9	0.159	9.94	- 0.09	0.0081
10	0.158	9.88	- 0.15	0.0225

$$\bar{X} = 10.030$$

$$\Sigma(X_i - \bar{X})^2 = 0.0920$$

$$\text{SD} = 0.1.$$

$$\text{Relative standard deviation} = 1\%$$

6.6 PERFORMANCE OF ON-LINE PRECONCENTRATION SYSTEM

The characteristic data for the performance of the on-line preconcentration system are summarized in Table 6.6.

Table 6.6 Analytical performance data for FI on-line preconcentration by FAAS method for cobalt and nickel determination

	Cobalt	Nickel
Linear range ($\mu\text{g/l}$)	0.5 – 20	0.5 – 20
Sensitivity enhancement ^a	725	600
Precision (RSD) ^b (at 10 $\mu\text{g/l}$)	0.87	1.0
Sample consumption (ml)	11.6	11.6
Loading time (min)	1	1
Sample frequency	30/h	30/h
Detection limit (3σ) ($\mu\text{g/l}$)	0.087	0.1

^acompared to conventional nebulization

^b $n = 5$

The efficiency of sorption was investigated by analyzing the previously collected column effluent from a standard solution of cobalt and nickel and using the same preconcentration technique. From the results obtained by the repeated preconcentration, a retention efficiency of > 99% was calculated for cobalt and nickel. The preconcentration elution sequence is highly reproducible, giving an overall precision of 0.87 and 1.0% for 10 successive determinations of 10 $\mu\text{g/l}$ of cobalt and nickel respectively (Table 6.4 and 6.5). One minute loading allows a sampling frequency of 30/h. Higher sensitivities can be obtained by modifying the method, ie. using a longer preconcentration period, at the expense of a lower sample throughput. A linear relationship was observed between loading time and enrichment factor upto 4 min of loading/preconcentration time. Thus, with a loading time of 1 min, 725 and 600 fold enhancement in sensitivity compared to conventional flame AAS was observed for cobalt and nickel with a detection limit of 0.087 $\mu\text{g/l}$ and 0.1 $\mu\text{g/l}$ corresponding to 3 times the standard deviation of the blank.

6.7 INTERFERENCE STUDIES

The tolerance of maximum concentration of neutral electrolytes and co-existing ions usually present in soils and hair in the determination of 10 µg/l of cobalt and nickel were systematically studied by the FIA-AAS procedure described under Section 6.5 Any deviation of 1.0% or more from the standard absorbance value was taken as interference. The maximum concentration of neutral electrolytes and co-existing ions which do not cause reduction in FIA-AAS signal of cobalt and nickel are given in Table 6.7 These observations suggest that the developed procedure can be used for the analysis of cobalt and nickel in soils and hair samples.

Table 6.7 Tolerance limits of foreign ions/electrolytes

S.No.	Interferent	Co (absorbance)	Ni (absorbance)
1	1.0 M NaCl	0.205	0.160
2	1.0 M NaNO ₃	0.200	0.165
3	1.0 M Na ₂ SO ₄	0.200	0.160
4	1.0 M MgCl ₂	0.205	0.160
5	Fe(II) (1 mg)	0.205	0.165
6	Zn (1 mg)	0.200	0.160
7	Cu(II) (1 mg)	0.200	0.165

6.8 APPLICATION

6.8.1 Analysis of standard reference material IAEA – soil 7 (supplied by IAEA, Vienna)

The accuracy of the developed preconcentration procedure was tested by analyzing a standard soil reference material (IAEA soil – 7) supplied by IAEA, Vienna. The soil-7 sample was mineralized by using the dissolution procedure described in the experimental section and was subjected to preconcentration and determination by adopting the general procedure given in the Experimental Section 6.9.4. The nickel content established by the present procedure agrees well with the reference values, whereas cobalt content is below the detection limit as the certified cobalt content is 8.9 µg/g of soil (Table 6.8).

6.8.2 Analysis of soil samples

As the co-existing species present in soils did not interfere and gave comparable values of nickel to those present in soil reference material (IAEA soil-7), it was decided to analyse for nickel in soil samples collected from two stations in Trivandrum. The soil samples were mineralized and subjected to analysis for nickel using the general procedure described in Experimental Section 6.9.4. Thus, as seen from Table 6.8, the SPE preconcentration method developed in present work enables simple and low cost instrument like FIA-FAAS to analyse soil samples containing ultratrace amounts of nickel.

