

**THE SORPTION OF URANIUM FROM  
AQUEOUS SYSTEMS**

By

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A Thesis  
Submitted to the Faculty of Graduate Studies  
in Partial Fulfillment of the Requirements  
for the Degree of

**DOCTOR OF PHILOSOPHY**

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**ABSTRACT**

The determination of uranium, together with other radionuclides, for monitoring purposes, has received enormous attention in recent years. While the average concentration of uranium in seawater is believed to be 3.3 ppb, commonly available instrumental techniques are unable to directly determine uranium (and other trace metals) at concentrations below 5 ppb in seawater. Recently developed instruments such as inductively-coupled plasma-mass spectrometer can detect uranium at this concentration but the instrument is relatively very expensive to be used in most analytical laboratories. Even when metal concentrations are relatively high, the sensitivity and detection limits of the commonly used techniques are seriously affected by the seawater matrix, resulting in inaccurate analysis. Consequently, sample preparation techniques must be employed to preconcentrate and to separate uranium from alkali and alkaline earth metals, so as to enhance the accuracy of uranium determination.

In our work, preconcentration was attempted by using modified polyurethane foams, modified polyacrylonitrile fabric, and some commercially available, but rare, chelating resins. Two new modified polyurethane foams, namely  $\beta$ -diketone foam and phosphonic acid foam, were made by separately incorporating benzoyl acetone and phenyl phosphonic acid into the foam during the foaming process. A modified Orlon fabric was made by using hydroxylamine to convert nitrile groups of the

polyacrylonitrile part of an Orlon™ fabric into amidoxime groups. These three new sorbents were evaluated for their ability to extract uranium from simple aqueous solutions with a wide range of pH and temperature. A continuous flow spectrophotometric method (CFSM), using a diode array spectrophotometer and Arsenazo III as the photometric reagent, was developed for the determination of uranium and was used for the evaluation of these three new sorbents.

The syntheses of  $\beta$ -diketone foam, phosphonic acid foam and the amidoxime modification of Orlon™ fabric were relatively simple and inexpensive to achieve. Both the  $\beta$ -diketone foam and modified Orlon fabric were found to be useful for sorbing uranium from simple aqueous solutions with pH values between 3 and 8, whereas phosphonic acid foams were effective for solutions with pH values between 5 and 8. Generally  $\beta$ -diketone foam performed best at room temperature or higher but this was not the case with the modified Orlon fabric, which performed best at 4°C.

Commercially available, but rare, chelating resins containing amidoxime or phosphonic acid as the functional group (i.e. Chelite N, Duolite ES 346, Duolite ES 467 and Chelite P) along with the commonly used Chelex 100 that had a iminodiacetic acid functional group, were evaluated for their capability to extract uranium from actual seawater using a Seastar™ in-situ sampler. From among these commercially available sorbents only those that contained an amidoxime group, namely Chelite N and Duolite ES 346, proved to be useful in sorbing uranium from seawater.

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## LIST OF ABBREVIATIONS

CFSM	Continuous flow spectrophotometric method
DCP-AES	Direct current plasma atomic emission spectrometer
ICP-AES	Inductively-coupled plasma atomic emission spectrometer
ICP-MS	Inductively-coupled plasma mass spectrometer
P $\beta$ DK	Poly- $\beta$ -diketone
PVA	Polyvinylalcohol



## CHAPTER I

### INTRODUCTION

#### 1 Introduction

Metal ions and their chemical compounds find their way into ocean waters from streams and rivers after weathering of rocks, minerals, ores and soils. Underwater volcanic activity, hydrothermal vents and the seafloor mineral deposits all contribute to the metal ions and their concentrations in these waters. In addition, a significant contribution is possible from all avenues of human endeavour, ranging from large industrial enterprises to home activities. A thorough understanding and characterization of ocean water calls for an accurate determination of trace elements and their species. The chemical speciation of metal ions in seawater is primarily determined by complexes formed by inorganic anions ( $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$  etc.) and organic complexing agents such as carboxylic, humic and fulvic acids. In this connection, trace elements are defined here as those elements that are present in ocean waters at concentrations less than 1 ppm ( $1 \mu\text{g}\cdot\text{mL}^{-1}$ ). They are difficult to determine directly by instrumental methods, mainly because of the high salt content in these waters.

Accurate analysis of ocean waters, especially at trace levels, is one of the most difficult and complicated analytical tasks, because the oceans contain many of the naturally-occurring elements and radioactive isotopes. The current interest of

analytical chemists in the constituents of ocean waters emphasizes determination at ppm levels or below, with special attention to monitoring of radionuclides. Despite their low concentrations, these latter constituents are of interest due to their bioaccumulation properties. The analyst is presented with a difficult task by the increasingly rigorous requirements of versatility, specificity, sensitivity and accuracy in the analyses.

During the past three decades rapid development of electronic instrumentation has created powerful analytical tools for trace element determination. However, these tools can give erroneous results for ocean water samples because of matrix effects, if the limitations of the devices go unheeded. Kantipuly and Westland<sup>1</sup>, in their review, made evident the matrix effects involved and the importance of separation chemistry in instrumental methods such as neutron-activation analysis, plasma-source emission and mass spectrometry, X-ray fluorescence spectrometry, atomic absorption and spectrophotometric methods. The best course to obtain reliable data is to separate the analytes of interest from the matrix constituents and determine them in the isolated state. This results in greater sensitivity, but calls for elegant separation and concentration techniques involving chelating resins and ion-exchange resins.

There have been several reviews<sup>2-8</sup> dealing with the use of chelating polymers in separation and preconcentration methods. A number of review papers<sup>9-15</sup> have been published recently that discuss the use of chelating polymers for the treatment of waste

water and for the removal of toxic trace metals from natural water systems. Other review papers<sup>16-23</sup> deal with the preparation, evaluation and characterization of polymeric chelating agents for the separation of trace metals from various matrices.

### **1.1 General properties of chelating polymers**

The chemistry underlying the use of ion-exchange and chelating polymers for the separation and preconcentration of trace elements is reasonably well understood<sup>24,25</sup> and progress today is mainly in the area of improving the specificity of the resins and the techniques of application.

The analytical application of chelating polymers depends on many factors. Normally a metal ion exists in ocean water as a hydrated ion or as a complex species in association with various anions with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and/or donor atom capable of forming complexes with the metal ions in solution, and it is logical to classify chelating polymers on this basis. Chelating polymers can be classified as shown in Figure 1.1. This method of classification is not meant to imply that these systems are mutually exclusive. Indeed some polymers can belong to more than one class, depending on experimental conditions.

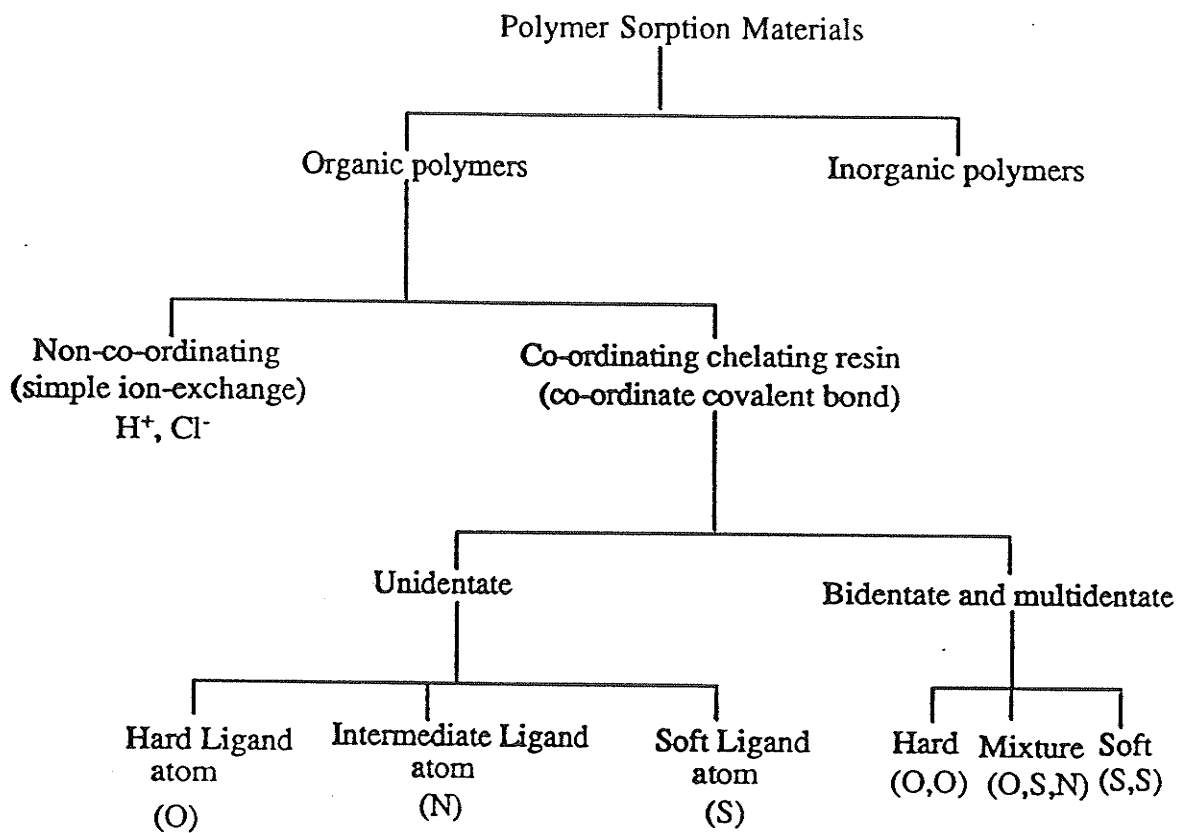


Figure 1.1 Classification of chelating polymers

## 1.2 Functional groups of chelating polymers

The functional group atoms capable of forming chelate rings usually include oxygen, nitrogen and sulphur. Nitrogen can be present as an amine, nitro, nitroso, azo, diazo, nitrile, amide or other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether, phosphoryl or other groups. Sulphur can be present in the form of thiol, thioether, thiocarbamate, disulphide groups, etc.. These functional groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbents from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix enables metal ions or metal species, under certain favourable conditions, to form chelate rings.

The selective concentration and separation of elements from natural water systems depend both on elemental speciation and the chelating properties of the polymer. The applications of chelating groups for the selective preconcentration of inorganic elements were reviewed by Myasoedova and Savvin<sup>2</sup>, but these authors did not include an important class of commercially available chelating resins, namely the Chelite, Duolite and Amborane series of resins. However, Schwochau<sup>3</sup> has documented the application of some of these resins for the extraction of metals from seawater and these form the basis of Table 1.1. An entire section of this review<sup>3</sup> was devoted to the extraction of uranium from seawater, and the data are included in Table 1.2.

Table 1.1 Sorbents used for the separation of metal ions from natural water systems<sup>3</sup>

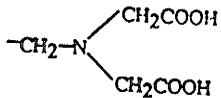
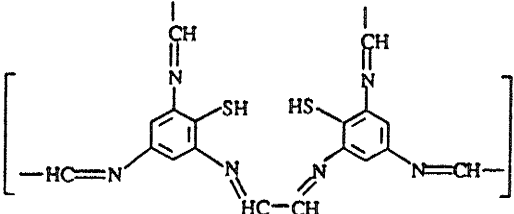
Systems	Metal ions	Remarks	References
Chelex 100, Dowex A1 	Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Mo, Ag, Cd, In, lanthanides, W, Re, Pb, Bi, Th, U, Al, Sn, Ti	Cation elution with dilute mineral acids, anion elution with 4M ammonia solution	26-45
Retardant 11-A8 -CH <sub>2</sub> COOH -CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> Cl <sup>-</sup>	Li	Concentration factor of 30 in the ethyl alcohol eluent	46
Amberlite CG400 -CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> SCN <sup>-</sup>	Ti, Co	Sorption after complexation with SCN <sup>-</sup> Elution with 2M mineral acids	47,48
Poly(tetraethylenepentamine)-polyurea resin	Ni, Cu, Zn	Nearly quantitative recovery at natural pH of seawater	49
Poly(glyoxaltriaminophenol)	Cu, U	Separation at natural pH of seawater; elution with dilute mineral acids	50,51
Poly(glyoxaltriaminothiophenol) 	Au	Separation at natural pH of seawater; elution with dilute mineral acids.	51

Table 1.1 Continued

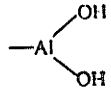
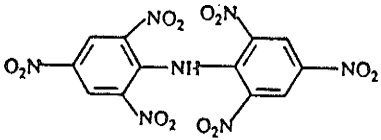
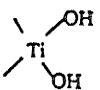
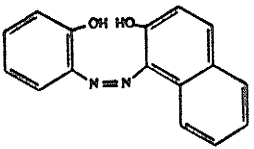
Systems	Metal Ions	Remarks	References
Hydrous aluminium oxide 	Li	Elution with boiling water; maximal concentration factor 46 in the eluate	52,53
Dipicrylamine 	K	Precipitation of the potassium salt elution of K <sup>+</sup> with mineral acids	54-56
Zirconium phosphate	K	Potassium capacity 25 mg.g <sup>-1</sup>	57
Hydrous titanium oxide 	Na, Mg, Al, Ca, V, Cr, Mn, Fe, Ni, Cu, Sr, Ba, U	Sorption at natural pH of seawater; elution with dilute mineral acids; selective elution of U with 2M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	58,59
Hyphan on cellulose or polystyrene 	Fe, Ni, Cu, Zn, Pb, U	Almost complete separation; elution with 1M HCl	60-62
Thiazoline on polystyrene	Hg	Extraction at pH 1; complete elution with 0.1 M HCl containing 5% thiourea	63

Table 1.1 Continued

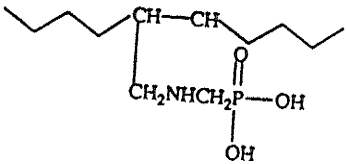
Systems	Metal ions	Remarks	References
8-Hydroxyquinoline on C <sub>18</sub> -bonded silica gel	Mn, Fe, Co, Ni, Cu, Zn, Cd	Concentration factors 50-100 in methanol eluate	64
1-Nitroso-2-naphthol-3,6-disulphonate	Co	Elution with titanium(III) chloride	65
4-(2-Thiazolylazo)resorcinol	Co	Elution with methanol-chloroform (1:1) mixture	66
Duolite CS-100 (carboxylic acid and phenolic hydroxyl groups)	<sup>137</sup> Cs, <sup>90</sup> Sr	Alkaline low-level radioactive wastes	67
Polyallylamine phosphonic acid 	U	-----	68
Sumichelate Q-10 (vinyl polymer with dithiocarbamate)	Hg	-----	69
ALM-125 (dithiocarbamate)	Hg	-----	70
MnO <sub>2</sub> -impregnated fibre filter	<sup>238</sup> Pu/ <sup>239</sup> , <sup>240</sup> Pu	Seawater	71
2,5-Dimercapto-1,3,4-thiadiazole loaded on silica gel (DMT-SG)	Bi	Preconcentration of trace amounts of Bi(III) from water samples; eluted with 0.05M EDTA	72



Table 1.1 Continued

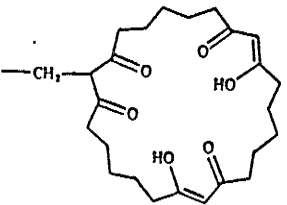
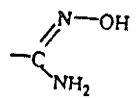
Systems	Metal ions	Remarks	References
Mercapto-modified silica	Zn <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup>	Elution with 3M nitric acid	73
Polystyrene-bound hexaketone	U	Seawater	74
			
Polystyrene-bound tetraketones	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup>	-----	75
Polystyrene-bound 1,3-diketone	UO <sub>2</sub> <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Fe <sup>3+</sup>	-----	76
Ethylenediaminetriacetic acid on porous glass	Cu, Zn, Pb	Seawater buffered at pH 5.6; elution with 1M HCl	77
<i>p</i> -Dimethylaminobenzylidenerhodamine on silica gel	Pd, Ag, Au	Quantitative retention from acidified seawater; elution with 0.1 M HCl containing thiourea	78
Chitin	Co, Sb, Au, Hg	Sorption at pH 7	79
Chitosan	Co, Zn, Cu, Mo, Pd, Sb, Cs, Ir, Au, Hg, U	Sorption at pH 7	79
Amidoxime		Sorption at natural pH of seawater; elution with dilute mineral acids	59,80-138

Table 1.1 Continued

Systems	Metal ions	Remarks	References
Dithiocarbamate cellulose derivative	Cu, Cd, Hg, Pb, U	Sea and tap water	139
Poly(maleic anhydride)	Pb	Tap Water	140
<i>Flotation Systems:</i> Iron(III) hydroxide + sodium dodecylsulphate	V, Mo, U	More than 80% recovery at the appropriate pH	141-143
Iron(III) hydroxide + dodecylamine Lead sulphide + stearylamine	Cu, Zn Ag	More than 90% recovery at pH 7.6 Almost quantitative separation at pH 2	143, 144 145
2-Mercaptobenzothiazole co-precipitate without surfactant	Ag	More than 95% recovery at pH 1	146
Cadmium sulphide + octadecyltrimethylammonium chloride	Hg	Quantitative separation at pH 1	147
<i>Complexing agents/organic solvents:</i> Ammonium pyrrolidine dithiocarbamate/methyl isobutyl ketone, chloroform or Freon TF	V, Cr, Mn, Fe, Co, Ni Cu, Zn, Cd, Pb	Extraction at pH 3-5	148-152
4-Benzoyl-3-methyl-1-phenol-5-pyrazolone/isoamyl alcohol or methyl isobutyl ketone	Cu, Mo	Extraction of Cu at pH 7, Mo extraction at pH 1.3	153, 154

Table 1.2 Uranium loading of selected sorbents<sup>3</sup>

Sorbent	Functional Group	Uranium loading	References
<i>Inorganic:</i> Hydrous aluminium oxide	$\begin{array}{l} \text{OH} \\ \diagup \\ \text{—Al} \\ \diagdown \\ \text{OH} \end{array}$	61 $\mu\text{g}\cdot\text{g}^{-1}$ Al	155
Hydrous iron(III) oxide	$\begin{array}{l} \text{OH} \\ \diagup \\ \text{—Fe} \\ \diagdown \\ \text{OH} \end{array}$	60 $\mu\text{g}\cdot\text{g}^{-1}$ Fe	155
Silica gel	$\begin{array}{l} \text{OH} \\ \diagup \\ \text{—Si} \\ \diagdown \\ \text{OH} \end{array}$	27 $\mu\text{g}\cdot\text{g}^{-1}$ sorbent	156
Hydrous lanthanum oxide	$\begin{array}{l} \text{OH} \\ \diagup \\ \text{—La} \\ \diagdown \\ \text{OH} \end{array}$	38 $\mu\text{g}\cdot\text{g}^{-1}$ La	155
Hydrous titanium oxide	$\begin{array}{l} \text{OH} \\ \diagup \\ \text{—Ti} \\ \diagdown \\ \text{OH} \end{array}$	550 $\mu\text{g}\cdot\text{g}^{-1}$ Ti 200 $\mu\text{g}\cdot\text{g}^{-1}$ sorbent	58,157
Hydrous titanium oxide (freshly precipitated)	-----	1550 $\mu\text{g}\cdot\text{g}^{-1}$ Ti	158
Basic zinc carbonate	-----	540 $\mu\text{g}\cdot\text{g}^{-1}$ Zn	156
Hydrous tin oxide	$\begin{array}{l} \text{OH} \\ \diagup \\ \text{—Sn} \\ \diagdown \\ \text{OH} \end{array}$	17 $\mu\text{g}\cdot\text{g}^{-1}$ Sn	156

Table 1.2 Continued

Sorbent	Functional Group	Uranium loading	References
Hydrous zirconium oxide	$\begin{array}{c} \text{OH} \\ \diagup \\ -\text{Zr} \\ \diagdown \\ \text{OH} \end{array}$	13 $\mu\text{g.g}^{-1}$ Zr	155
<i>Organic:</i> Polystyrene-methylene phosphonic acid	$-\text{CH}_2\text{PO}(\text{OH})_2$	24 $\mu\text{g.g}^{-1}$ sorbent	155
Resorcinolarsonic acid/ formaldehyde copolymer	$-\text{AsO}(\text{OH})_2$	1112 $\mu\text{g.g}^{-1}$ sorbent	155
Duolite ES 467	$-\text{CH}_2-\text{NH}-\text{CH}_2-\text{PO}_3\text{Na}_2$	45 $\mu\text{g.g}^{-1}$ sorbent	158
Duolite ES 346			
Poly(acrylamidoxime)	$\begin{array}{c} \text{OH} \\ \diagup \\ -\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	3600 $\mu\text{g.g}^{-1}$ sorbent	59,81
Oxamidoxime-terephthalic acid chloride condensation polymer (fibres)	$\begin{array}{c} \text{HO} \quad \quad \quad \text{OH} \\ \diagdown \quad \quad \quad \diagup \\ \text{N} \quad \quad \quad \text{N} \\ \diagup \quad \quad \quad \diagdown \\ \text{C} \quad \quad \quad \text{C} \\ \diagdown \quad \quad \quad \diagup \\ \text{H}_2\text{N} \quad \quad \quad \text{NH}_2 \end{array}$	240 $\mu\text{g.g}^{-1}$ sorbent	159

Table 1.2 Continued

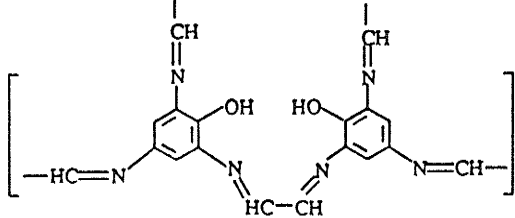
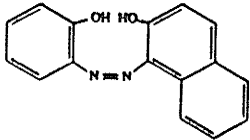
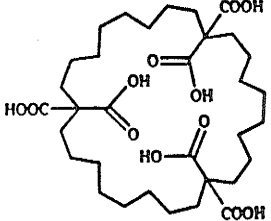
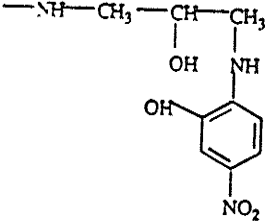
Sorbent	Functional Group	Uranium Loading	References
Poly(glyoxaltriaminophenol)		45 $\mu\text{g}\cdot\text{g}^{-1}$ sorbent	156
Hyphan on cellulose		80 $\mu\text{g}\cdot\text{g}^{-1}$ sorbent	160
Macrocyclic hexacarboxylic acid on polystyrene		70 $\mu\text{g}\cdot\text{g}^{-1}$ sorbent	161
Macrocycloimide resin 508		930 $\mu\text{g}\cdot\text{g}^{-1}$ sorbent	162

Table 1.2 Continued

Sorbent	Functional Group	Uranium Loading	References
<i>Biological:</i>			
Halimeda opuntia (green alga)	----	1.85 $\mu\text{g.g}^{-1}$ sorbent	163
Laurencia papillosa (red alga)	----	0.66 $\mu\text{g.g}^{-1}$ sorbent	163
Dictyota divaricata (brown alga)	----	2.14 $\mu\text{g.g}^{-1}$ sorbent	163
Oscillatoria spec (Blue-green alga)	----	2.00 $\mu\text{g.g}^{-1}$ sorbent	164
Phytoplankton (North Pacific Ocean)	----	0.86 $\mu\text{g.g}^{-1}$ sorbent	165
Zooplankton (North Pacific Ocean)	----	0.31 $\mu\text{g.g}^{-1}$ sorbent	165
Chitosan phosphate	----	2.60 $\mu\text{g.g}^{-1}$ sorbent	166

A recent review from our laboratory<sup>17</sup> dealt with the application of chelating polymeric resins for the separation and concentration of trace metals from oceans, rivers, streams, and other natural water systems. Commercially available resins, specially prepared polymers and a selection of other sorbents were described and their uses outlined. Special emphasis was placed on the preconcentration of uranium from seawater. A similar paper by Egawa<sup>18</sup> deals primarily with the author's work that includes classification, application and the relationship between the structure of the resin and the properties exhibited by the resins.