Table 6.8 Analysis of soil samples

Sl.No.	Sample	Amount of Ni, $\mu\text{g/g}$ of soil (95% confidence interval)	
		Present methods	Certified value
1	IAEA-soil 7	24.7 (21.30)	26 (31.37)
2	Soil sample from Station I	14.8 (14.18)	-
3	Soil sample from Station II	62.2 (55.70)	-

6.8.3 Analysis of human hair samples

The factors that influence trace elements of hair samples are (i) the distance of the sample from the scalp, (ii) age and sex of the donor, (iii) the geographical habit of donors and (iv) his or her dietary supplements and medication. However, factors (i) and (iv) were eliminated by the careful sampling procedure adopted in this study. We have eliminated factor (iii) by choosing the hair samples from subjects of different age and sex of same geographical location. These samples were washed and analysed by FIA-FAAS procedure described in Experimental Section 6.9.5 for cobalt and nickel. The results obtained are shown in Table 6.9 from which the following observations can be deduced, even though the number of samples analysed are only 12 collected from single city, i.e. same geographical location.

- (1) The cobalt content in case of samples 6-9 and 11-12 is below the detection limit of the developed FIA-FAAS procedure.
- (2) Except sample 10, other subjects contain ~0.4-0.62 $\mu\text{g/g}$ of cobalt.
- (3) The nickel content is below the detection limit of the developed FIA-FAAS procedure for samples 4-6.
- (4) Nickel contents of hair sample are ~0.97-1.70 $\mu\text{g/g}$ except for samples 4-6.
- (5) In case of male subjects, the nickel content increases with increase of age. On the other hand, nickel content in female subjects significantly decreases with increasing age. The increase in nickel content in male subjects with age can be attributed to occupational exposure.

Table 6.9 Analysis of human hair samples ($\mu\text{g/g}$ of hair)

Sl.No.	Sex (age)	Cobalt	Nickel
1	F (20)	0.62+0.02	1.70±0.03
2	F (30)	0.55±0.02	1.45±0.03
3	F (35)	0.50±0.02	1.40±0.03
4	F (47)	0.45±0.01	< 0.01
5	F (7)	0.44±0.01	< 0.01
6	M (22)	< 0.01	< 0.01
7	M (25)	< 0.01	0.97±0.02
8	M (30)	< 0.01	1.00±0.02
9	M (36)	< 0.01	1.45±0.03
10	M (37)	< 0.01	1.50±0.03
11	M (48)	< 0.01	1.70±0.03
12	M (62)	< 0.01	1.69±0.03

6.9 EXPERIMENTAL

6.9.1 Instrumentation

A Perkin Elmer model A AnalystTM 100 atomic absorption Spectrometer (Perkin Elmer Life and Analytical Sciences, Shelton, CT, USA) with deuterium background correction and Perkin-Elmer Lumina[®] hollow cathode lamps were used. The hollow cathode lamp current, wavelength and spectral band pass were

10 & 10 mA, 240.7 & 232.0 nm and 0.7 & 0.7 nm for cobalt and nickel respectively. A standard air acetylene stainless steel nebulizer and a 10 cm path length system were operated at an air flow rate of 4.0 l/min and acetylene flow rate of 1.0 l/min. The burner height was adjusted to about 30 mm from base for optimum sensitivity. The nebulizer uptake rate was adjusted to provide optimum response for conventional sample aspiration.

A Perkin-Elmer FIAS-400 flow injection system connected to the atomic absorption spectrometer (Perkin-Elmer AAnalyst 100) was used for on-line preconcentration of cobalt and nickel, which is shown in Fig.6.6. The FIAS-400 has two peristaltic pumps and a 5-port valve. Two peristaltic pumps with two channels are used to transport the various liquids through the system. Each pump can be fitted up to four magazines which hold the pump tubing. The magazines are slid into the pivots and pressure is applied using the pressure adjustment lever (Fig 6.7). The flow is from left to right for magazines placed above the pump rotor and right to left for magazines placed below the pump rotor. The 5-port injection valve is used for the injection of defined volume of sample into the carrier stream during preconcentration. The automatic operation of the injection valve to switch from the load to elute position and the two multichannel peristaltic pumps were programmed using the spectrometer software. Tygon pump tubes were used to propel the sample (11.6 ml/min) and reagent solutions (4.0 ml/min). A PTFE tubing of 0.3 mm i.d. was used for all connections in order to minimize the dead volume. A commercially available conically shaped micro column of 50 μ l capacity (Perkin-Elmer, Uberlingen, Germany) packed with 20 mg of C₁₈ bonded silica gel (40-60 μ M) was used. Time resolved absorbance signals of cobalt and nickel were displayed on the computer monitor and printed with peak height and integrated absorbance values.