The recovery of uranium from seawater was viewed as an important future application, and special emphasis<sup>3,17,18,80-138</sup> was placed on the extraction of uranium from seawater due to the increasing attention it has received over the past three decades.

### **1.3 Selection of chelating polymers**

Synthetic chelating polymers have, for the most part, replaced inorganic ion-exchange polymers, with a few exceptions, such as, metal phosphates (zirconium and stannic phosphates) and some oxides ( $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  gel, etc.).

Conventionally, the resin materials can be classified into three main divisions: (a) cation-exchangers, (b) anion-exchangers, and (c) chelating polymeric resins. These can be subdivided into strong, weak, or intermediate types, depending on the functional group.

The choice of an effective chelating resin and its value in analytical method development is dictated by the physicochemical properties of the resin materials. These are the acid-base properties of the metal species and the resin materials, polarizability, selectivity, sorptive capacity, kinetic, physical and chemical stability of the resin.

In view of the complex nature of seawater, the selection of the proper chelating polymeric material for a specific suite of trace metals is of great importance. Akaiwa and Kawamoto<sup>167</sup> have discussed the advantage of having a synergic agent on a chelating resin to improve the sensitivity and separation of trace metals. The distribution coefficient of the analyte of interest should differ from that of the matrix constituents in seawater by several orders of magnitude. One of the rules of selection is based on the concept of hard and soft acids and bases.<sup>168,169</sup> The functional groups in the chelating polymer materials usually act as bases. Oxygen-containing functional groups are hard and sulphur-containing groups soft bases; functional groups with a basic nitrogen atom have an intermediate character.

Two aspects of extraction of uranium from seawater have to be considered: analytical reproducibility and commercial recovery. These are not necessarily incompatible, although they may have different requirements with regard to capacity, cost, re-use, etc. Since uranium acts as a hard acid, chelating polymers which have oxygen-containing functional groups can be used to extract uranium from seawater. It is also



reasonable to use sulphur-containing functional-group materials for soft acids such as the precious metals, Hg, Ag, etc. Although this guide is highly useful in the practical selection and synthesis of chelating polymers, it should be borne in mind that there is a substantial difference in the stability of complexes formed by metal ions with macromolecular and low molecular-weight functional ligands. This is primarily caused by the polymeric structure of the resin material.

The kinetic characteristics of a chelating polymer are of considerable importance and depend on the nature and properties of the polymeric matrix and the degree of cross-linkage. Whereas in the ordinary type of exchanger the exchange processes are more rapid and controlled mainly by diffusion, in a chelating exchanger the exchange processes are slower and controlled either by a particle-diffusion mechanism or by a second-order chemical reaction. For complexation or sorption to occur, it is not sufficient that surface functional groups are present; they must also be accessible for the chelation of the metal ion without steric hindrance. Thus, within chelating resin particles, many surface functional groups may remain inactive in complexation, because equilibrium cannot be attained. On comparing the kinetic properties of different chelating sorbents, it quickly becomes obvious that the sorbents with the best characteristics are those based on hydrophilic macroporous co-polymers or cellulose, or on fibrous materials as the rate of sorption is not only dependent on the surface area but also the availability of the functional groups for metal chelation without steric hindrance. A new type of chelating sorbent has been proposed, which is made of fine

fibrous materials with a porous structure and which holds very fine particles (up to several  $\mu\text{m}$ ) of chelating sorbents.<sup>170,171</sup> These sorbents have high selectivity and excellent kinetic properties, i.e., equilibrium time is only a few minutes.

## 1.4 Novel chelating polymers

### 1.4.1 Iminodiacetic acid polymers

Among the earliest chelating resins to be studied were analogues of EDTA, viz. Dowex A1, Chelex 100 and Chelex 20. The uses of Chelex resins have been well documented<sup>39,40</sup> and these resins continue to be useful in a wide variety of systems. El-Sweify *et al.*<sup>41</sup> described the ion exchange behaviour of  $\text{UO}_2^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Am}^{3+}$  with Chelex 100 from a thiocyanate medium. They reported that Chelex 100 can act as an anion exchanger at  $\text{pH} < 2$  and at  $\text{pH} > 2$  it acts as a cation and chelate exchanger. They also showed that the distribution coefficients were high at  $\text{pH} > 3.5$  from aqueous solutions containing 0.2 or 5.0M  $\text{NH}_4\text{SCN}$ . Mathur and Khopkar<sup>42</sup> used Chelex 100 to develop an ion-exchange chromatographic procedure for the separation of  $\text{Pu}^{4+}$  from  $\text{UO}_2^{2+}$ . They also reported several actinides and lanthanides can be extracted by Chelex 100.

Gladney *et al.*<sup>43</sup> have reported the use of Chelex 100 to isolate uranium from natural waters. Impurities were removed by hexone extraction and by the use of an ion exchange resin, Dowex AG 1X8. This was done to develop a procedure for the

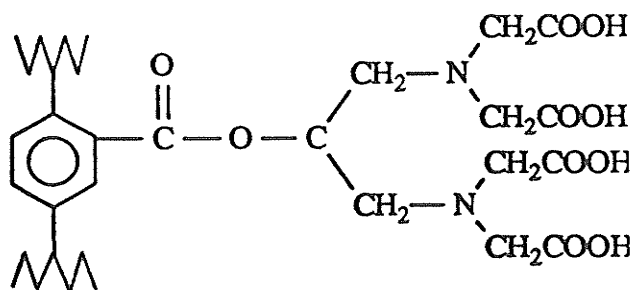
determination of the  $U^{235}/U^{238}$  ratio in water samples containing trace levels of uranium, for monitoring purposes. Chelex 100 was also used for the separation of uranium from fresh water<sup>29</sup> and was done by carefully conditioning the resin with a buffer solution of pH 4.6. The fresh water sample was adjusted to have a pH value between 3.9 and 4.7 prior to passing it through the Chelex 100 column. Hirose<sup>44</sup> reported that a trace amount of uranium in seawater could be preconcentrated on Chelex 100. The resin was then used as a support for thermal neutron irradiation.

Some of the metals extracted from seawater and other systems with Chelex 100 and Dowex A1 are listed in Table 1.1. Van Berkel *et al.*<sup>27</sup> and Paulson<sup>28</sup> studied the effects of flow-rate and pretreatment of the resin on the extraction of trace metals from estuarine coastal seawater and artificial seawater. In an interesting paper, Chiba *et al.*<sup>31</sup> examined the effect of using a magnetic field during the extraction of metal ions by Dowex A1. They reported an increase of 1-6 % in the amount sorbed per unit mass of resin. Sasaoka *et al.*<sup>32</sup> used a chelating filter paper ("Expapier F-2", 2-hydroxypropyliminodiacetic acid loaded on cellulose fibre) to preconcentrate and separate thorium from monazite. They also used this chelating paper<sup>33</sup> to preconcentrate and separate  $Sc^{3+}$  and  $Zr^{4+}$  from  $Fe^{3+}$  and  $Al^{3+}$  using the pH dependence of the extractions. Various matrices or resins<sup>172-174</sup> containing aminoacetic acid or iminodiacetic acid have been synthesized, mainly to improve the physical and chemical stability.

Kaczvinsky *et al.*<sup>175</sup> have described the synthesis of porous phenol-formaldehyde polymers containing iminodiacetic acid. The porosity was introduced by the addition of a finely divided solid material ("a template") that was insoluble under the reaction conditions, and was removed by dissolution after the polymerization was complete. Silica gel, carbonates and various other salts were used as templates. Resins containing different phenols were synthesized and their effectiveness examined for the removal of radioactive cesium and strontium from alkaline concentrated sodium salt solutions, which typify the soluble nuclear waste from the defence industry.

#### 1.4.2 Propylenediaminetetra-acetic Acid Polymers

Moyers and Fritz<sup>176</sup> have synthesized, by an esterification reaction, a new chelating resin containing propylenediaminetetra-acetic acid functional groups attached to a carboxylic acid divinylbenzene resin.



The resin was found to retain multivalent metal cations at  $\text{pH} \geq 3$ . It retained  $\text{Cu}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Zr}^{4+}$  from more acidic solutions. A scheme was given for a clean, rapid chromatographic separation of the last three elements from each other. The resin

was claimed to retain quantitatively a number of trace elements from simulated seawater. A macrocyclic hexacarboxylic acid resin<sup>161</sup> has been used to remove uranium from seawater in a batch process.

#### 1.4.3 Poly- $\beta$ -diketone resins

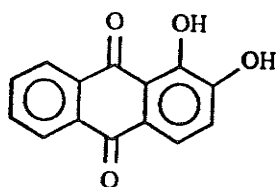
A water-insoluble poly- $\beta$ -diketone chelating resin has been prepared by the controlled oxidation of poly(vinyl alcohol) (PVA) with chromic acid.<sup>177</sup> This polymer forms stable complexes with cations, such as  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Au}^{3+}$  and  $\text{UO}_2^{2+}$ , and removes them completely from dilute aqueous solution. The ions may be recovered quantitatively from the resin complex by elution with dilute aqueous acid and it is claimed that the resin is re-usable.

Tabushi *et al.*<sup>178</sup> described the preparation of a macrocyclic hexaketone (tris- $\beta$ -diketone) and cyclic tetraketone (bis- $\beta$ -diketone) which were effective in extracting  $\text{UO}_2^{2+}$  selectively. The hexaketone was subsequently bonded to a polystyrene resin,<sup>74</sup> to give a product that was highly selective for extracting  $\text{UO}_2^{2+}$  from seawater. Similar cyclic bis- $\beta$ -diketone resins were synthesized<sup>75</sup> and shown to extract  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . Djamali and Lieser<sup>76</sup> have synthesized a resin with a 1,3-diketone as an anchor group by treating aminopolystyrene with diketene; the product was shown to extract  $\text{UO}_2^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$ .

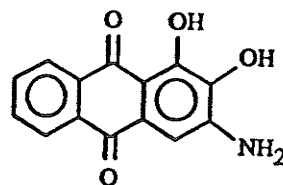
#### 1.4.4 Immobilized polyhydroxyanthraquinones

Nine polyhydroxyanthraquinones and two polyhydroxynaphthoquinones have been screened to determine which have the greatest ability to accumulate uranium.<sup>179</sup>

1,2-Dihydroxyanthraquinone and 3-amino-1,2-dihydroxyanthraquinone had extremely high accumulation abilities and to improve their absorption characteristics they had been immobilized by coupling with diazotized aminopolystyrene.



1,2-Dihydroxy-  
anthraquinone



3-Amino-1,2-dihydroxy-  
anthraquinone

The immobilized 1,2-dihydroxyanthraquinone had the most favourable features, i.e. high selectivity, rapid sorption rate, and applicability in both column and batch methods. The authors found the relative order of magnitude of metal sorption to be  $\text{UO}_2^{2+} > \text{Cu}^{2+} \gg \text{Ni}^{2+} > \text{Cd}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+} > \text{Mn}^{2+}$ . The sorbent takes up far larger amounts of uranyl and copper ions than other metal ions and can recover uranium almost quantitatively from natural seawater. Almost all the uranium extracted could be desorbed in 1M hydrochloric acid. The ability of the resin to extract uranium from seawater was found not to decrease after ten sorption/desorption cycles, showing good chemical stability.

#### 1.4.5 *Tris(dithiocarbamate)*

Tabushi *et al.*<sup>180</sup> synthesized a linear tris(dithiocarbamate) specific for the extraction of uranium from dilute carbonate solutions. Strong ligands specific for a given metal ion have generally been designed by considering (a) the size-fitting factor, (b) the nature of the ligand-metal interaction and (c) the orientation in the binding. These authors have designed and synthesized several uranophiles, **1**, **2**, **3** and **4**, which are specific for the uptake of uranyl ions as shown in Figure 1.2. In particular, O<sup>-</sup> or S<sup>-</sup> groups were introduced into the ligands, since the formation of U-O<sup>-</sup> or U-S<sup>-</sup> bonds is generally favoured.

It is of interest that molecule **4** showed a macrocyclic effect which unexpectedly led to slow rate-determining U-S<sup>-</sup> bond formation. This finding prompted the design of uranophiles capable of rapid U-ligand bond formation together with satisfactorily high stability constants. The same authors also reported the successful "kinetic design" of a new type of uranophile, **3**, having high values of both the formation rates and stability constants. The macrocyclic uranophile **4** showed a much slower exchange rate than the monomeric uranophile Et<sub>2</sub>(NCS)<sub>2</sub><sup>-</sup>. On this basis, it was predicted that fast uranyl binding might be achieved by avoiding such a restricted transition state, while maintaining the high stability constant by using intramolecular terdentate ligands. A linear tris(dithiocarbamate) should satisfy both requirements.

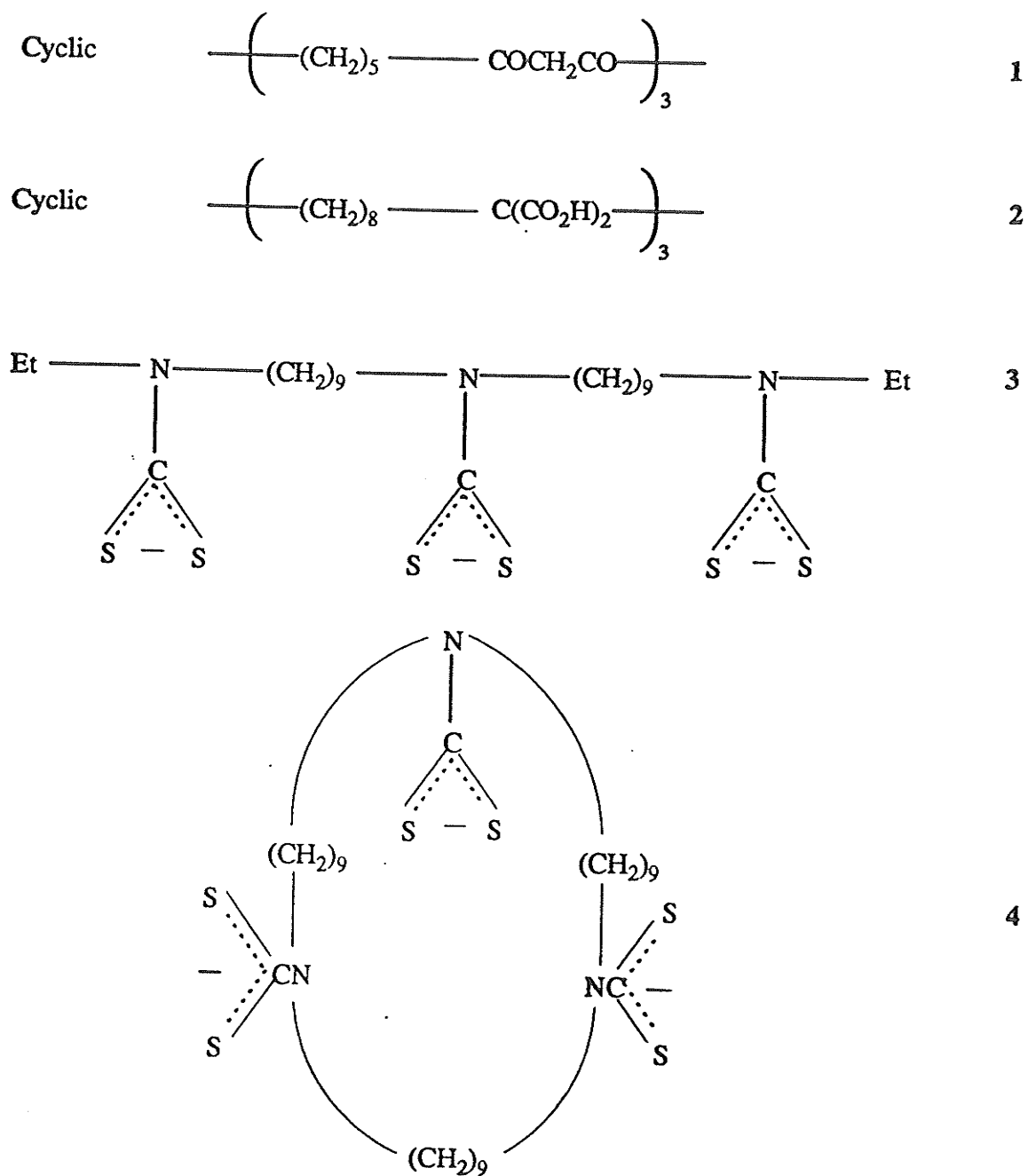


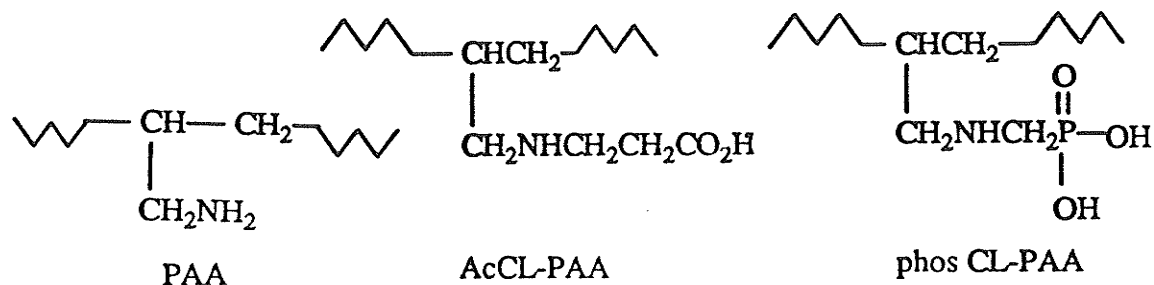
Figure 1.2 Uranophiles synthesized by I. Tabushi *et al.*<sup>180</sup>



Compound 3 binds  $\text{UO}_2^{2+}$  strongly and may be useful for extracting it from seawater in a rapid ocean current.

#### 1.4.6 Poly(allylamine)

The chelating properties of poly(allylamine) (PAA) for  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{UO}_2^{2+}$  have been examined quantitatively. Three resins for the recovery of uranium from seawater were studied; cross-linked PAA (CL-PAA), PAA modified by acrylic acid, and cross-linked (AcCL-PAA), and CL-PAA modified with phosphorous acid and formaldehyde (phos CL-PAA).<sup>68</sup>



The last resin (phos CL-PAA) showed the highest sorption for uranium, viz. 500 mg of resin recovered 12.9 mg of uranium from 5 litres of seawater at 25°C within 24 hours, which corresponds to 78% of the uranium in the original seawater.

Other nitrogen-containing polymers, such as those of pyridine, have been well documented. It has been shown that poly(4-vinylpyridine) can bind  $\text{Co}^{2+}$ ,<sup>181</sup> as well as

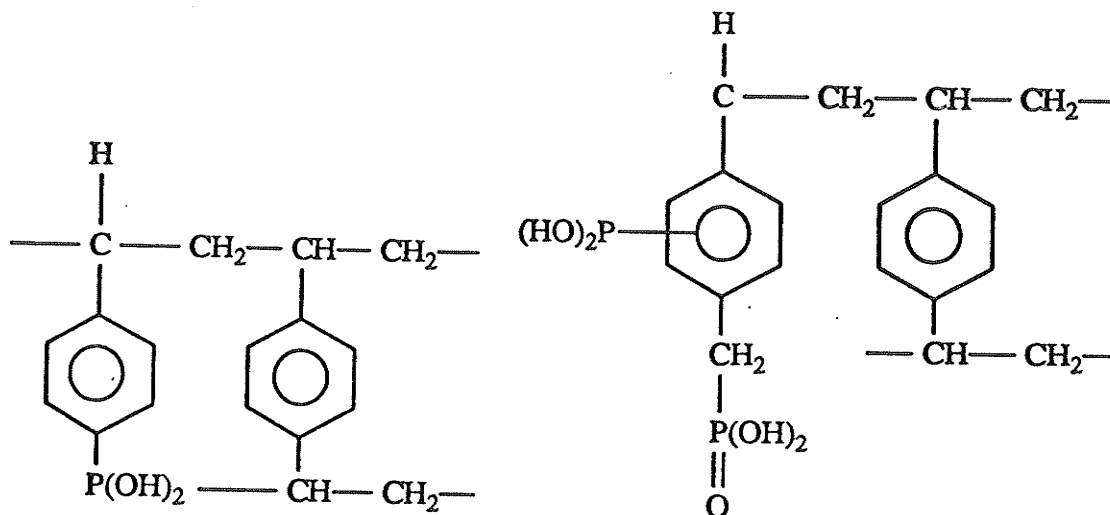
$\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .<sup>182</sup> A summary of their uses in separation and concentration of metal ions has been given by Sugii *et al.*<sup>183</sup> More varied pyridine resins<sup>184</sup> have been used for the extraction of  $\text{Cu}^{2+}$  in the presence of  $\text{Zn}^{2+}$ .

#### 1.4.7 Chelating resins containing phosphorus

Marhol and co-workers<sup>185,186</sup> have described the preparation and extraction properties of several phosphorus-containing ion-exchange resins. Manecke *et al.*<sup>187</sup> synthesized a polymer containing a methylphosphonic acid functional group and studied its ability to bind  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$ . A polystyrene-divinylbenzene tributyl phosphate resin has been used for the extraction chromatography of U, Pu, Np, Nb, Ru, Rh, and Am.<sup>188</sup> Akio and Yoshiaki<sup>189</sup> synthesized a chelate resin containing methylene phosphonate groups and reported that this resin was selective for extracting uranium from seawater.

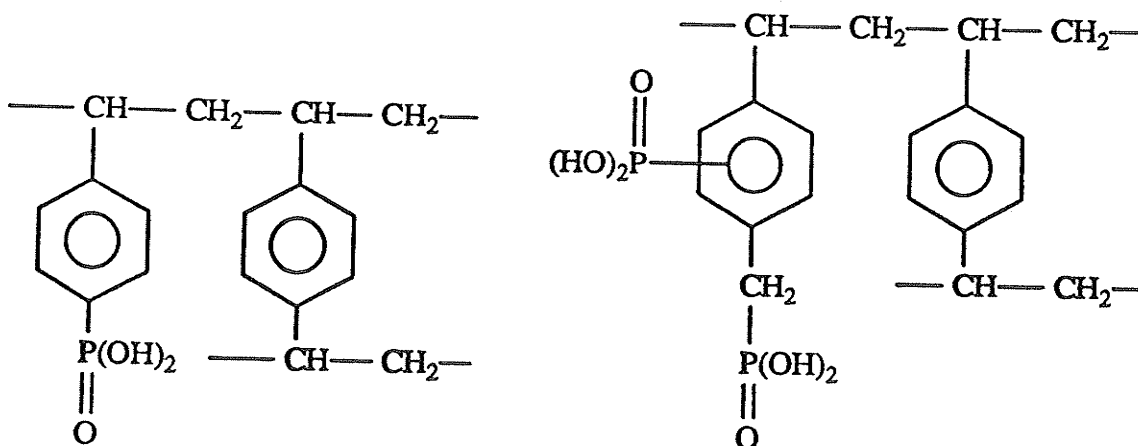
Macroreticular chelating resins (RSP, RSPO, RCSP and RCSPPO) containing dihydroxyphosphino and or phosphono groups were prepared and their sorption capacity for  $\text{UO}_2^{2+}$  and the recovery of uranium from seawater were investigated by Egawa *et al.*<sup>190</sup> The order of recovery of uranium from seawater with these four resins was RCSPPO – RCSP > RSPO > RSP. Uranium was eluted with 0.25-1M sodium carbonate or bicarbonate in batch and column methods. The average recovery of uranium from seawater with the  $\text{Na}^+$ -form and  $\text{H}^+$ -form RCSP in 10 recycles were 84.9% and 90.5% respectively when 20 litres of seawater were passed through the

column (resin 4 cm<sup>3</sup>, 50 x 10 mm) at 60 bed-volumes per hour. RCSP exhibited high sorption capacity, sorption rate of uranium from seawater, chemical and physical stability, and should be an excellent resin for recovery of uranium from seawater.



RSP

RCSP



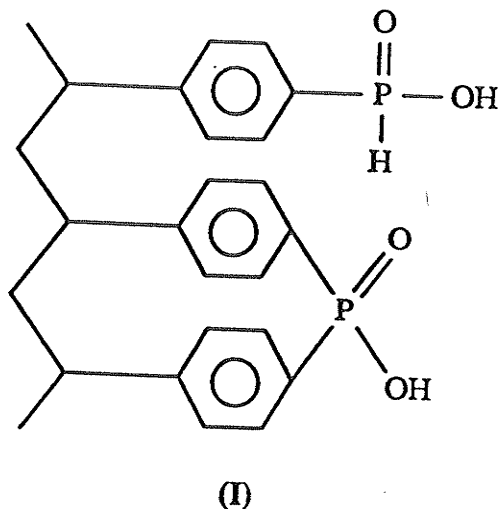
RSPO

RCSPO

The H<sup>+</sup>-form of RCSP gave a higher recovery of uranium from seawater. The Na<sup>+</sup>-form was more favourable for the recovery of uranium because, after elution, the resin could be reused immediately. Furthermore, the sorption capacity for UO<sub>2</sub><sup>2+</sup> was claimed not to decrease even after treatment of the resin with 1M sodium hydroxide or hydrochloric acid at 60°C for 24 hours, showing that the resin had high resistance to acid and alkali.

Alexandratos *et al.*<sup>191</sup> have synthesized bifunctional resins that complex metal ions by both ion-exchange and coordination. These resins are a class of polymer-supported bifunctional complexing agents for specific metal-ion extraction by a dual mechanism. They synthesized bifunctional ion-exchange coordination resins containing phosphonic acid ligands for ion-exchange, and phosphonate ester or amine ligands for coordination to the metal ion. Initial extraction studies with these resins were focussed on complexation of americium from 4M nitric acid and from varying amounts of sodium nitrate at different pH values.

The phosphinic acid resins (**I**) have been studied<sup>192</sup> for the extraction of europium, thorium, uranium, americium and plutonium from acidic nitrate media as a function of acid concentration and ionic strength.

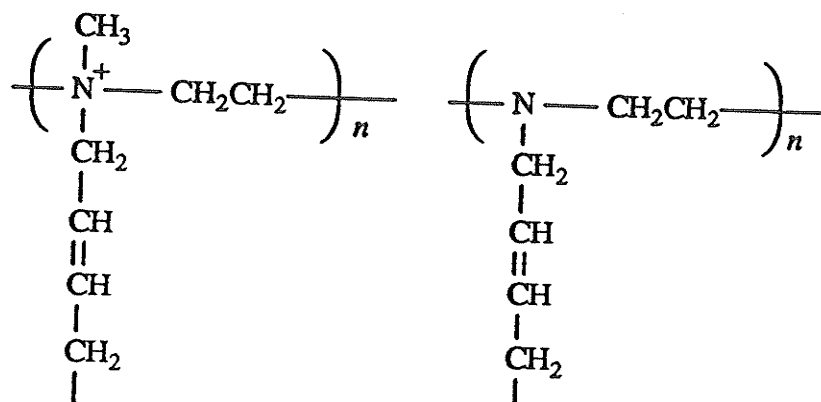


The phosphinic acid resins show better extraction than the sulphonic acid resins for these ions, especially from more acid solution (4M nitric acid) owing to the superior coordination ability of the phosphoryl oxygen atom. The resins also exhibit a higher selectivity relative to sodium, for the ions tested. Under conditions where sulphonic acid resins absorb 85% of the plutonium in solution, the phosphonic acid resins absorb 99.7% of the plutonium in solution.

#### 1.4.8 Polyethyleneimine

Rivas *et al.*<sup>193</sup> synthesized resins by cross-linking polyethyleneimine with 1,4-dibromo-2-butene and subsequent alkylation with dimethyl sulphate to produce resins with good retention properties for  $\text{Cu}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . The resin 1M-1 did not retain copper appreciably at  $\text{pH} < 1$ . However at  $\text{pH}$  values between 2 and 4 it retained 94% of the copper added. The resin 1M-1M did not extract copper

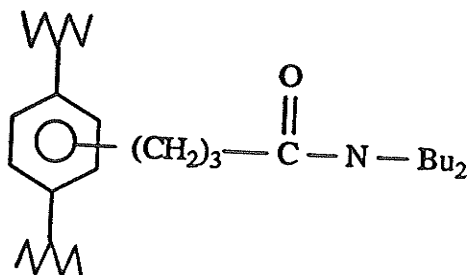
between pH values of 0 and 4 but selectively retained 44.8 – 99.9% of the uranium present. Also, this resin had a greater maximum capacity for uranium (3.2 meq.g<sup>-1</sup>) than 1M-1 (2.8 meq.g<sup>-1</sup>).

1M - 1M1M - 1

According to these results the resins retain copper and uranium by different mechanisms. Usually copper is retained by ion-exchange and possibly by chelate ring formation; uranium was apparently held by adduct formation with the protonated tertiary amine group. Rivas and co-workers have also synthesized several other resin materials,<sup>194-196</sup> by cross-linkage of polyethyleneimine with 1,4-dibromo-2-butene, 1,9-dibromononane and 1,10-dibromodecane, and subsequent alkylation with dimethylsulphate. The influence of pH on the retention, maximum load capacity and elution was studied for Cu<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup>.

#### 1.4.9 Amide resins

Synthetic routes for the incorporation of a tertiary aliphatic amide group in a macroporous polystyrene-divinylbenzene resin have been discussed.<sup>197</sup>

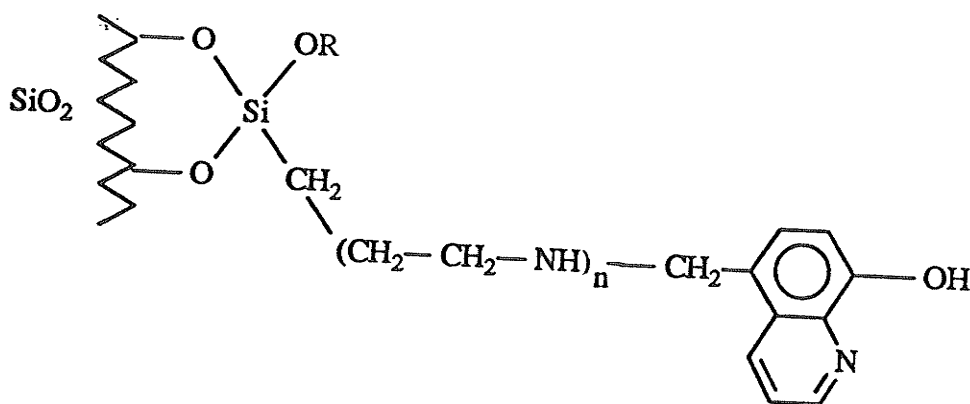


The amide resin retains  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Zr}^{4+}$  selectively from aqueous solution at  $\text{pH} = 3.0$ . A liquid chromatographic separation scheme using the resin was developed. Quantitative results were obtained for uranium in synthetic and actual samples, and for thorium in synthetic samples.

#### 1.4.10 Immobilized 8-hydroxyquinoline

Simple methods for the immobilization of 8-hydroxyquinoline on silica have been described.<sup>198,199</sup> The suitability of the immobilized quinolinol for trace enrichment has been tested for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  in the pH range from 4 to 6. The metal uptake capacities were found to range from 0.2 to  $0.7 \text{ meq.g}^{-1}$  and the distribution ratios from  $1 \times 10^3$  to  $9 \times 10^4$ . Immobilized 8-hydroxyquinoline on silica was also used for preconcentration of trace metals<sup>200-202</sup>

from seawater samples, with the final analytical determination performed by inductively-coupled argon plasma-mass spectrometry (ICP-MS).



The synthesis and characteristics of nine chelating groups immobilized on silica have been described and their use in metal-ion separation by liquid chromatography was evaluated.<sup>203</sup> The use of macroporous resins (XAD-4 and XAD-7) impregnated with 7-dodeceny-8-quinolinol for the preconcentration of trace metals from seawater has also been evaluated.<sup>204</sup> The bonding of 8-hydroxyquinoline to glycidyl methacrylate gel,<sup>205</sup> epoxide "separon"<sup>206</sup> and styrene-ethylene dimethacrylate co-polymer<sup>207</sup> has been studied for the uptake of Cu<sup>2+</sup>. The preconcentration and complexation properties of poly-(7-acetyl-8-hydroxyquinoline-5-aldehyde) chelating polymer have been described.<sup>208</sup> The rate of attainment of equilibrium was established for UO<sub>2</sub><sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Mn<sup>2+</sup>.



#### 1.4.11 Polyurethane foams

Korkish *et al.*<sup>209</sup> reported the use of polyurethane foam (polyether type) loaded with organic extractants, such as ethyl acetate, for the recovery of uranium from nitrate solutions. Polyurethane foams impregnated with trioctylphosphine oxide<sup>210</sup> (TOPO), were capable of quantitatively separating uranium from many other elements in 1M HCl containing ascorbic acid. Pearson and Bowen<sup>211</sup> found the separation of uranium from aqueous solution could be facilitated with the use of a polyurethane foam impregnated with TOPO. Uranium and TOPO could be desorbed independently.

Akiba and Hashimoto<sup>212</sup> investigated the sorption of uranium by using open cell polyurethane foam impregnated with 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63). At pH = 4.5, more than 99.5% of uranium was sorbed onto the LIX 63-impregnated foam and uranium was desorbed with dilute acid. Trace uranium has been extracted from aqueous solutions using polyurethane foams loaded with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one.<sup>213</sup> Anions such as  $\text{PO}_4^{3-}$  interfere slightly but  $\text{CrO}_4^{2-}$  and  $\text{F}^-$  interfere severely.

Gesser and Ahmed<sup>214</sup> reported the use of open cell polyurethane foam coated with long chain tertiary amines (Adogen) for the extraction of uranium from solution with pH values between 1 and 3;  $\text{Co}^{2+}$  had a significant adverse effect on the uranium extraction. When polyurethane foams were loaded with di-(2-ethylhexyl)phosphoric acid<sup>215</sup> in nitrobenzene, these foams were capable of extracting uranium from sulphuric

acid solutions, except at low acidities. When polyurethane foams were loaded with di-(2-ethylhexyl) phosphoric acid and tributylphosphate in o-dichloro-benzene,<sup>216,217</sup> these foams were capable of extracting uranium from nitric acid solutions. Huang *et al.*<sup>218</sup> used polyurethane foams for the extraction of uranium from aqueous solutions containing nitrate salts and reported that these foams did not extract uranium when the nitrate salts were absent.

### 1.5 Commercially available polymers

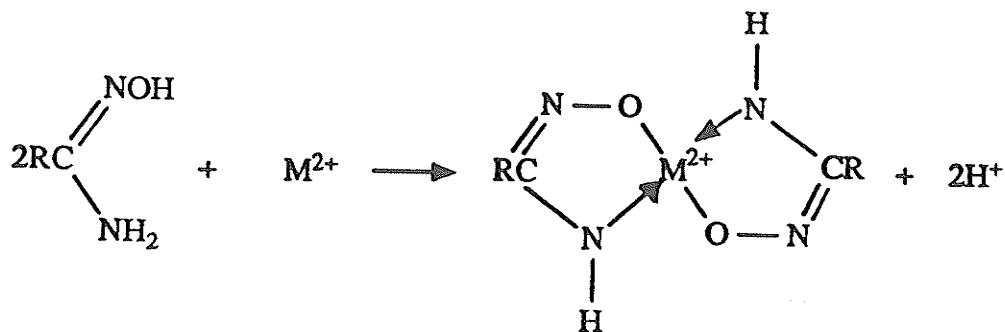
A few selected commercially available chelating resins that are suitable for extracting uranium and other trace metals from seawater are listed in Table 1.3. The donor atoms listed are those which may be covalently bound to the metal ions or metal species in solution. Duolite resins can be used in solving problems of water and process-liquid treatment, and for many applications in the pharmaceutical, food, nuclear and hydrometallurgical industries and environmental protection. The principal application of these chelating resins is in removing calcium and magnesium from the brine feed for chloralkali cells. Duolite ES 467 is capable of reducing the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to a few  $\mu\text{g.L}^{-1}$ , as required for the membrane cells.<sup>219</sup> The Chelite series of resins have complex-forming chemical configurations fixed to a porous matrix.<sup>220</sup> They can specifically retain and remove various multivalent cations from solutions. Furthermore, they have ion-exchange properties; hence it is necessary to equilibrate the resins with the matrix solution before use to avoid changes in the overall ionic composition of the liquid phase.

Table 1.3 Commercially available chelating resins that are suitable for extracting uranium and other trace metals from seawater

Trade name	Functional group	Nature of functional group	Donor atoms	Company
Chelex 100 Duolite ES466	$\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ $\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$	Iminodiacetate Iminodiacetate	N, O, O N, O, O	Bio-rad Duolite
Not named Duolite ES467 Chelite P Duolite ES465 Chelite S	$\text{CH}_2\text{NCH}_2\text{PO}(\text{OH})_2$ $\text{CH}_2\text{NCH}_2\text{PO}(\text{OH})_2$ -SH -SH	8-Hydroxyquinoline Aminophosphonic acid Aminophosphonic acid Mercapto Mercapto	N, O N, O, O N, O, O S S	Seakem Duolite Duolite Duolite Duolite
Duolite ES346	$\text{H}_2\text{N}-\text{C}=\text{N}-\text{OH}$	Polyacrylate with amidoxime	O, N	Duolite
Chelite N	$\text{H}_2\text{N}-\text{C}=\text{N}-\text{OH}$	Macroporous polymer with amidoxime	O, N	Duolite
MISSO ALM KRUPTOFIX 22IB CR20	$\text{NCS}_2\text{H}$ Cryptand $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N})_n-\text{H}$	Dithiocarbamic acid Cryptand Polyamine	N, S, S N, O N	Nippon Soda Parish Mitsubishi
Amborane 345	$\text{P}-\text{BH}_3$	Amine-borane	--	Rohm & Haas

### 1.5.1 Duolite ES 346 and Chelite N

These resin materials are cross-linked co-polymers containing amidoxime groups,  $-\text{C}(\text{NH}_2)=\text{NOH}$ . They contain a small proportion of hydroxamic acid groups which function in the higher pH ranges. Because of their three-dimensional cross-linked structure, these resins are insoluble in common organic and aqueous solvents. They offer a number of possibilities for the separation and isolation of trace metals from various matrices, including seawater.<sup>80,82</sup> The amidoxime group forms strong complexes<sup>221</sup> with a wide variety of metal ions (i.e.  $\text{Cu}^{2+}$ ,  $\text{Au}^{3+}$ ,  $\text{Ru}^{3+}$ ,  $\text{V}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{VO}^{2+}$ ,  $\text{VO}_2^+$ ,  $\text{UO}_2^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mo}^{6+}$ ,  $\text{Th}^{4+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Pb}^{2+}$ ) but does not chelate with alkali and alkaline-earth metal ions. These resins can be employed for the removal of unwanted ions, such as copper and iron from water or other polar solvents, and for the recovery of trace amounts of valuable materials (such as noble metals) from metal-finishing wastes. Also, a resin containing an amidoxime functional group has been employed to recover gallium from Bayer liquor,<sup>222</sup> and a similar resin was used to preconcentrate vanadium.<sup>223</sup> A possible chelation mechanism for the complexation is:



Since the resin contains a weak-base functional group, the chelation and ion-exchange capacity depends on the pH. Regeneration with mineral acid converts the weak-base functional group into its protonated form. If it is not neutralized, this conjugate acid will dissociate in the succeeding loading cycle and may depress the pH below the point of optimum chelation. In such cases, the resin should be buffered to a suitable pH following acid regeneration.

Owing to the immense worldwide interest during the last three decades in the extraction of uranium from seawater, there have been many papers dealing with this problem. Amidoxime-containing sorbents are usable for this purpose and this has prompted a number of papers mainly dedicated to the synthesis<sup>80-138</sup> of these materials.

Egawa *et al.*<sup>83,84</sup> prepared a macroreticular chelating resin containing amidoxime by reacting acrylonitrile-divinylbenzene co-polymer beads with hydroxylamine. They reported an average recovery of 82.9% in the extraction of uranium from seawater. A number of polyacrylamidoxime resins made from various co-polymers of acrylonitrile and cross-linking agents<sup>85</sup> have been synthesized and tested for the extraction of uranium.

Recently, Egawa *et al.*<sup>86</sup> have synthesized macroreticular chelating resins containing amidoxime groups with various degrees of cross-linking, which was obtained by using various amounts of ethyleneglycol dimethacrylate, dimethyleneglycol dimethacrylate,

triethyleneglycol dimethacrylate, tetraethyleneglycol dimethacrylate and enneaethyleneglycol dimethacrylate as cross-linking reagents. The effect of cross-linking reagents on the pore structure, ion-exchange capacity, swelling ratio, and sorption ability for uranium in seawater was investigated. Simultaneous use of divinyl benzene and ethylene glycol dimethacrylate or tetraethylene glycol dimethacrylate produced a resin with improved chemical and physical stability.