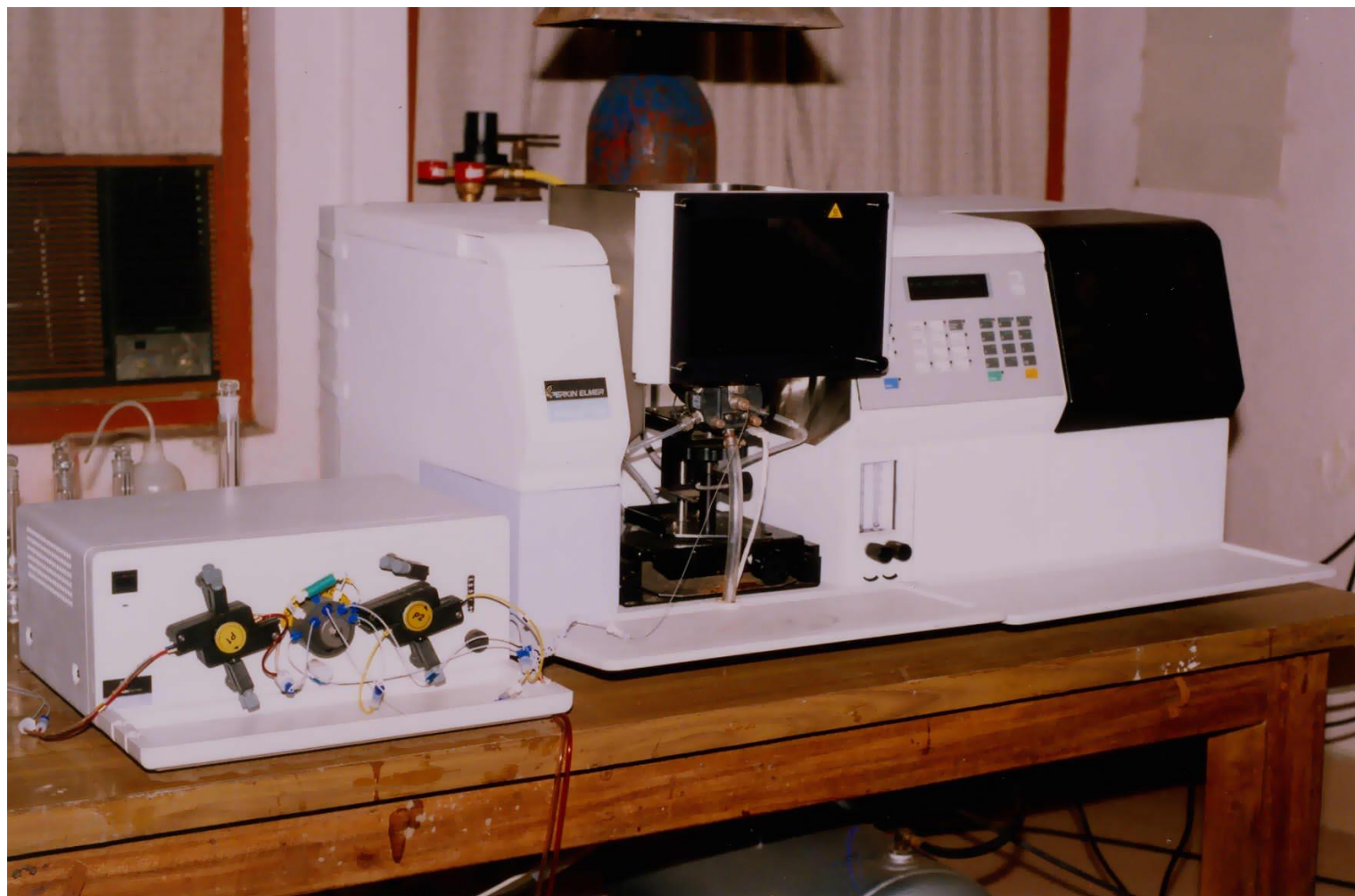


Fig. 6.6 Flow injection – FAAS for online preconcentration and determination

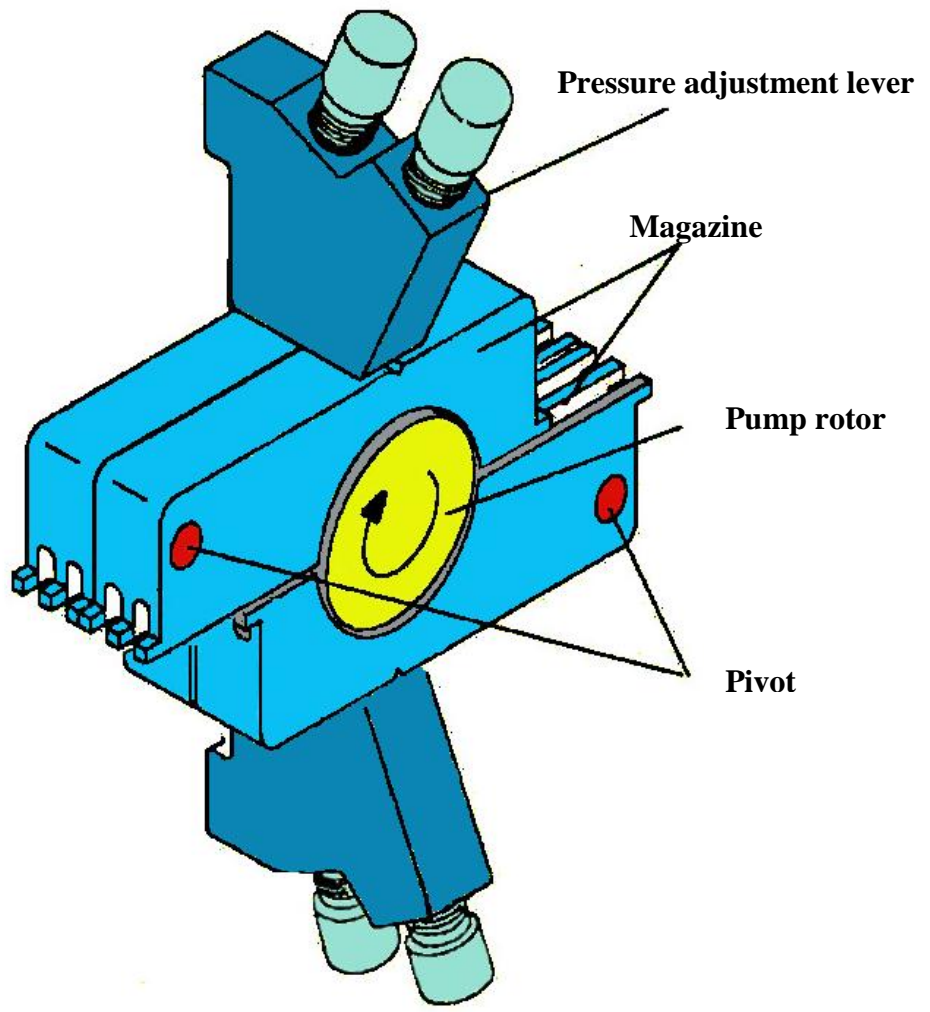


Fig. 6.7 Peristaltic pump

6.9.2 Reagents

All reagents used were of analytical reagent grade. 2,3-Dihydroxy naphthalene (DHN) 0.1% (Aldrich, Milwaukee, WI, USA) was prepared in 0.075 M ammonia solution as it is not soluble in pure water. Acidified methanol (pH ~2 with HNO₃) was used for elution of the Co and Ni adsorbed on the microcolumn. 0.1 M (pH 5) sodium acetate – acetic acid buffer was used for all pH adjustment. Stock standard solution of 1 mg/l of cobalt and nickel were prepared by dissolving appropriate amounts of CoCl₂.6H₂O and NiSO₄.6H₂O (Aldrich, USA) in 250 ml of deionized water. These solutions were standardized by using the EDTA titration procedure. The working solution was prepared by suitable dilution.