To improve the flow-rate through the column and the mechanical stability of the resin, various fibres carrying amidoxime groups were synthesized. Commercial acrylonitrile fibres were treated with hydroxylamine in methanol to give the required acrylonitrile amidoxime fibres.<sup>85,130</sup> Fibres were also made by radiation-induced graft polymerization of acrylonitrile onto polymeric fibres, followed by amidoximation.<sup>88,89</sup>

## 1.6 Summary

Chelating polymer resin materials are mainly used in analytical, industrial and radiochemical laboratories, but only to a limited extent in solving environmental problems. Metal pollution of the environment poses unique problems. Predominantly, metal pollution originates from trace contamination in waters and soil systems. The behaviour of trace metals in the environment is primarily determined by the particular species of the metals rather than by their bulk concentrations. Since metals are not subject to biodegradation, for practical purposes, they have infinite lifetimes.

The most promising way to decontaminate aqueous systems such as waste water treatment sludges, and to recover the trace metals from them, is by employing specific chelating resin materials. Even though almost all common chelating polymers are non-selective, research efforts are being directed to synthesize selective chelating polymers, with good physical and chemical stability, for metal extraction. It can be seen that methods to synthesize chelating resins with functional groups that are selective for the extraction of uranium can be very complex.

The objective of this study is to develop and evaluate sorbents for the sorption of uranium from aqueous systems. Chapter II describes the different analytical plasma techniques used for this study along with the development of a continuous flow spectrophotometric method for the analysis of uranium. An evaluation of commonly available sorbents to determine the effectiveness of various functional groups for the sorption of uranium from simple and complex aqueous solutions is described in Chapter III. Chapter IV will describe simple methods of preparation of sorbents with functional groups that are selective for the extraction of uranium. This includes the preparation of polyurethane foams with phosphonic acid or  $\beta$ -diketone functional groups and a modified polyacrylonitrile (Orlon™) fabric with amidoxime functional groups. These materials were evaluated for their uptake of uranium from aqueous solutions with a wide range of pH and temperature values. Commercially available resins that have seldom been used in analytical chemistry, because they were only recently introduced into the market, were evaluated for the uptake of uranium from

actual seawater and the results were compared to the commonly used Chelex 100 resin; these results are discussed in Chapter V.

The preconcentration procedures based on chelating polymers seem to offer unexplored opportunities that deserve the attention of scientists concerned with environmental pollution abatement in general, and with the removal of hazardous species in particular. These chelating polymers would play a vital role in environmental monitoring of toxic trace metals. Preconcentration with chelating sorbents improves the sensitivity and reliability of the analytical determination of elements for a wide variety of samples, including natural waters, geological, biological and industrial materials.



## CHAPTER II

## ANALYTICAL TECHNIQUES

**2 Introduction**

Four different techniques were used for the determination of uranium due to limitations associated with the availability and suitability of these techniques for our use. A brief evaluation of the techniques used for the determination of uranium will be discussed in this chapter.

The determination of trace metals for monitoring purposes, particularly of radionuclides in seawater, has received enormous attention in recent years and a number of analytical methods are presently used for the analysis of trace metals in seawater. The instrumental techniques available include x-ray fluorescence,<sup>49</sup> laser fluorescence,<sup>224</sup> neutron activation,<sup>225,226</sup> isotope dilution mass spectrometry,<sup>227</sup> inductively-coupled plasma-mass spectrometry,<sup>200</sup> anodic stripping voltammetry<sup>228</sup> and atomic absorption spectrometry.<sup>229</sup> None of these analytical techniques is able to perform a direct determination of trace elements in seawater at concentrations below 5 ppb (the concentrations of uranium and thorium in seawater are 3.3 ppb and 0.03 ppb respectively). Even when metal concentrations are relatively high, the sensitivities and detection limits are seriously affected by the seawater matrix. As a result of these limitations, a sample preparation technique is usually employed to preconcentrate the radionuclides as well as separate them from alkali and alkaline

earth metals.

A number of review papers have been published for the analysis of uranium using various techniques.<sup>231-242</sup> The different techniques reviewed for the analysis of uranium were spectrophotometric,<sup>240,242</sup> electrochemical,<sup>237</sup> ion probe,<sup>236</sup> nuclear magnetic resonance,<sup>238</sup> radiochemical,<sup>235,241</sup> neutron activation,<sup>226,234,236</sup> inductively-coupled plasma atomic emission spectrometry,<sup>234,241</sup> inductively-coupled plasma mass spectrometry,<sup>232,234,236</sup> mass spectrometry<sup>231,233,235,236,241</sup> and fluorescence spectrometry.<sup>230,234,239,241</sup>

Many of the techniques for the determination of trace uranium were either not suitable or not available in our laboratory. Emission spectroscopic techniques appeared to offer high sensitivity with suitable selectivity. Initially in this work the analysis of uranium was done using an inductively-coupled plasma atomic emission spectrometer (ICP-AES) which was available for our use on a limited time basis at the Ward Technical Services Laboratory of the Province of Manitoba (Winnipeg, Canada). However, large delays were involved in getting this instrument back into working condition when it required repairs. These recurring delays led us to seek alternative methods of analysis and this resulted in the use of a direct current plasma atomic emission spectrometer (DCP-AES) located in the Fresh Water Institute, a Canadian Government facility on the University of Manitoba campus. Unfortunately, similar problems occurred with the DCP-AES, thus limiting the availability of the instrument

for our use because of its normal workload and because of long delays required for repairs. These difficulties led us to develop a continuous flow spectrophotometric method (CFSM) for the quick and accurate analysis of uranium in our laboratory.

The analysis of uranium for the evaluation of various sorbents was done using either ICP-AES, DCP-AES or CFSM. One of the criteria used for the evaluation was percent extraction, which was obtained by comparing the initial and final concentration of uranium. Uranium content of the eluates for actual seawater experiments was determined by an inductively-coupled plasma mass spectrometer (ICP-MS) which was located in the Geological Survey of Canada (Ottawa, Ontario). ICP-AES, DCP-AES or CFSM were unable to analyze for uranium content in these eluates due to severe problems associated with matrix interferences.

## 2.1 Reagents

All chemicals [Arsenazo III (Aldrich Co. WI, USA), uranyl acetate (BDH, England) and thorium nitrate (Fisher Sci. Co. NJ, USA)] were of reagent grade and were used without further purification. Water used was first purified by reverse osmosis followed by a Barnstead Nanopure II™ system.

A 2000 ppm uranium stock solution was prepared by dissolving 3.5640 grams of uranyl acetate [ $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] in 1 litre of deionized water. Uranium standard solutions ranging from 1 to 10 ppm were prepared by successive dilution of the 2000

ppm stock solution.

A 2000 ppm thorium stock solution was prepared by dissolving 2.3800 grams of thorium nitrate ( $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ) in 500 mL of deionized water. Thorium standards ranging from 0.1 to 10 ppm were prepared by successive dilution of the 2000 ppm stock solution.

For the evaluation of the sorbents, we were interested in only the relative concentration (i.e. concentration before and after using the sorbent). Hence, no attempt was made to determine the uranium content of the stock solution accurately.

## 2.2 Equipment

### 2.2.1. *Inductively-coupled plasma atomic emission spectrometer (ICP-AES)*

The spectrometer was a Jarrell-Ash Atom Comp series 800 (MA, USA) equipped with a MAK™ nebulizer and a Gilson Minipuls peristaltic pump with a flow rate of  $1.3 \text{ mL} \cdot \text{min}^{-1}$ . The argon plasma creates a hot zone, with a temperature in the range of 8,000 to 10,000 K, in which excited atoms are produced from the sample solution. At these temperatures chemical interference from organic or inorganic anions is generally eliminated.

ICP-AES measures the intensity of the characteristic emitted light which is

proportional to the concentration of atoms in the sample. The photomultiplier tube monitors the emission line intensity at a wavelength characteristic of the element to be analyzed.

The Jarrell-Ash Atom Comp instrument has the capability of determining ten elements simultaneously, as shown in Figure 2.1. The elements, wavelengths, and the detection limits for the ten elements are given in Table 2.1. The detection limit is defined as twice the standard deviation of background noise. The computer uses calibration standards to produce concentration values from the raw intensity data. Background correction (i.e. baseline intensity of the peak), was measured at 0.1 nm in the high wavelength side of the analytical line and was automatically subtracted for each sample. This was done using a spectrum shifter with a motor driven quartz refractor plate which is located behind the entrance slit. The integration time for each sample was 10 seconds and each analysis was performed in duplicate or triplicate.

### *2.2.2 Reproducibility of ICP-AES results*

When a 40 ppm uranium standard was analyzed as a sample, the average of the three readings was found to be  $40.6 \pm 0.4$  ppm. When a 1 ppm solution was analyzed the average was found to be  $1.09 \pm 0.04$  ppm uranium. The above results show good reproducibility, i.e. the relative error for the "high" standard was within 1% and for the "low" standard within 4% of their respective average readings. A major portion of the

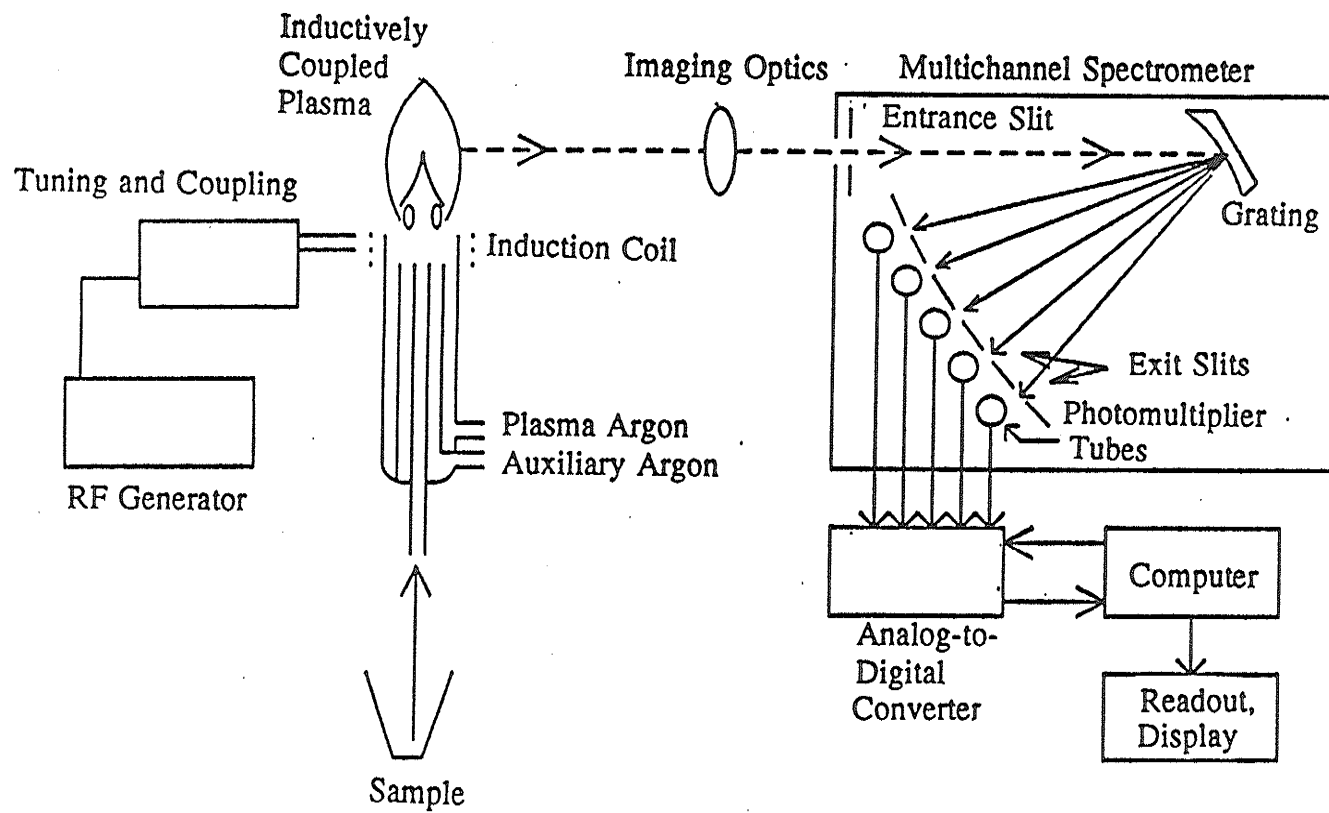


Figure 2.1 Schematics of an inductively-coupled plasma atomic emission spectrometer (ICP-AES)

**Table 2.1 ICP-AES detection limits and emission wavelengths**

<b>Element</b>	<b>Wavelength (nm)</b>	<b>Detection limit (ppm)</b>
Ca	317.9	0.5
Mg	279.5	0.5
Na	589.0	1.0
Cu	324.7	0.01
Zn	213.8	0.01
Fe	259.9	0.02
Mn	257.6	0.02
Pb	220.3	1.0
Ni	231.6	0.01
U	385.9	0.20

Data for Jarrell-Ash Atom Comp Series 800 Instrument

analysis using this instrument was performed by Mr. D. Chan of the Ward Technical Service Laboratory.

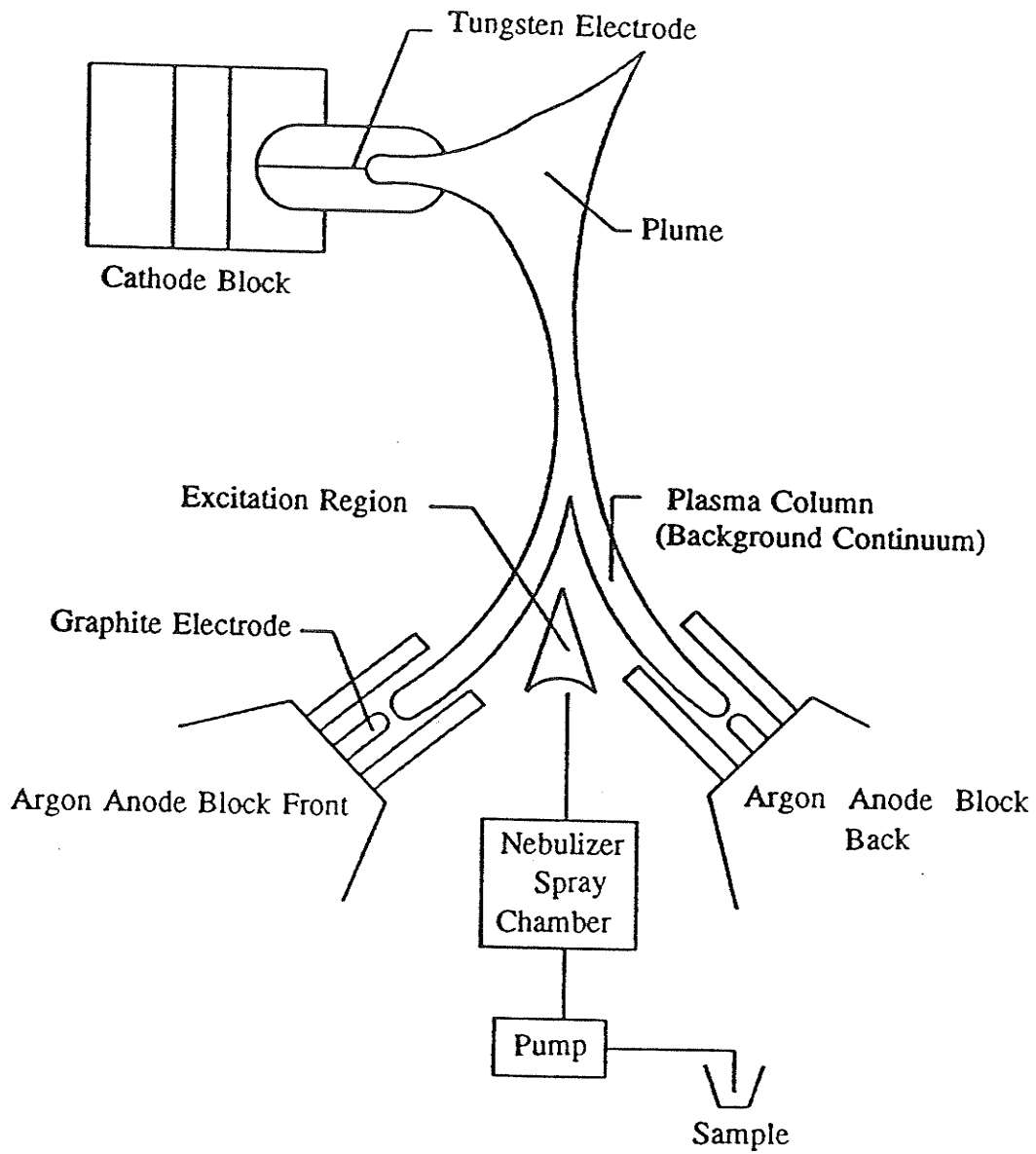
### *2.2.3 Direct current plasma atomic emission spectrometer (DCP-AES)*

The spectrometer used was a Beckman Spectrospan V (Spectra Metrics Inc., MA, USA) with a high resolution echelle grating. The high energy dc plasma excitation source consists of a front and rear graphite anode and a top tungsten cathode forming an inverted "Y" configuration, as shown in Figure 2.2. The peristaltic pump transfers the sample to the nebulizer at a rate of approximately 2 mL.min<sup>-1</sup>.

The uranium emission wavelength was found by scanning the spectrum from 200 to 700 nm while a 100 ppm uranium standard was being aspirated into the plasma. The most sensitive line was found to be at 424.17 nm with an intensity of 6000 (arbitrary units). To confirm that this line at 424.17 nm was due to uranium, a deionized water sample was aspirated and the intensity dropped to 326 (arbitrary units), indicating that the line at 424.17 nm was not due to the background or other interferences. This line at 424.17 nm was also recommended by the instrument manufacturer for the analysis of uranium.<sup>243</sup>

The DCP-AES spectrometer was capable of digitizing the analytical peak spectrum and displaying it as a plot of wavelength versus intensity measurements. The intensity





**Figure 2.2 Schematics of a direct current plasma atomic emission spectrometer (DCP-AES)**

measurements at every 0.052Å displacement from the centre of the analytical peak on both sides of peak were measured and displayed as a spectrum called Digiscan™. A Digiscan™ showing the digital scan of both sample and background spectrum when a 10 ppm uranium standard solution and deionised water were aspirated is given in Figure 2.3. The spectrum displayed in Figure 2.3 is centred on the wavelength 424.17 nm.

The DCP-AES instrument was calibrated by aspirating two uranium standard solutions, a 10 ppm "high" standard and a 1 ppm "low" standard. The calibration software supplied with the instrument prepares a straight line calibration curve using the intensity measurements of these standards and converts sample signal measurements into concentration values as shown in Figure 2.4. The software extends the curve beyond the "high" and "low" values to accommodate measurements falling outside of that region<sup>243</sup> (for values up to about twice the high standards.) The background correction (i.e. base line intensity of the peak) was obtained by measuring the emission intensity at 0.416 Å on the high wavelength side of the analytical line as shown in Figure 2.5 and automatically subtracted for each sample.

#### ***2.2.4 Reproducibility of DCP-AES results***

Two samples, one approximately 5.7 ppm and the other 1.0 ppm, were analyzed successively by DCP-AES. The analysis was performed after calibrating the instrument with a 10 ppm as "high" standard and 1 ppm as "low" standard.