6.9.3 Procedure

The FI manifold (0.3 mm i.d. type) (Fig. 6.8) used for online preconcentration and elution consists of two main steps. In the loading step (Fig. 6.8a), the injection valve was in the fill position, while sample or standard solution and ammoniacal 2,3-dihydroxy naphthalene solution were pumped by Pump 1 simultaneously and mixed online before passing through the column. In this position, the stream flows through the column between ports 2 and 4 to preconcentrate the sample. The eluent (methanol) stream flows continuously to the detector. The preconcentration time was usually 60 s for sorption of cobalt and nickel. The programme for the injection valve in load (fill) and elute (Inject) positions are given in Table 6.10. Sample loading and elution sequence are shown in fig.6.8a and 6.8b respectively. The cobalt and nickel complex sorbed on C₁₈ bonded silica gel column was eluted with methanol acidified to pH ~2.0 between the port 2 and 4. The eluted cobalt and nickel 2,3-dihydroxy naphthalene complex was transported to the nebulizer. The peak height of the transient signal was proportional to the cobalt and nickel concentration in the sample, and was used for all measurements. Triplicate measurements were carried out in all instances. Linear calibration graph was obtained for 1-20 µg l⁻¹ of cobalt and nickel using aqueous standard solutions.

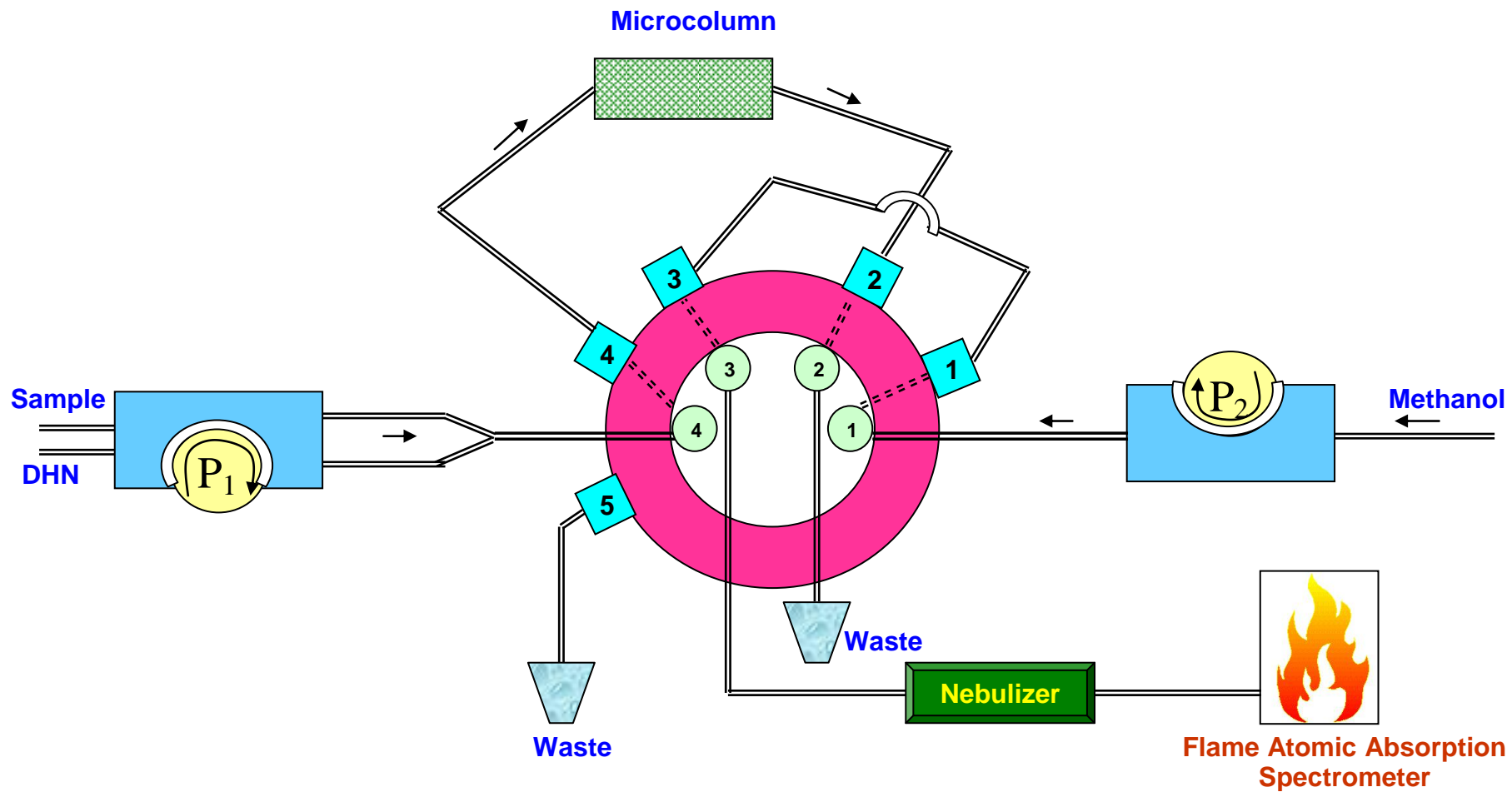


Fig. 6.8a Sample loading sequence in Flow Injection Analysis System

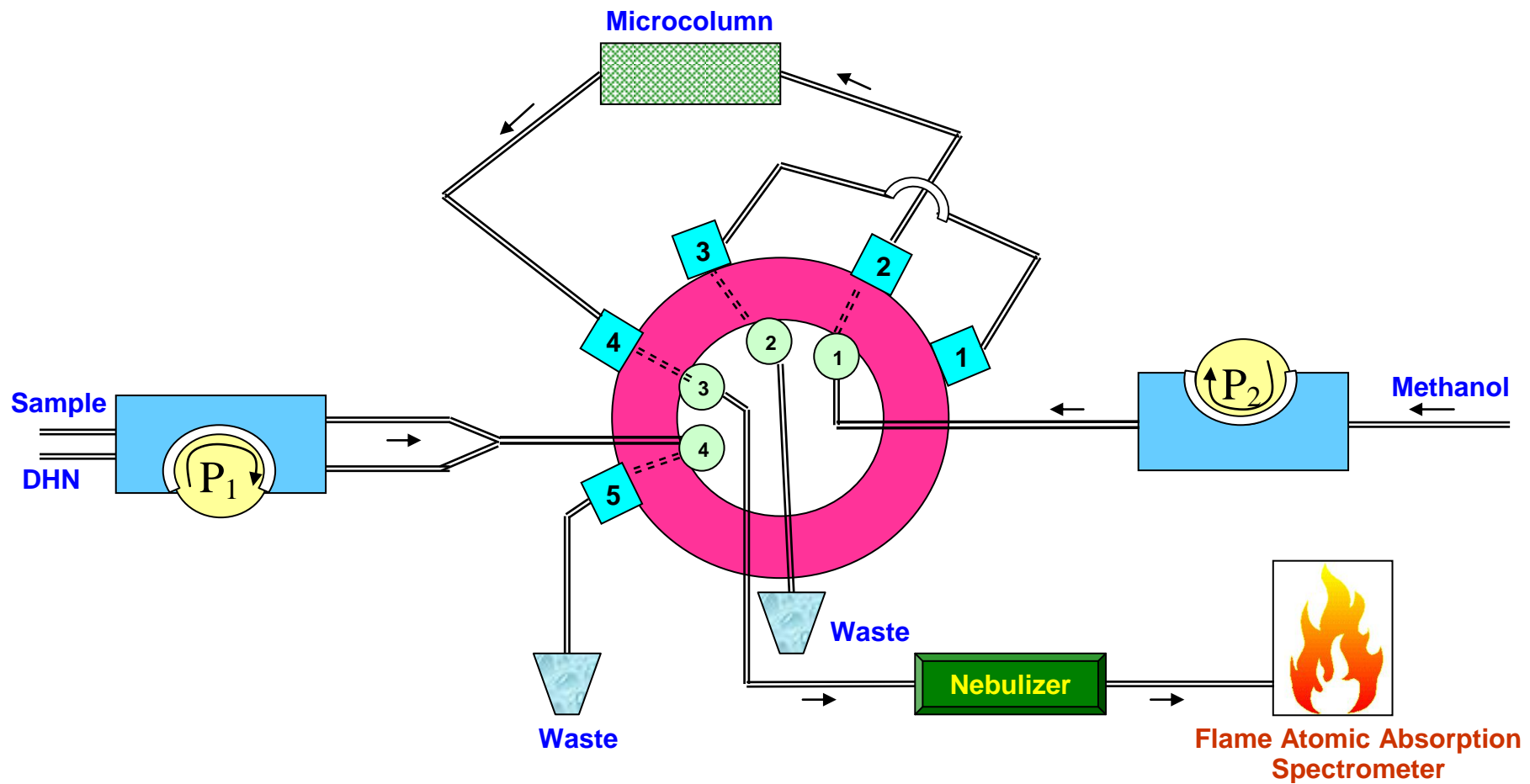


Fig. 6.8b Elution sequence in Flow Injection Analysis System

Table 6.10 Programme for the injection valve in load (fill) and elute (Inject) positions

Step	Time	Pump 1	Pump 2	Valve position
Prefill	20	100	120	Elute
1	40	100	0	Load
2	20	100	120	Load
3	20	0	120	Elute

6.9.4 Analysis of standard reference material (IAEA-soil 7) and soil

A sample of 0.5 g of soil was taken in a platinum crucible; 5 ml of HF and 1 ml of Conc. H₂SO₄ were added and heated to 150°C on a hot plate. The process was repeated thrice. The residue was cooled and fused with 2 g KHSO₄ at 800°C in an electric bunsen for 30 min. The melt was cooled and dissolved in 50 ml deionised water and was made up to 100 ml. Suitable aliquots were taken and subjected to preconcentration and determination by the procedure described above. The cobalt and nickel content of soil samples were established by reference to a calibration graph prepared as per the above procedure.

6.9.5 Analysis of hair samples

The sampling protocol and washing procedures were carried out as described by Airey [56], Ryabukin [57] and Assarian and Oberleen [58]. 1g of hair sample was dissolved in 10 ml of mixture of conc. HNO₃ + 30% H₂O₂ (4:2 v/v) at the temperature of 150°C kept for 30 min [59]. The pH of the solutions was adjusted to ~5.0±3.0 and subjected to FIA-AAS determination as per the procedure described above.

6.10 CONCLUSIONS

The flow injection online preconcentration flame AAS procedure developed above allows the determination of as low as 0.1 µg/l of nickel in soil and nickel and cobalt in hair samples. The developed procedure is precise and

rapid and allows the analysis of 30 samples per hour with a loading time of 60 s. In addition, online FI preconcentration is an ideal tool for the separation of analyte from large amounts of neutral electrolytes present in complex real samples such as soils and hair. Again, FI provides a simple means of total automation, eliminating manual operations resulting in better precision. The online FI manifold used in the present study permits high sampling loading rates and thus resulting in higher preconcentration/enrichment factors. The enrichment factors were 725 and 600 for cobalt and nickel respectively with a 1 min preconcentration time compared to conventional FAAS signal. These enrichment factors are far superior to already developed on-line preconcentration procedures for inorganics. The instrumentation adopted in the present study allows much simpler equipment and low maintenance costs compared to costlier ICP-AES or ICP-MS instruments.