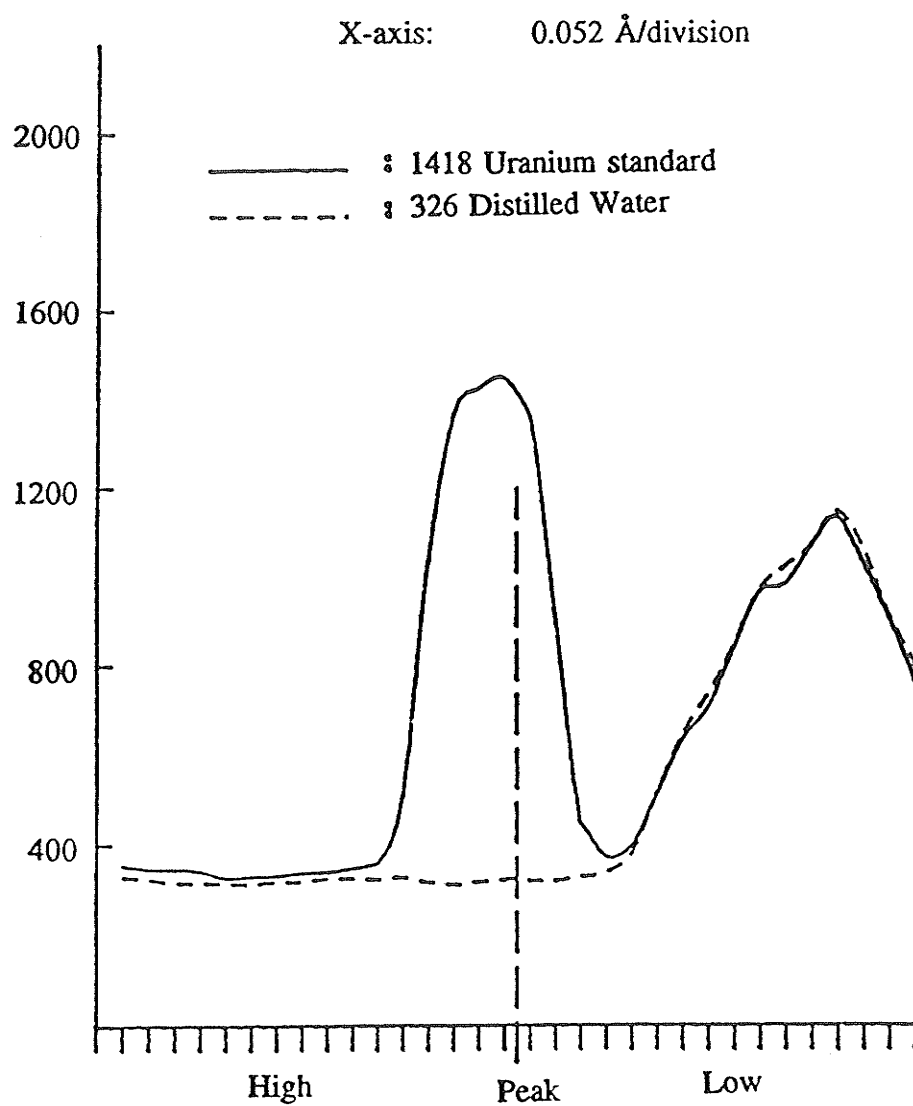


Figure 2.3 Digital scan of a 10 ppm uranium standard and background by DCP-AES at 424.17 nm

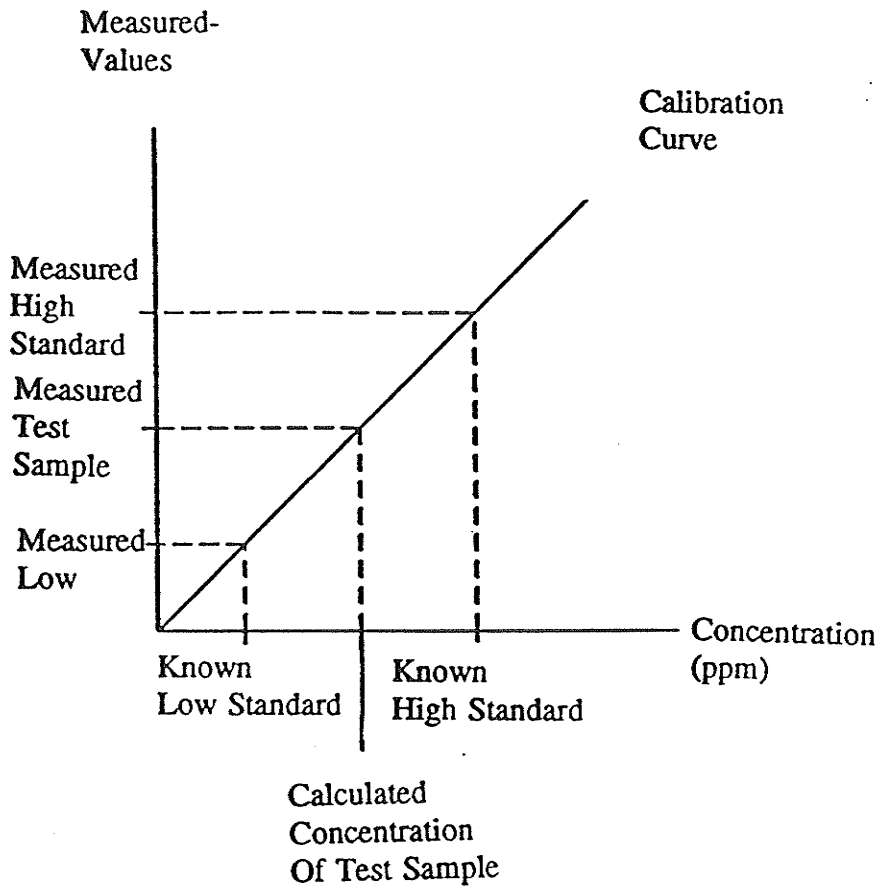


Figure 2.4 System calibration for DCP-AES

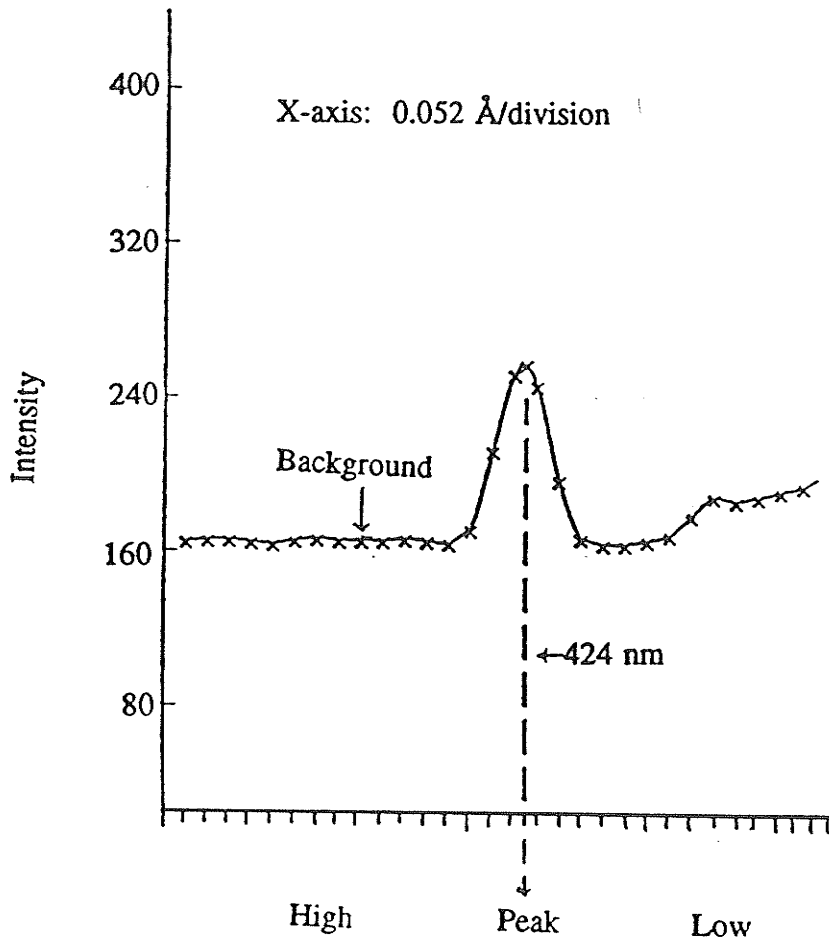


Figure 2.5 Background correction for the uranium analytical line by DCP-AES

The results are given in Table 2.2 for the 5.7 ppm uranium solution. The "low" standard, i.e. 1 ppm, was analyzed as a sample six times and the results are given in Table 2.3. It can be seen from Tables 2.2 and 2.3 that the DCP-AES is capable of analyzing uranium with reasonable reproducibility, i.e. within  $\pm 0.05$  ppm uranium.

### *2.2.5 Inductively-coupled plasma mass spectrometry (ICP-MS)*

In ICP-MS, the ICP acts as an ion source as described earlier for ICP-AES. The ions produced in the ICP are transferred into a mass spectrometer with a quadrupole mass analyzer which acts as a mass filter. The spectrometer used was a Perkin-Elmer Sciex Model 250 (Ontario, Canada). The schematics of a Sciex instrument are shown in Figure 2.6. The solution uptake was controlled with a Gilson Minipuls 2 peristaltic pump. Calibration was accomplished using Johnson Matthey Specpure™ calibration standards. The uranium isotope ratios were determined by monitoring the ion intensity of  $U^{235}$  and  $U^{238}$  separately. Data were accumulated on the less abundant isotope such that a minimum of 10,000 counts were obtained to improve counting statistics. The value obtained for the isotope ratio was calculated from an average of five separate determinations. Mass discrimination corrections were made using NBS Standard Reference Material 982 isotopically analyzed and certified equal atom lead isotopic standard<sup>244</sup>. ICP-MS was used for the analysis of Zr, Hf, Ta, Th and U in the eluates for the actual seawater experiments; the rest of the elements in the eluates were analysed by ICP-AES. The ICP-AES used was a Jobin-Yvon Model 48 simultaneous ICP-AES emission spectrometer with a 2400 groove  $mm^{-1}$  holographic grating. The

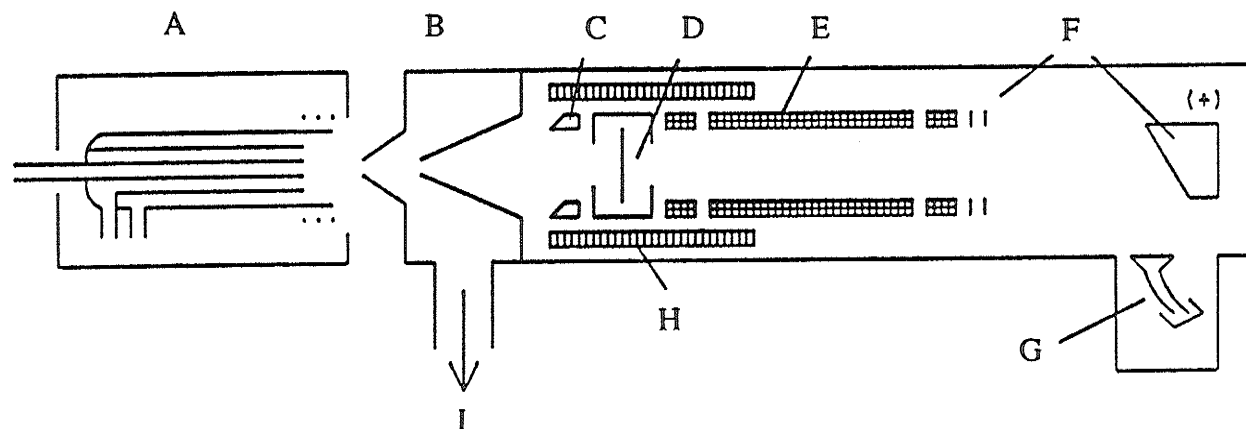
**Table 2.2** Reproducibility results for DCP-AES when a 5.70 ppm uranium solution was analysed

<b>Serial No.</b>	<b>DCP-AES Results (ppm)</b>	<b>Deviation from Average (ppm)</b>
1	5.79	+ 0.01
2	5.77	- 0.01
3	5.77	- 0.01
4	5.73	- 0.05
5	5.61	- 0.17
6	5.83	+ 0.03
7	5.79	+ 0.01
8	5.83	+ 0.05
9	5.89	+ 0.11
10	5.76	- 0.02
Average	5.78	± 0.05

**Table 2.3** Reproducibility results for DCP-AES when a 1.00 ppm uranium solution was analysed

<b>Serial No.</b>	<b>DCP-AES Results (ppm)</b>	<b>Deviation from Average (ppm)</b>
1	1.03	+ 0.04
2	1.01	+ 0.02
3	1.00	+ 0.01
4	0.98	- 0.01
5	1.00	+ 0.01
6	0.93	- 0.06
Average	0.99	$\pm 0.03$





- A. ICP torch and shielding box
- B. Ion extraction interface with sampler and skimmer cones
- C. Ion lens elements
- D. Bessel box (plasma photon filter)
- E. Quadrupole mass analyzer
- F. Ion optical elements for deflecting ions into detector
- G. Offset electron channel multiplier
- H. Cryogenic pumping surfaces
- I. Line to mechanical vacuum pump

Figure 2.6 Schematics of an inductively-coupled plasma mass spectrometer (ICP-MS)

nebulizer used was a Meinhard "C" concentric glass type nebulizer. Calibration was accomplished using Spex™ ICP standard solutions prepared in acid of strength matching that of sample solution. Measurements by ICP-AES were obtained by integration for 3 minutes and the relative standard deviations were between 1.5 and 2.0<sup>244</sup>. The ICP-MS and ICP-AES used (for the analysis of the eluates for the seawater experiments) were located in Geological Survey of Canada (Ottawa, Canada) and all analyses were performed by Dr. Gregoire and Ms. Bertrand of the Geological Survey of Canada.

#### **2.2.6 *Continuous flow spectrophotometric method (CFSM)***

The analysis of uranium by ICP-AES or DCP-AES is rapid, convenient and relatively free from matrix effects, but the analysis became very restrictive because the Chemistry Department at the University of Manitoba did not have these instruments. These instruments were being used for routine analysis by the owners of the instrument. Instrumental parameters had to be changed for our analysis which restricted our use of the instrument to a time when routine analysis was not being performed by the owners. Due to the large number of samples that had to be analyzed, the inconvenient location of equipment, and the occasional availability of the instrument for our use, we developed a continuous flow spectrophotometric method (CFSM) for the analysis of uranium.

The continuous flow technique consists of simultaneously pumping Arsenazo III (the

photometric reagent) and the uranium solution into a flow mixer to form the Arsenazo III-uranium complex. This complex then enters a flow cell wherein the absorbance measurements were recorded with a diode array spectrophotometer. The advantages of using a flow cell, as compared to a conventional cell, is that the flow cell requires less time per sample (because the tedious process of cleaning and rinsing is avoided) and the time for complex formation is always a constant in a flow cell. The pumping of Arsenazo III and uranium solutions through the flow cell was done by a peristaltic pump which did not come into direct contact with the solution, thereby reducing the possibility of contamination.

CFSM is a simpler technique mechanically than flow injection analysis. Flow injection analysis of uranium would involve the injection of uranium sample into a carrier stream with the use of a switching valve. This sample is merged with the reagent stream into the flow cell. In CFSM the reagent and the sample are continuously passed into the flow cell thereby eliminating the use of a carrier solution and the use of a complex switching valve to inject the uranium sample.

Arsenazo III(2,2'-(1,8-dihydroxy-3,6-disulphonaphthylene-2,7-bisazo)-bisbenzenearsonic acid, FW 776.37) reacts with wide variety of metal ions in weakly acidic to alkaline aqueous solutions, but reacts with only a few metals in strong mineral acid, forming highly coloured complexes (molar absorptivity approximately  $10^5$ ). Arsenazo III has been recommended as a highly sensitive and selective

photometric reagent for Mg, Zr, U, Th and rare earths.<sup>245</sup> Arsenazo III is commercially available as either a free acid or disodium salt and is stable both as a solid and in dissolved form.

More than 150 papers have been published in the last three decades,<sup>246-253</sup> wherein Arsenazo III is the preferred choice of chromogenic reagent for the spectrophotometric determination of uranium. Uranyl ions form a 1:1 complex in moderately acidic media<sup>251,253</sup> and the stability constant for the complex is  $\log \beta_1 = 5.42$ <sup>254</sup>. For our analysis the concentration of Arsenazo III was always higher than that of uranium or thorium.

### **2.2.7 Apparatus for CFSM**

Absorbance measurements were obtained with a Hewlett-Packard Model 8452A Diode Array Spectrophotometer (Hewlett-Packard Company, CA, USA). The spectrophotometer is a microprocessor-controlled, single beam uv-visible spectrophotometer operated by a Tandy™ 1000 personal computer with Hewlett-Packard uv-visible software. A deuterium lamp that emits light over the 190 to 820 nm wavelength range is used as a light source. A single, collimated beam of light is passed through the sample, and then dispersed by a grating onto the diode array. The diode array is a 2 mm x 18 mm semiconductor with 328 photodiodes etched on to it. Each photodiode is assigned 2 nm; this permits simultaneous access to the whole wavelength range between 190 and 820 nm. A few photodiodes on either end of the array were not

used.<sup>255</sup> This instrument is capable of obtaining the full spectrum in 0.1 seconds with a photometric range up to 3.3 AU (absorbance units).

A quartz flow cell with 0.5 cm path length (Markson Science Inc., CA, USA) was used for the spectrophotometric analysis. The solution was pumped through the flow cell using a Piper Pump™ Model P10T (Dungey Inc., Ontario, Canada) peristaltic pump. The Markson™ flow cell is a quartz cell enclosed in a metallic casing which fits into the 1 cm cuvette holder of the diode array spectrophotometer. The structure and dimensions of the quartz flow cell are given in Figure 2.7. The liquid to be analyzed flows into the cell from the top and escapes from the bottom. The path length of the beam that passes through the solution was found to be 5 mm.

A 1.5 mm x 5 mm slit cover jacket on the cell was used for all our analysis as this provided a more linear calibration graph.

### **2.2.8 *Flow mixers for CFMS***

Initially a flow mixer of the simple type as shown in Figure 2.8a was used to thoroughly mix the Arsenazo III and uranium solutions. On careful examination, it was observed that the resulting solution was not of uniform colour intensity. Looking at the solution against light, there appeared to be a laminar flow of different layers which resulted in differently coloured segments of solution that were passing into the flow cell. Absorbance measurements of the segmented flow showed poor reproducibility because the differently coloured solutions that were entering the flow

## Markson™ Flow Cell

Side View

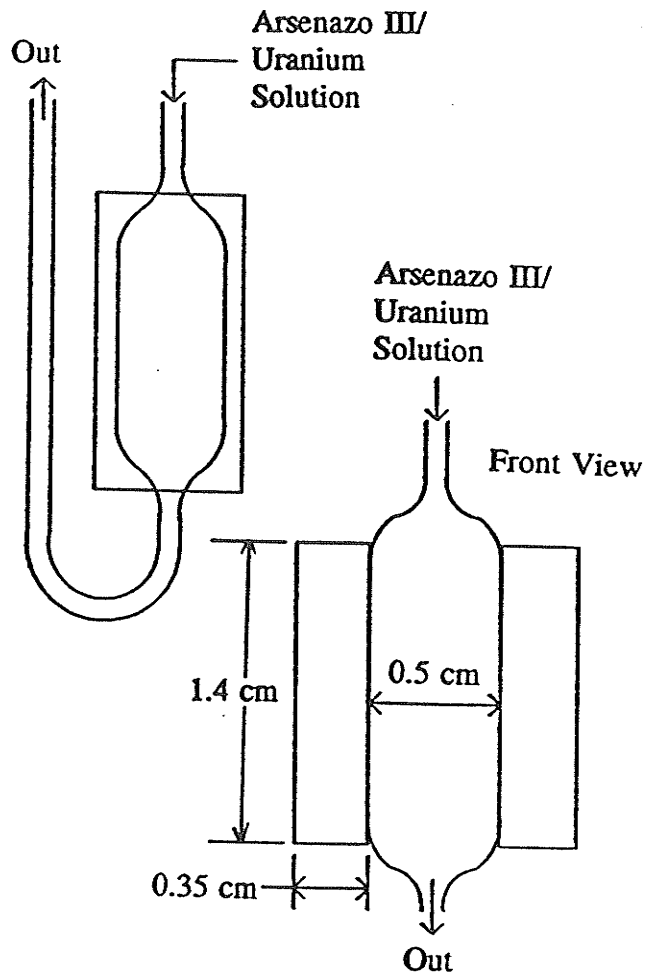


Figure 2.7 Structure and dimensions of a Markson™ flow cell

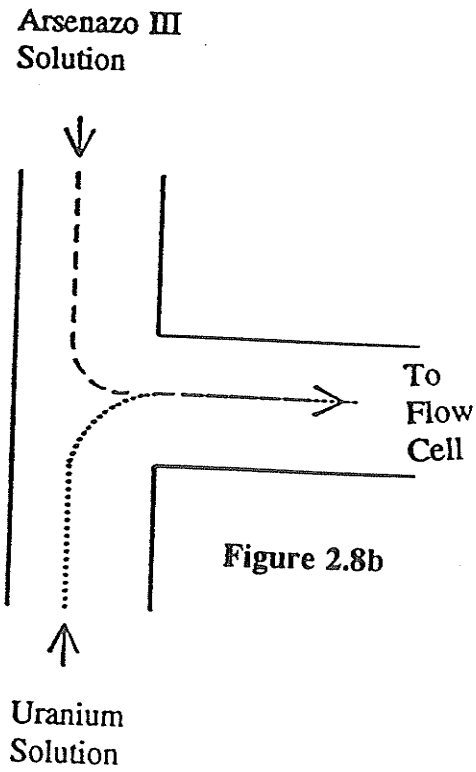
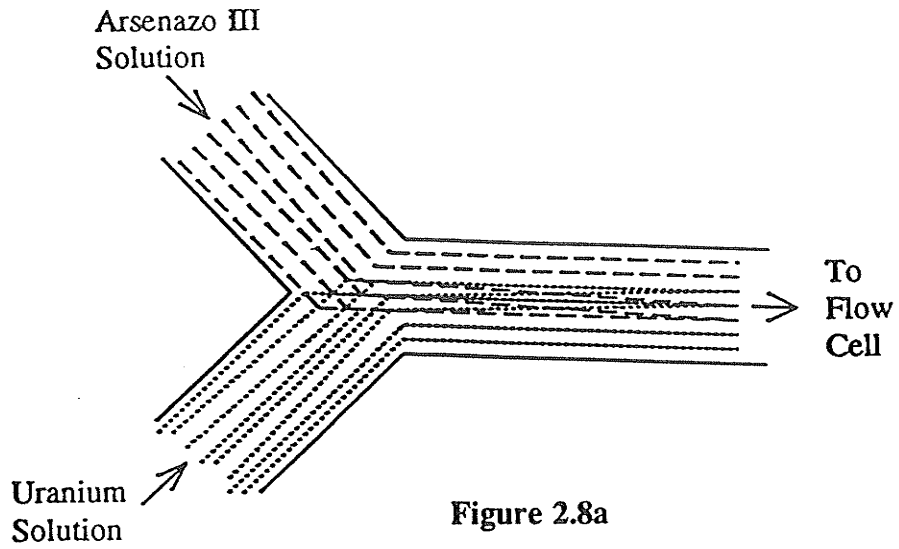