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CHAPTER 7

CONCLUSIONS

The introductory part of the thesis brings out the need for developing newer and newer preconcentrative separation procedures for inorganics based on solid phase extraction for the determination of toxic/nutrient elements. The work described in subsequent chapters has shown the development of solid phase extraction (SPE) procedures for preconcentration/removal of mercury (II), uranium(VI), thorium(IV), cobalt(II) and nickel(II). These procedures have several advantages over the existing ones and utilize simple, reliable, low cost and readily available molecular/atomic spectrometric instruments.

Quinoline-8-thiol modified naphthalene was prepared and used for the preconcentration of mercury(II) from aqueous solutions and biological samples (hair) in a offline (Batch) mode due to the greater flexibility, operational stability and simplicity of the equipments required. This SPE preparation is very simple and the mercury(II) sorbed on naphthalene can be simply dissolved in acetone for subsequent determination by UV-visible spectrophotometry.

Several researchers have tested the effectiveness of mercury(II) removal from industrial wastes using activated carbon in recent years. However, the problem of disposal solid activated carbon and non-quantitative recoveries at trace levels of mercury culminated in searching for chelate modified SPE materials. Therefore, TAN modified activated carbon has been prepared to remove mercury(II) very effectively. TAN shows the selectivity towards the mercury(II) because of the high stability constant of Hg(II) with TAN. Further, TAN is somewhat bigger organic molecule, therefore it is easily adsorbed on activated carbon. Because of the fast kinetics of sorption, high reuse capability, the problem

due to contamination of mercury(II) from brine sludge and effluents can be solved by preparation of TAN modified activated carbon filters which have to be designed and installed in on-line.