Figure 2.8 Flow mixers evaluated for use with CFM

Figure 2.8 Continued

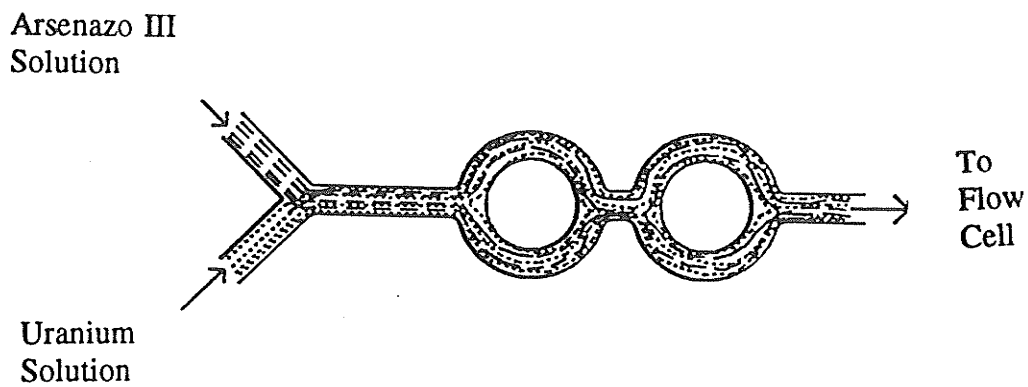


Figure 2.8c

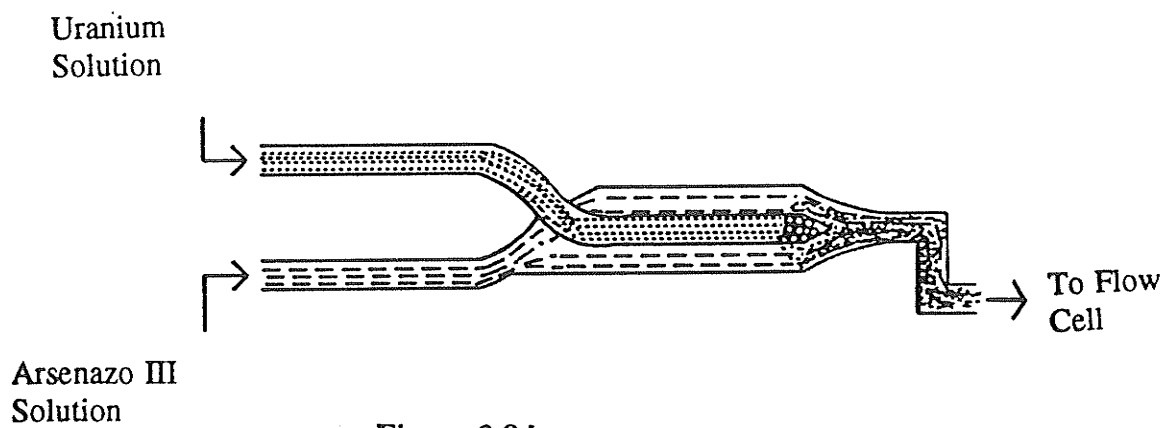


Figure 2.8d



cell due to the poor mixing ability of the flow mixer. In order to obtain better mixing several other designs were investigated. The mixer in Figure 2.8b was designed to make more complete mixing possible as the two solutions were moving in opposite directions. A laminar flow still existed with this model, but to a smaller extent compared to the mixer in Figure 2.8a.

In Figure 2.8c, a mixer was designed to increase the mixing by providing additional places where the two streams of solution would meet in opposite directions.

Unfortunately, the paths taken by the solutions were never consistent, which resulted in problems during the changing of samples as some solution from the previous sample was trapped in a ring thereby contaminating the second sample.

The above mixers were abandoned when the mixer in Figure 2.8d was obtained from Dr. Queen of this Department. It showed a good capability in mixing the solutions, resulting in uniformly coloured solutions entering the flow cell. The flow mixer consists of two glass concentric tubes with the uranium solutions passing through the inner tube while the Arsenazo III solution passes through the outer jacket. The inner tube has a number of small holes at the end to enable the release of uranium solution in all directions into the Arsenazo III dye solution.

### **2.2.9 Analysis of uranium by CFMS**

The uv-visible spectrum of Arsenazo III is shown in Figure 2.9 and the spectrum of

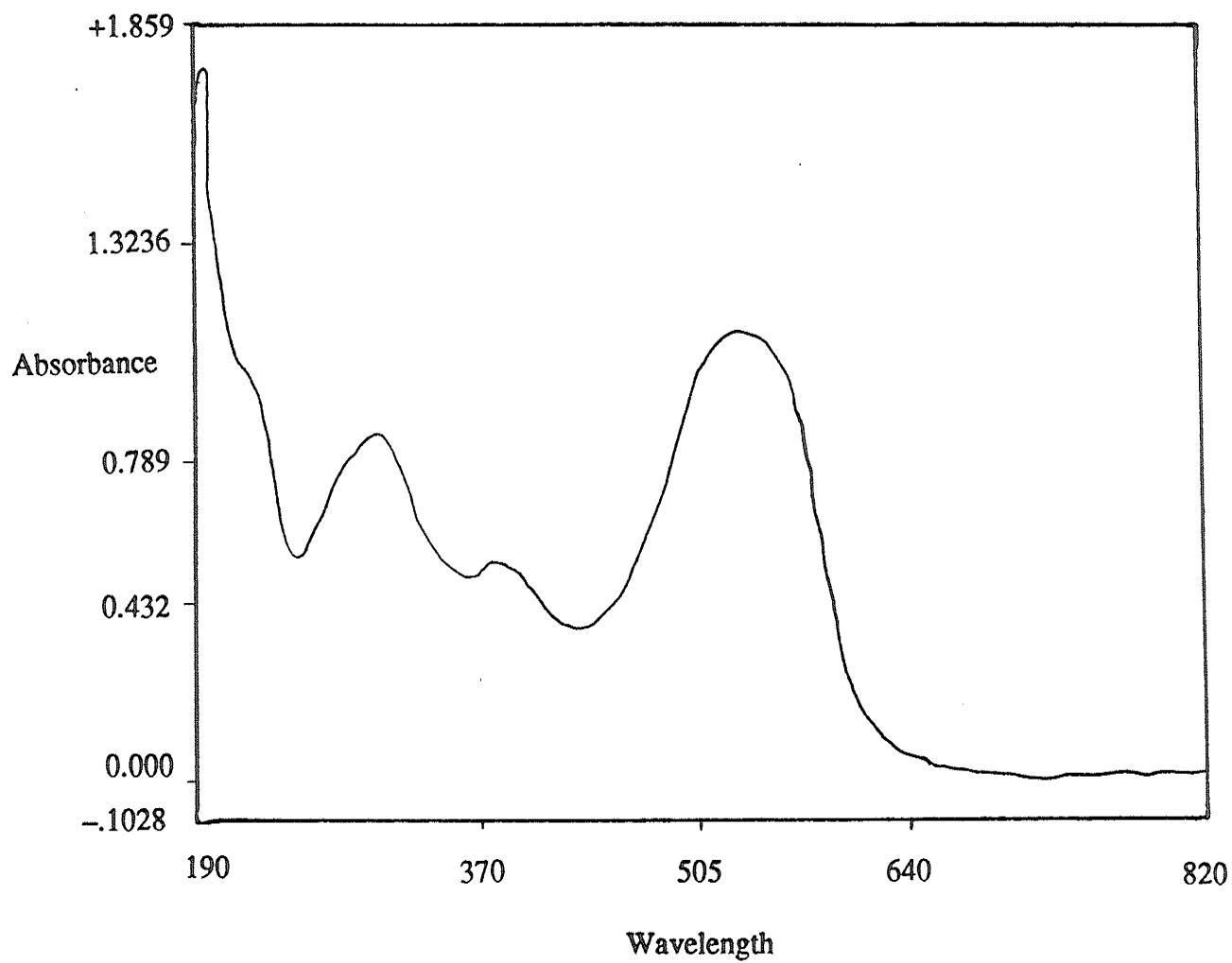


Figure 2.9 UV-visible spectrum of the Arsenazo III dye solution

Arsenazo III - uranium complex is given in Figure 2.10. The absorption maximum is at 532 nm for the dye and at 650 nm for the Arsenazo III - uranium complex as shown in Figure 2.10. The reference wavelength for the Arsenazo III - uranium complex can be at any wavelength greater than 726 nm. The spectrum for Arsenazo III - uranium complex was obtained when the instrument was blanked (i.e. to show zero absorption) with Arsenazo III solution as shown in Figure 2.11.

Initially, the analysis was done using two peristaltic pumps which had to be synchronised with respect to the movement of the rollers in their respective pump heads. To eliminate any discrepancies in the movement of rollers of the two pumps, the two silicone tubes were simultaneously passed through the same pump head. The flow rates of the reagent solution and sample solution were each  $8 \text{ mL}\cdot\text{min}^{-1}$  with a combined flow rate of  $16 \text{ mL}\cdot\text{min}^{-1}$  when reaching the flow cell. This flow rate was chosen because it was capable of forcing out the air bubbles that frequently adhere to the flow cell. An internal referencing method was used where the absorbance at the reference wavelength was subtracted from the absorbance at the analytical wavelength. This absorbance difference was used to obtain the calibration curve and for sample analysis. The reference wavelength of 768 nm was selected at a point along the baseline beyond the sample absorbance. Internal referencing was done to improve the precision of the results by minimizing the impact of any changes that cause a baseline shift due to dust or other particles, air bubbles or a drift in lamp intensity.

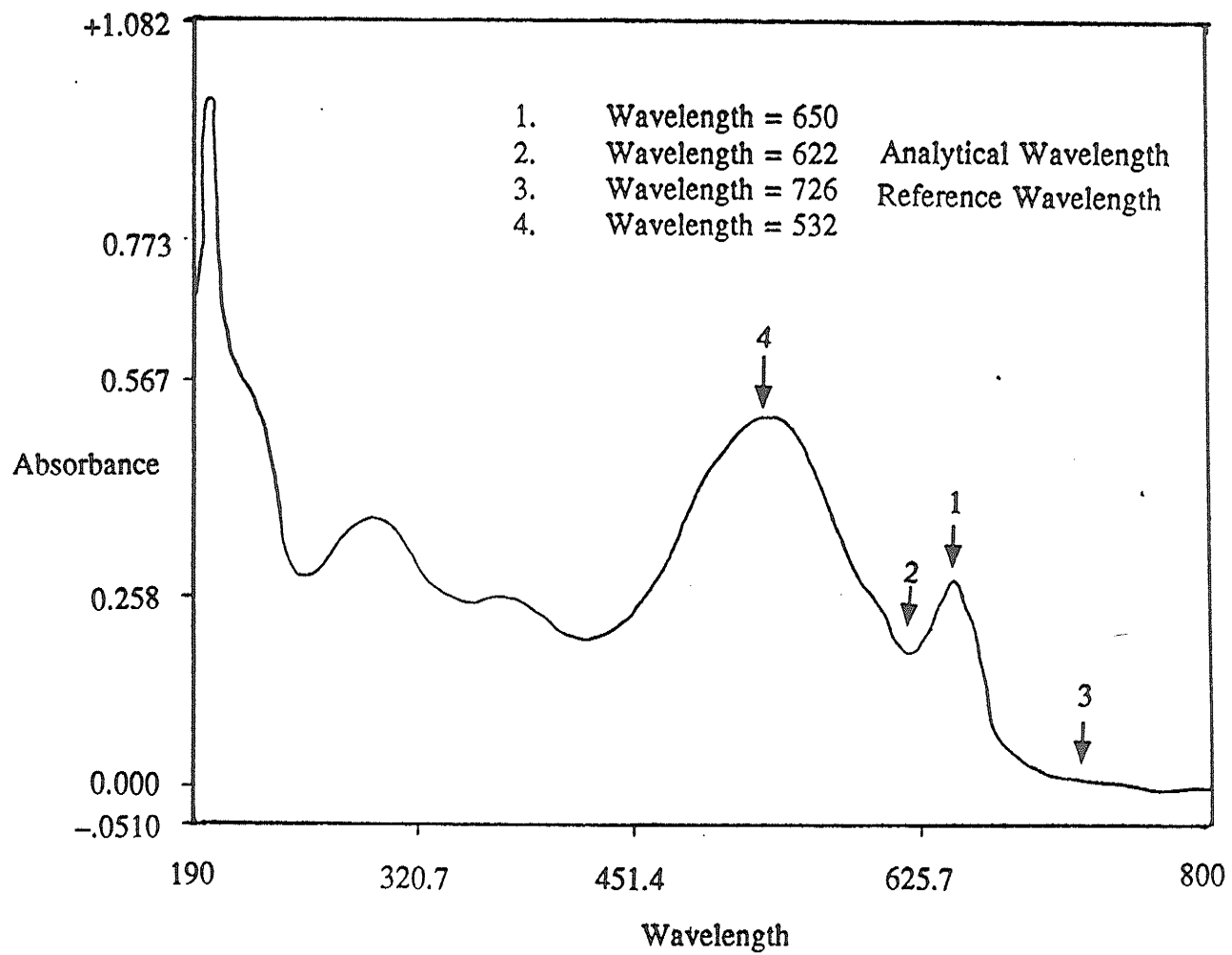


Figure 2.10 UV-visible spectrum of the Arsenazo III - uranium complex

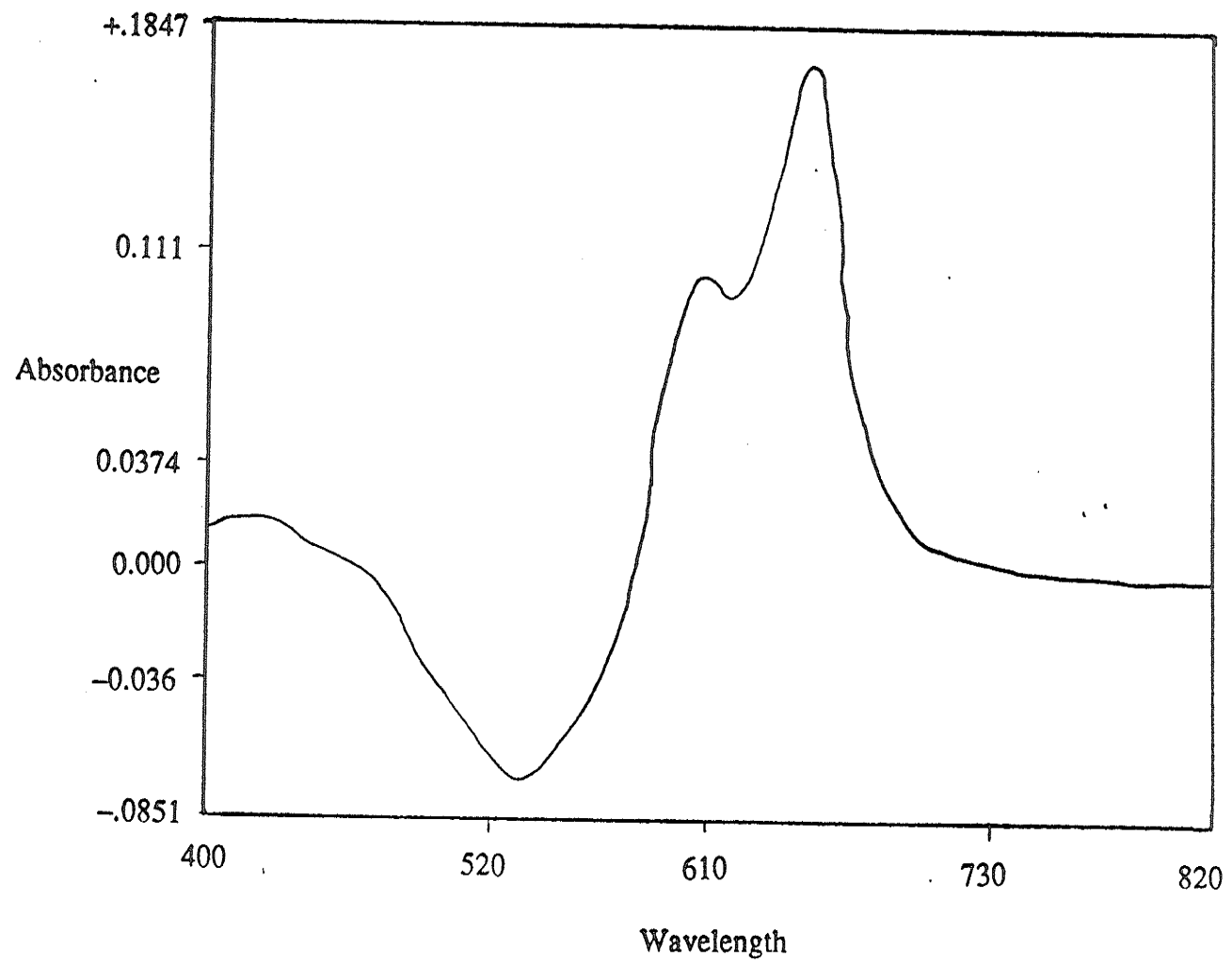


Figure 2.11 Visible spectrum of Arsenazo III - uranium complex  
The spectrophotometer was blanked with Arsenazo III solution.

Quantitative analysis was performed by using the "Quantitation" program which was part of the software menu for the Hewlett-Packard system. Uranium standards ranging from 1 to 10 ppm uranium were used to obtain the calibration graph. The calibration curve in Figure 2.12 was obtained using a second order curve fit. The equation used was  $C = K_2A^2 + K_1A$  where  $K_1$  and  $K_2$  are constants for the curve,  $C$  is the concentration obtained and  $A$  is the measured absorbance. The absorbance readings displayed were an average of the readings integrated for 10 seconds and are given in Table 2.4.

The 0.006% Arsenazo III (wt/vol) reagent solution was prepared by dissolving 0.1500 grams of Arsenazo III solid in 2.5 litres of 0.12M HCl. Concentrations higher than 0.12M HCl resulted in larger errors when analyzing uranium solutions with lower pH, and concentrations lower than 0.12M HCl resulted in larger errors when analyzing uranium solutions with higher pH values. The acidity of 0.12M HCl was chosen as the optimal concentration as it was capable of analyzing uranium solutions whose pH ranged between 1 and 11, as shown in Table 2.5.

#### **2.2.10 Final analytical technique**

The spectrometer was turned on for an hour prior to use to allow all components to stabilize. The instrument was blanked by a 0.006% Arsenazo III solution in 0.12M HCl and deionized water. The pumping rate was maintained at  $8 \text{ mL}\cdot\text{min}^{-1}$  through each tube, with a combined flow rate of  $16 \text{ mL}\cdot\text{min}^{-1}$ . Calibration and

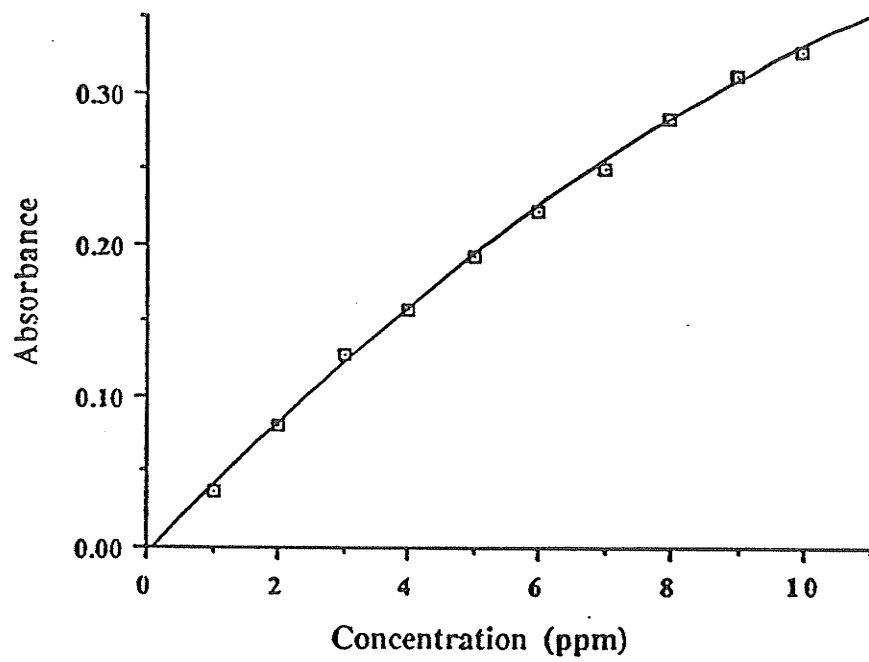


Figure 2.12 Calibration graph for uranium standards between 1 and 10 ppm

A 5 mm Markson™ flow cell and 0.006% Arsenazo III solution were used.

**Table 2.4 Calibration for uranium standards between 1.0 and 10 ppm  
using 0.006% Arsenazo III solution**

<b>STD#</b>	<b>Concentration (ppm)</b>	<b>Absorbance</b>	<b>Reference</b>	<b>Abs-Ref</b>
1	1.0000	0.0387	0.0018	0.0369
2	2.0000	0.0831	0.0027	0.0805
3	3.0000	0.1325	0.0051	0.1275
4	4.0000	0.1641	0.0061	0.1580
5	5.0000	0.1993	0.0069	0.1924
6	6.0000	0.2287	0.0069	0.2218
7	7.0000	0.2582	0.0076	0.2507
8	8.0000	0.2960	0.0123	0.2837
9	9.0000	0.3222	0.0104	0.3118
10	10.0000	0.3382	0.0102	0.3281

A 5 mm Markson™ flow cell was used.



**Table 2.5 CFSM analysis of a 10.0 ppm uranium solution at different pH values**

<b>Sample No.</b>	<b>Wavelength</b>	<b>Absorbance</b>	<b>Abs-Ref</b>	<b>Concentration (ppm)</b>
1 pH = 1.0	Analytical	+0.5424	+0.5370	9.89
2 pH = 3.0	Analytical	+0.5344	+0.5307	9.77
3 pH = 5.3	Analytical	+0.5525	+0.5420	9.98
4 pH = 8.3	Analytical	+0.5404	+0.5373	9.90
5 pH = 11.0	Analytical	+0.5513	+0.5490	10.12

A 5 mm Markson™ flow cell was used.

analysis involved the continuous flow of the Arsenazo III solution. The sample sipper was placed into each sample for analysis and because the pump was continuously pumping, air bubbles entered the flow cell during the sample change.

Every sample change was followed by rinsing with water; this was achieved by placing the sample sipper in deionized water for 10 seconds. The sample sipper was then wiped dry with Kleenex™ tissue paper before placing it into the next sample. The sample was then allowed to flow through the flow cell for 20 seconds before a reading is taken. The analytical wavelength and reference wavelength chosen for the analysis are 650 and 768 nm respectively. All absorbance measurements are an average obtained during a 10 second integration time.

Calibration was done using 1 to 10 ppm uranium standards prior to each analytical set of samples. A 10 ppm uranium standard was introduced for every fifty samples analyzed to check for any instrumental drift and a recalibration was performed after every one hundred samples.

#### ***2.2.11 Reproducibility of CFSM results***

A 10 ppm uranium standard solution was analyzed ten times to determine the accuracy and precision of the analysis as shown in Table 2.6. The average for the 10 ppm uranium standard was  $10.00 \pm 0.03$  ppm. Deionized water was then analyzed as a sample and the results are given in Table 2.7. The average concentration of uranium

**Table 2.6** Reproducibility results for the analysis of a 10.0 ppm uranium solution by CFSM

Sample No.	Wavelength	Absorbance	Abs-Ref	Concentration (ppm)
1	Analytical	+0.3466	+0.3344	10.03
2	Analytical	+0.3460	+0.3349	10.05
3	Analytical	+0.3446	+0.3327	9.96
4	Analytical	+0.3447	+0.3333	9.98
5	Analytical	+0.3432	+0.3331	9.98
6	Analytical	+0.3420	+0.3322	9.94
7	Analytical	+0.3445	+0.3338	10.00
8	Analytical	+0.3435	+0.3338	10.01
9	Analytical	+0.3461	+0.3347	10.04
10	Analytical	+0.3460	+0.3347	10.04

Average Concentration =  $10.00 \pm 0.03$  ppm uranium. A 5 mm Markson™ flow cell was used.

**Table 2.7** Reproducibility results for the analysis of deionised water (0.0 ppm uranium) by CFMS

Sample No.	Wavelength	Absorbance	Abs-Ref	Concentration (ppm)
1	Analytical	+0.0020	-0.0004	0.00
2	Analytical	+0.0022	-0.0004	0.00
3	Analytical	+0.0018	-0.0005	0.00
4	Analytical	+0.0021	-0.0001	0.00
5	Analytical	+0.0020	-0.0001	0.00
6	Analytical	+0.0018	-0.0005	0.00
7	Analytical	+0.0019	-0.0003	0.00
8	Analytical	+0.0022	-0.0001	0.00
9	Analytical	+0.0022	-0.0000	0.00

Average Concentration =  $0 \pm 0$  ppm uranium. A 5 mm Markson<sup>TM</sup> flow cell was used.

in deionized water was found to be  $0 \pm 0$ . In Table 2.7 it can be seen that the difference between the analytical and reference wavelength absorbances were very small negative numbers; the Quantitation software reported these negative values as zero uranium concentration but in actuality it should have reported as  $-0.01$  ppm uranium concentration. The above results for the 10 ppm uranium standard solution indicates that CFSM shows good reproducibility as the relative error was within 0.3% of the average reading.

#### *2.2.12 Analysis of thorium by CFSM*

Arsenazo III has been proven to be a sensitive photometric reagent for both uranium and thorium analysis<sup>245</sup>, so it was decided to test if thorium could be analyzed using Arsenazo III and the continuous flow technique.

The apparatus used for this analysis is identical to that described previously for uranium analysis. The commercially available flow cell (Markson Sciences Inc., CA, USA) along with 0.006% Arsenazo III dye solution was used for this analysis.

Initially a scan of the thorium-Arsenazo III complex was obtained using a 10 ppm thorium with 0.006% Arsenazo III dye solution to determine the analytical wavelength required for analysis. The instrument was blanked on 0.006% Arsenazo III and deionized water. From the spectrum in Figure 2.13 it can be seen that the absorption maximum for the complex was at 664 nm.

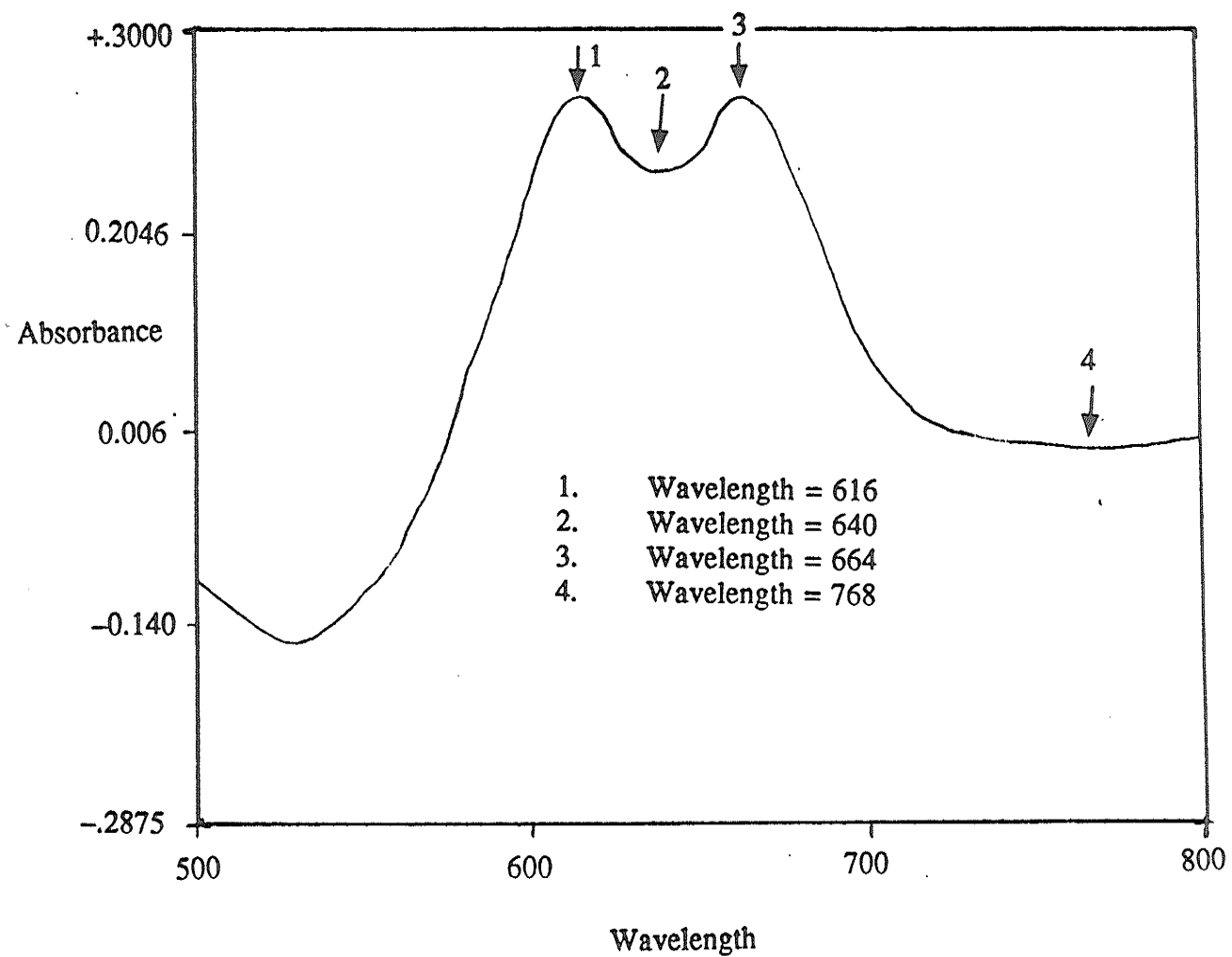
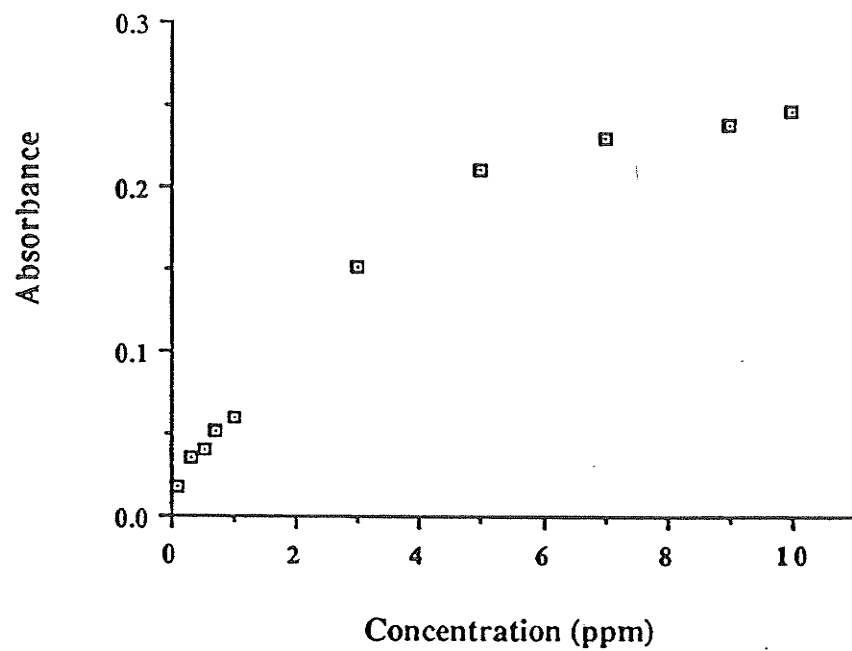


Figure 2.13 Visible spectrum of Arsenazo III - thorium complex  
The spectrophotometer was blanked with Arsenazo III solution.

The calibration graph and absorbance data obtained for thorium standards using 0.006% Arsenazo III solution are given in Figure 2.14 and Table 2.8. On careful observation of the calibration graph one can conclude that concentrations higher than 1 ppm thorium were not consistent with those below 1 ppm. In Figure 2.14 it can be seen that two calibration curves can be obtained, one for thorium standards that were less than 1 ppm and another for thorium standards greater than 1 ppm. The calibration curve that was obtained, when thorium standard solutions with concentrations less than 1 ppm were used, is shown in Figure 2.15. When additional thorium standards were made (i.e. between 1 ppm and 5 ppm thorium) the calibration curve obtained is as shown in Figure 2.16. From Figure 2.15 and 2.16 it can be seen that the continuous flow technique can be used for the analysis of thorium whose concentrations are between 0.1 and 1 ppm thorium and also when the concentrations are between 1 and 5 ppm thorium.

To evaluate if Arsenazo III and the flow cell can be used for the simultaneous analysis of uranium and thorium the two Arsenazo III complexes of thorium and uranium were recorded and the results are shown in Figure 2.17. Both complexes absorb in the same region except for a few nm at 650 nm where uranium complex shows maximum absorption. Simple simultaneous analysis of uranium and thorium would be difficult to perform due to their overlapping spectra as shown in Figure 2.17. Blanco *et al.*<sup>256</sup> reported that the mixed spectra of uranium and thorium can be resolved with the use of a multicomponent analytical program based on a least-squares fitting algorithm.



**Figure 2.14** Calibration graph for thorium standards between 1.0 And 10.0 ppm

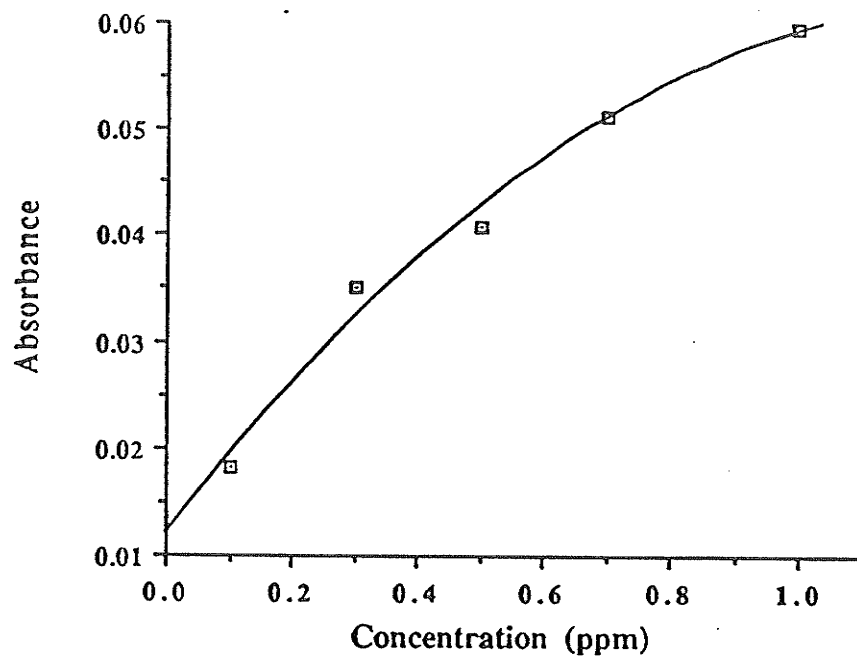
A 5 mm Markson™ flow cell and 0.006% Arsenazo III solution were used.



**Table 2.8 Calibration data for thorium standards between 0.1 and 10.0 ppm using 0.006% Arsenazo III solution**

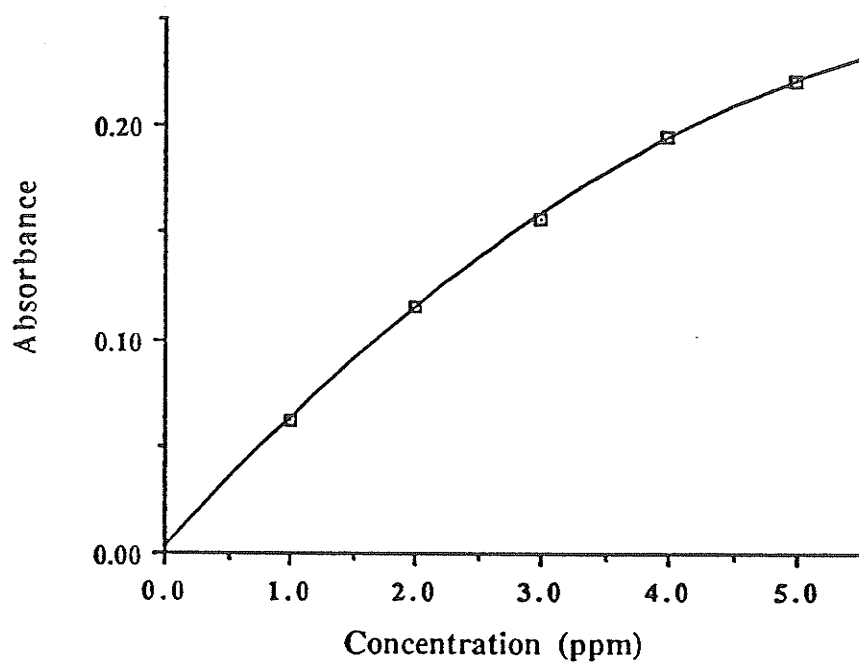
<b>STD #</b>	<b>Concentration (ppm)</b>	<b>Absorbance</b>	<b>Reference</b>	<b>Abs-Ref</b>
1	0.100	0.0193	0.0010	0.0183
2	0.300	0.0360	0.0010	0.0350
3	0.500	0.0419	0.0011	0.0408
4	0.700	0.0525	0.0011	0.0513
5	1.000	0.0598	0.0002	0.0596
6	3.000	0.1522	0.0011	0.1511
7	5.000	0.2121	0.0007	0.2113
8	7.000	0.2314	0.0007	0.2307
9	9.000	0.2413	0.0019	0.2394
10	10.000	0.2475	0.0015	0.2460

A 5 mm Markson™ flow cell was used.



**Figure 2.15 Calibration graph for thorium standards between 0.1 and 1.0 ppm**

A 5 mm Markson™ flow cell and 0.006% Arsenazo III solution were used.



**Figure 2.16** Calibration graph for thorium standards between 1.0 and 5.0 ppm

A 5 mm Markson™ flow cell and 0.006% Arsenazo III solution were used.

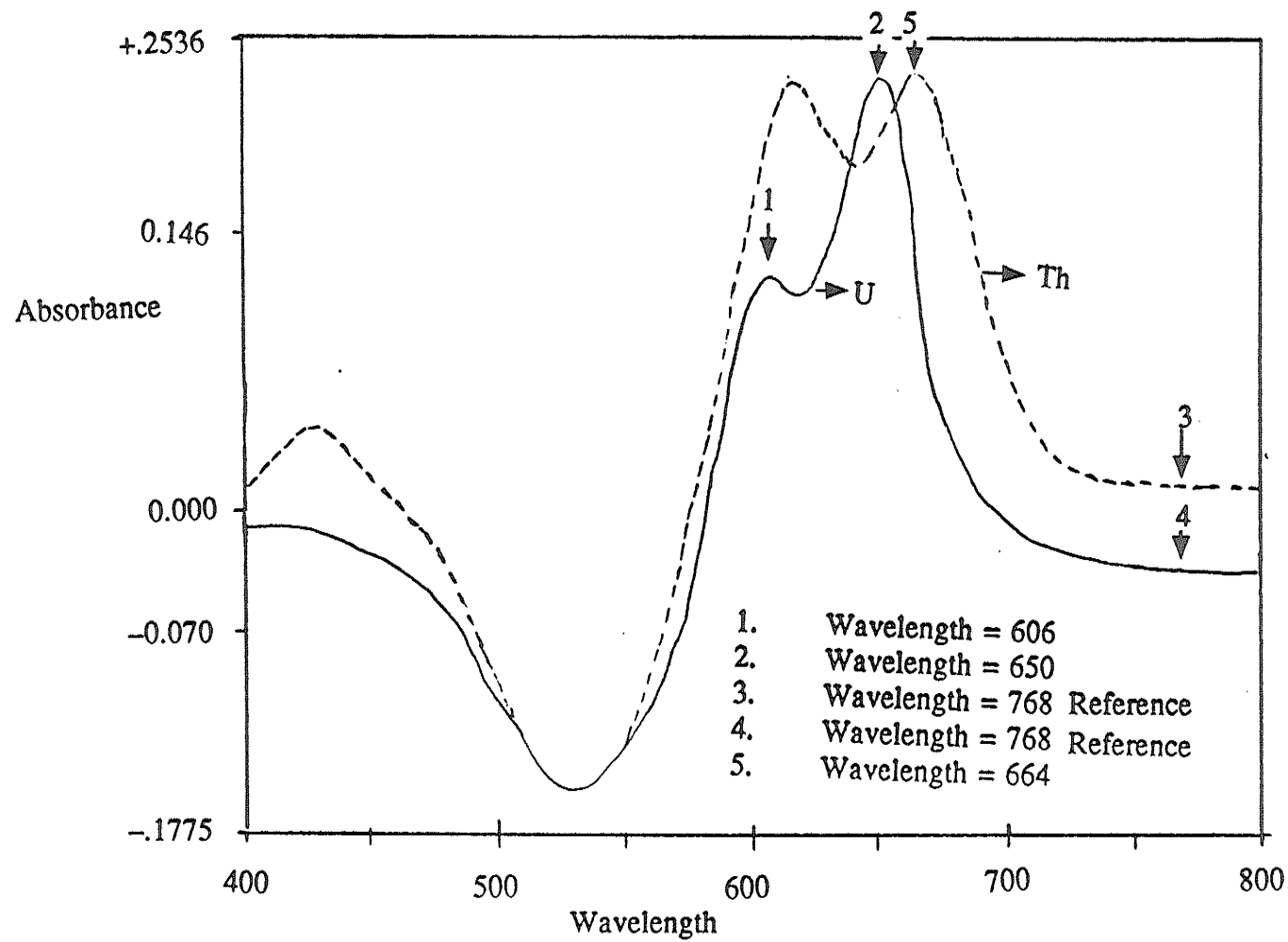


Figure 2.17 Visible spectra of uranium-Arsenazo III and thorium-Arsenazo III complexes. The spectrophotometer was blanked with Arsenazo III solution.

The Quantitation program used by the HP8452A was not capable of resolving the mixed spectra.

### ***2.2.13 Design and use of longer flow cells for CFMS***

The commercially available flow cell proved to be satisfactory when analyzing uranium solutions with concentrations between 1 and 10 ppm uranium. It was of interest to see if the uranium solutions with concentrations below 1 ppm uranium could be analyzed with cells with longer path lengths. A number of 5 cm and 10 cm flow cells were designed and their use in the analysis of uranium solutions (concentrations below 1 ppm uranium) were evaluated. A 10 cm glass flow cell with glued (Crazy Glue™) quartz windows was made as shown in Figure 2.18.