On scrutinization of various SPE's that have been used for preconcentration of uranium(VI), it is clearly appears that there is a scope for developing new SPE materials based on sorption of activated carbon with various chelating agents. Diarylazobisphenol, a ligand with azo and phenolic -OH, was synthesized for selective chelation with uranium(VI). The synthesis of diarylazobisphenol, having two binding sites with in the same molecule, is easy to synthesize. This SPE preparation is also very simple because of the bigger size of the ligand and high surface area of the activated carbon. Further, because of the fast kinetics and higher loading capacity, it can be applied to analyse the uranium(VI) in various environmental matrices including nuclear wastes.

Functionalized polymers provides good selectivity and retention capacity for metal ions and greater flexibility in working conditions compared to ligand modified materials which are plagued by ligand leaching problems. Hence, Amberlite XAD-4 functionalized with various β -diketone shows the effectiveness for the preconcentration of thorium(IV). Though the degree of functionalization is lesser with 4-fluoro benzoyl substituent, it makes the more percentage enolisable form of one of the keto group. Therefore, higher acidic conditions or basic conditions are not required for the complexation. At the higher alkaline side, thorium(IV) show hydroxide formation on the other hand, at the highly acidic side, completion form H^+ ions results in non-quantitative recoveries. The studies clearly shows the complexation of thorium(IV) around the neutral pH. Therefore, it is an interesting one to select this preconcentration material for thorium(IV) because other lanthanides do not form a complex at around pH 4. This observations has been employed to pre-concentratively separate trace amounts of thorium(IV) from rare earth chlorides (containing various lanthanides) prior to

determination by spectrophotometry. Amberlite XAD-4 was chosen as polymeric adsorbent as it has excellent physical, chemical and thermal stability. This SPE material can be reused via repeated cycles approximately 40-50 in column mode.

Manually operated separation and preconcentration procedures (batch or column) are usually tedious and involve large sample volumes, time and reagent consumption with a risk of losses and contamination. On the otherhand, on-line flow injection SPE preconcentration approach have several virtues over the above mentioned off-line SPE procedures, viz. i) improved precision as it is computer controlled ii) high sample throughput iii) low sample and reagent consumption iv) higher sensitivity due to SPE preconcentration v) better selectivity as separation from concomitant species occurs during online SPE preconcentration. The flow injection online preconcentration flame AAS procedure developed allows the determination of as low as 0.1 $\mu\text{g/l}$ of nickel in soil and cobalt in human hair samples. The developed procedure is precise and rapid and allows the analysis of 30 samples per hour with a loading time of 60 s. The online FI manifold used in the present study permits high sampling, loading rates and thus resulting in higher preconcentration/enrichment factors of ~ 725 and 600 for cobalt and nickel respectively with a 1 min preconcentration time compared to conventional FAAS signal. These enrichment factors are far superior to hitherto developed on line preconcentration procedures for inorganics. The instrumentation adopted in the present study allows much simpler equipment and low maintenance costs compared to costlier ICP-AES or ICP-MS instruments.

7.1 SUGGESTIONS FOR FUTURE WORK

Future avenues for the present investigation are

- i) Synthesis of new materials for SPE based on organic, inorganic and organic-inorganic hybrid materials.
- ii) Developing chelate functionalized polymers and highly crosslinked polymers with higher degree of functionalization.

- iii) Use of new SPE materials in automated systems resulting in high sample throughput.
- iv) Developing combinatorial methods for the replacement of tedious trial and error procedures in the optimization of parameters
- v) Developing new molecularly/ion imprinted polymers in order to detect and remove a wider range of toxic pollutants in water samples.

LIST OF PUBLICATIONS

1. Quinoline-8-thiol functionalized solid phase extractant for the preconcentration of ultra trace amounts of mercury(II),
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4. Solid phase extractive preconcentration of thorium(IV) using β -diketone anchored Amberlite XAD-4 (to be communicated).
5. Online solid phase extraction preconcentration of ultratrace amounts of cobalt and Nickel in soil and human hair samples for determination by flow injection flame AAS,
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