A number of uranium standards ranging from 0.010 ppm uranium to 1 ppm uranium were used to evaluate the usefulness of this cell. When a 0.006% Arsenazo III solution and deionized water was passed through the cell, the spectrometer was unable to blank this solution (i.e. to show zero absorption). The solution showed strong absorption in the 400 to 800 nm range, whereas ideally it should have shown a straight line across the wavelength range with zero absorption. Initially it was thought that the instrument was unable to blank the dye solution probably due to the strong absorption by the glue that was used to attach the quartz windows. However, when a 10 cm quartz tube which was bent as a flat "U" was used, the instrument still could not blank the solution. Therefore the problem was not due to the glue, but it was thought to be

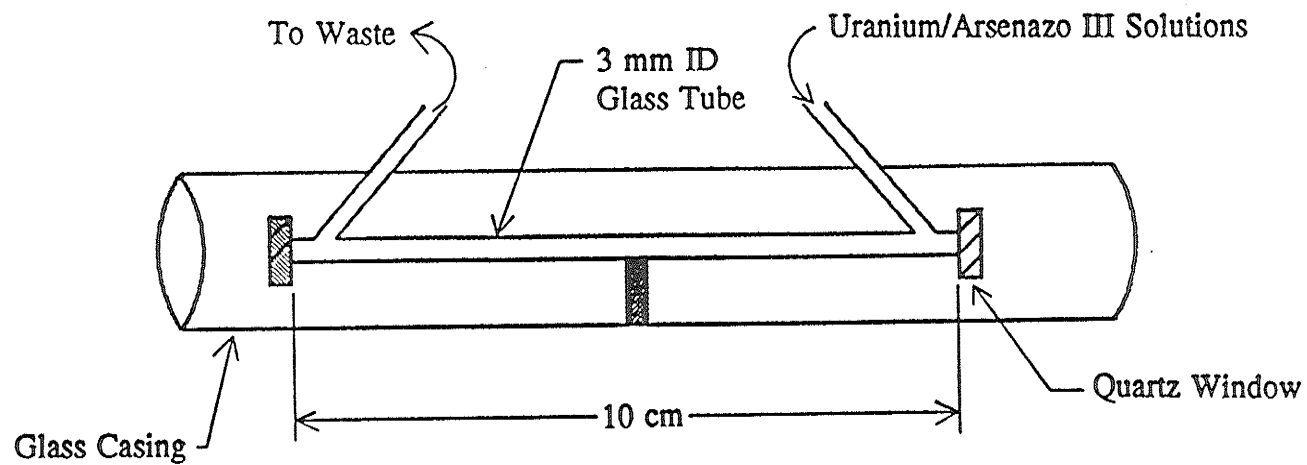


Figure 2.18 Cross-sectional view of a 10 cm glass flow cell

caused by either internal reflection from the glass walls or from dispersion occurring along the path length.

In an attempt to avoid any problems introduced by reflection of glass, flow cells made out of a Teflon™ cylinder were investigated. Flow cells of 5 cm and 10 cm were made by drilling a solid Teflon™ cylinder as shown for a 10 cm cell in Figure 2.19. Unfortunately, this cell showed the same effect as the previous cells. It was now suspected that the cause of the strong absorption in the 400 nm to 800 nm range was not due to cell design.

When the 5 cm Teflon™ cell was used, it was observed that the absorption was not as prominent as with the 10 cm Teflon™ cell and that it was occurring at the dye absorption maximum of 532 nm. This suggested that the concentration of the dye (i.e. 0.006%) was too high for the instrument to blank properly with the longer flow cells. The problem could be solved by diluting the Arsenazo III dye solution. To test this, Arsenazo III solutions of 0.0001, 0.0006, 0.0012 and 0.0025% were prepared by diluting the 0.006% Arsenazo III solution. These solutions were tested to check the optimal concentration of Arsenazo III required for the 10 cm glass flow cell.

Previously, air bubbles that were trapped near the windows of the 10 cm cell were removed by gently tapping the cell in an upright position and replacing the cell in its original alignment with the beam, but this proved to be too difficult. Hence to prevent air bubbles from entering the flow cell, the peristaltic pump was stopped during

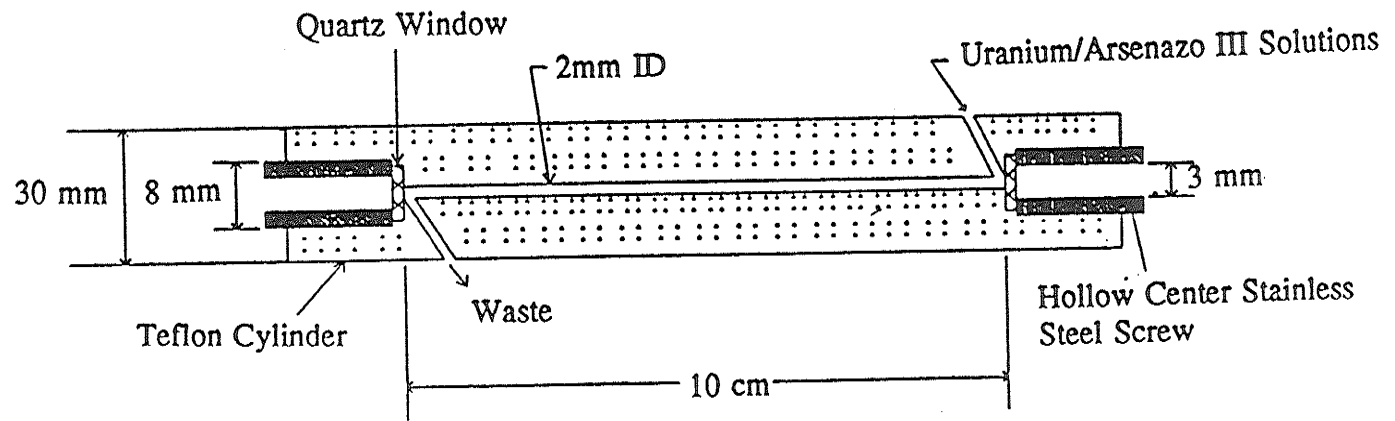


Figure 2.19 Cross-sectional view of a 10 cm Teflon™ flow cell



sample change. It was found that 0.0001, 0.0006 and 0.0012% Arsenazo III solutions were able to be blanked (i.e. zero absorption) by the instrument and so they were used to determine if the 10 cm flow cell could be used to analyze uranium at low concentrations. Different uranium standards were made by successively diluting a 100 ppm uranium stock solution. The standards made were from 0.010 to 0.500 ppm uranium and the calibration data obtained for 0.0001% Arsenazo III solution are given in Table 2.9.

It can be seen in Table 2.9 that standards 0.010, 0.025 and 0.050 ppm uranium, all showed very small corrected absorbance values. On eliminating the above standards, the resulting calibration graph is reasonably linear between 0.1 and 0.5 ppm uranium as shown in Figure 2.20. Although the calibration graph is linear between 0.1 and 0.5 ppm uranium, the absorbance values for the 0.5 ppm uranium was very low, i.e. 0.0387 with 0.0001% Arsenazo III solution. There are larger errors inherent to these measurements because of the low absorbances.

When the same standards were used with 0.0006% Arsenazo III, the absorbance generally increased as shown in Table 2.10 compared to when 0.0001 % Arsenazo III solution was used. On eliminating standards lower than 0.1 ppm uranium (due to the small absorbance values), a calibration graph between 0.1 and 0.5 ppm uranium resulted as shown in Figure 2.21.

**Table 2.9 Calibration data for uranium standards between 0.010 and 0.500 ppm using 0.0001% Arsenazo III solution**

STD #	Concentration (ppm)	Absorbance	Reference	Abs-Ref
1	0.010	-0.0006	-0.0032	0.0026
2	0.025	-0.0016	-0.0047	0.0031
3	0.050	-0.0011	-0.0057	0.0046
4	0.075	-0.0017	-0.0070	0.0053
5	0.100	0.0001	-0.0072	0.0073
6	0.150	0.0045	-0.0092	0.0137
7	0.250	0.0097	-0.0108	0.0205
8	0.350	0.0188	-0.0112	0.0299
9	0.500	0.0278	-0.0108	0.0387

A 10 cm glass flow cell was used.

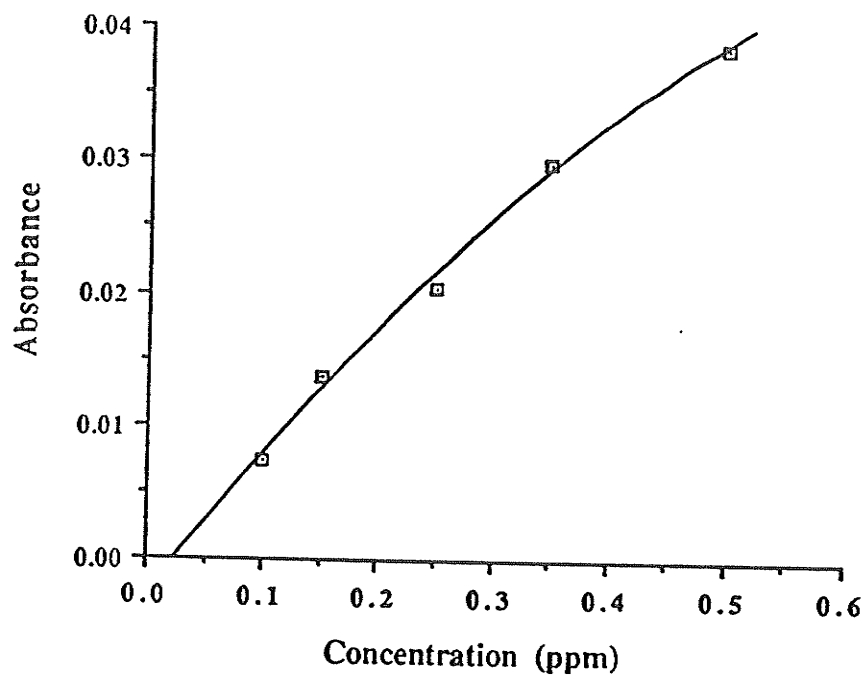


Figure 2.20 Calibration graph for uranium standards between 0.100 and 0.500 ppm using 0.0001% Arsenazo III solution

A 10 cm glass flow cell was used.

**Table 2.10 Calibration data for uranium standards between 0.025 and 0.500 ppm using 0.0006% Arsenazo III solution**

STD #	Concentration (ppm)	Absorbance	Reference	Abs-Ref
1	0.025	0.0073	-0.0005	0.0078
2	0.050	0.0114	-0.0007	0.0121
3	0.075	0.0163	-0.0022	0.0185
4	0.100	0.0202	-0.0019	0.0222
5	0.150	0.0469	-0.0011	0.0480
6	0.250	0.0787	-0.0002	0.0789
7	0.350	0.1211	0.0018	0.1194
8	0.500	0.1710	0.0032	0.1678

A 10 cm glass flow cell was used.

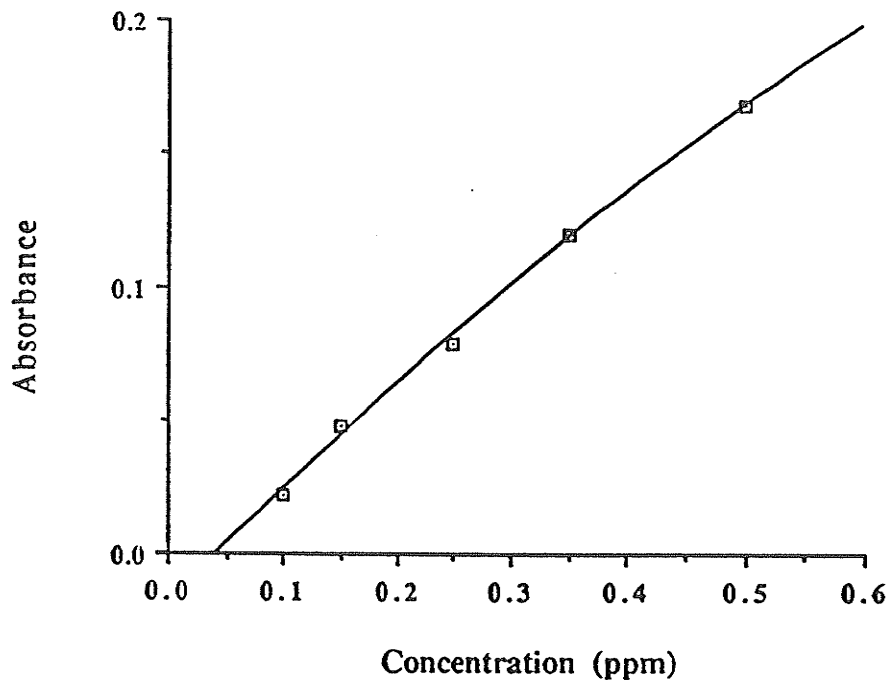


Figure 2.21 Calibration graph for uranium standards between 0.100 and 0.500 ppm using 0.0006% Arsenazo III solution

A 10 cm glass flow cell was used.

When the Arsenazo III concentration was increased to 0.0012%, a further increase in absorbance was obtained as shown in Table 2.11 compared to when 0.0006% or 0.0001% Arsenazo III solution was used. When standards lower than 0.1 ppm were eliminated (due to the small absorbance values), recalibration resulted in a linear graph between 0.1 and 0.5 ppm uranium as shown in Figure 2.22.

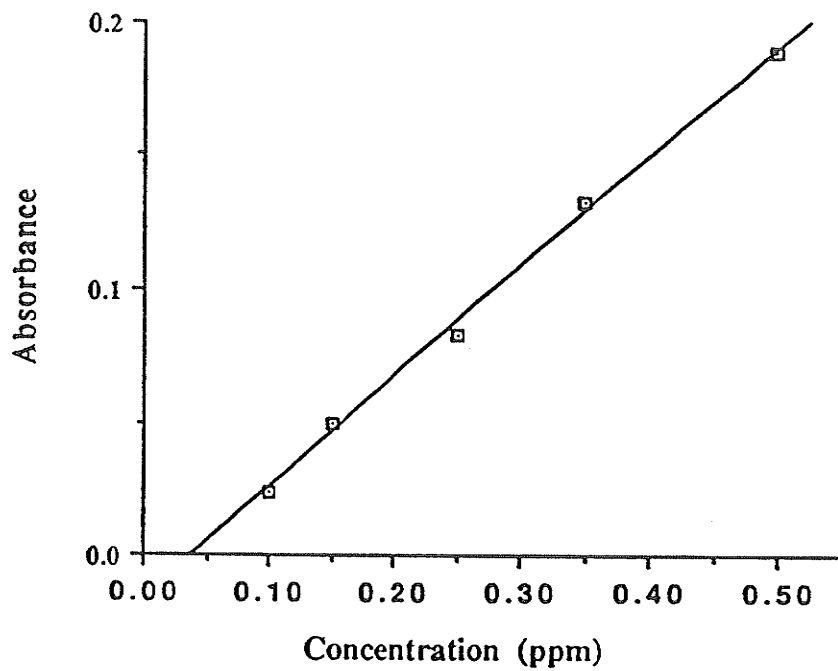
Even though the calibration curve was found to be linear between 0.1 and 0.5 ppm uranium with the use of a 10 cm quartz tube and 0.0012% Arsenazo III solution, there were practical problems associated with the use of these cells. Air bubbles get trapped, usually near the windows along the path of the beam, which needed to be removed by gently tapping the cell in an upright position. Teflon™ flow cells were not useful because any bubble formation was not visible due to the nature of Teflon™ used. Proper machining of the glass quartz tubes along with better design structure, especially, at the corners might prevent bubbles from lodging at the windows.

Rather than pursue a solution for the use of these longer cells, it was decided to perform all uranium analyses using the commercial 5 mm cell with uranium concentrations between 1 and 10 ppm U. The 5 mm flow cell (Markson™ Science Inc.) proved to be very convenient in minimizing any air bubble problem and avoiding alignment problems because it can be clamped firmly and reproducibly in a cell holder of the instrument. Even though the concentration of uranium in seawater is 3.3 ppb, the analysis of uranium in our laboratory using CFSM was limited to 1 to 10 ppm

**Table 2.11** Calibration data for uranium standards between 0.010 and 0.500 ppm using 0.0012% Arsenazo III solution

STD #	Concentration (ppm)	Absorbance	Reference	Abs-Ref
1	0.010	0.0081	0.0007	0.0075
2	0.025	0.0077	0.0005	0.0072
3	0.050	0.0138	-0.0004	0.0142
4	0.075	0.0195	0.0000	0.0195
5	0.100	0.0241	0.0000	0.0241
6	0.150	0.0506	0.0006	0.0500
7	0.250	0.0841	0.0019	0.0822
8	0.350	0.1346	0.0026	0.1319
9	0.500	0.1931	0.0045	0.1886

A 10 cm glass flow cell was used.



**Figure 2.22** Calibration graph for uranium standards between 0.100 and 0.500 ppm using 0.0012% Arsenazo III solution

A 10 cm glass flow cell was used.



uranium. This made the evaluation of the sorbents that were developed in our laboratory, which required the analysis of a large number of samples, more convenient.

### **2.3 Evaluation of the different analytical techniques**

Experiments performed by Dr. Kantipuly and Mr. Chan of our laboratory showed that the presence of calcium as a matrix constituent enhances the apparent uranium concentration when the analysis was carried out by ICP-AES and depresses it when carried out by DCP-AES. They have shown that when a 10 ppm uranium solution was spiked with 400 ppm of calcium and analyzed by ICP-AES, it reads a concentration of 11.6 ppm uranium and when the same solution was analyzed by DCP-AES it reads a concentration of 7.8 ppm uranium. The increase in ICP-AES measurements was attributed to a calcium line (385.96 nm) lying very close to the uranium analytical line. The decrease in DCP-AES measurements was attributed to physical or broadened spectral interferences. This enhancement of uranium signal in ICP-AES and the decrease in DCP-AES can be attributed to the different emission lines that were used for the analysis and also due to the different plasma generating systems that were used for the determination of uranium. The existence of matrix effects in argon plasma atomic emission spectrometers has been well documented in the literature.<sup>257,258</sup>

A correction factor for calcium was applied to solve the problem; this correction factor required an accurate and precise knowledge of the amount of calcium present. The

standard additions method, which has been regarded as a general remedy for matrix effects, was found to be too time-consuming when large numbers of samples had to be analyzed.

Evaluation of sorbents in our laboratory, in most cases, involved the analysis of uranium solutions with a simple matrix. The concentrations of uranium solutions were usually between 1 and 10 ppm. The above procedure of using a simple matrix and higher concentration of uranium (as compared to uranium in seawater) was undertaken so that the analysis of uranium could be performed in our laboratory.

To determine if the resins were capable of sorbing uranium from actual seawater, the resins were evaluated by testing in actual seawater (Patricia Bay, Sydney, B.C., Canada). The eluates from the resins for seawater samples were analyzed by ICP-MS and ICP-AES. Matrix interferences that were noticed in the plasma emission techniques (due to spectral line interferences) were eliminated when ICP-MS was used as it uses a mass spectrometer that detects the uranium isotopes. Of the three techniques used for the analysis of uranium from seawater matrix (i.e. ICP-AES, DCP-AES and ICP-MS), ICP-MS performed much better as far as matrix problems were concerned.

To analyze uranium with a simple aqueous solution as the matrix, CFMS with Arsenazo III proved to perform adequately for small concentrations of uranium (0.1 to

0.5 ppm uranium) when a 10 cm flow cell was used. When a 5 mm Markson™ flow cell was used, the analysis of uranium solutions whose concentrations fell between 1 and 10 ppm uranium, proved to be rapid and accurate.

## 2.4 Conclusion

Four analytical techniques were used for the analysis of uranium in our work, i.e. ICP-AES, DCP-AES, ICP-MS and CFMS. The three plasma techniques use expensive instruments which are not commonly available in many laboratories. CFMS is relatively less expensive and is capable of analyzing for uranium or thorium individually, provided they are in a simple aqueous matrix. Th, Zr, Hg and rare earths interfere with the determination of uranium with Arsenazo III but, with the use of selective masking agents, this problem can be avoided.<sup>245</sup>

Of the four techniques used, ICP-MS is the most sensitive (i.e. low detection limit) with minimal matrix interferences. Spectral line overlap, which is an inherent problem with ICP-AES and DCP-AES, is caused by a variety of elements that are present in the matrix. In ICP-MS, this problem of spectral overlap is avoided as it uses a quadrupole mass analyser as a filter. Another advantage of ICP-MS over ICP-AES or DCP-AES is that it can determine isotope ratios for the elements of interest. The determining of isotope ratios could prove useful in the monitoring of radionuclides in the environment. For example, only a certain isotope of an element may be radioactive or needed to be monitored for health reasons (for example, nuclear testing,

radioactive fallout, monitoring of nuclear plants, etc.) or the isotope ratio may be indicative of the source of the element.

ICP-MS is not generally suitable for solutions with high salt content, i.e. > 0.2% as the salt gets deposited on the orifice located at the interface between the ICP and MS. This causes a drift in the slope and/or the intercept of the calibration curve.<sup>259</sup> A preconcentration step may still be required for determining trace or ultra trace metals in seawater.

Uranium solutions with concentrations between 1.0 and 10.0 ppm or thorium solutions with concentrations between 1.0 and 5.0 ppm or between 0.1 and 1.0 ppm can be analyzed with a 5 mm flow cell and 0.006% Arsenazo III solution. Uranium solutions with concentrations between 0.1 and 0.5 ppm can be analyzed with a 10 cm flow cell and 0.0012% Arsenazo III solution. The 10 cm flow cell needs better designing or machining to prevent air bubbles from getting stuck in the tube. An alternative way would be to prevent air bubbles from entering the flow cell by stopping the peristaltic pump before sample change. An advantage of using a flow cell over a normal cell is that it takes less time to perform an analysis, i.e. over 60 samples can be analyzed in an hour. The tedious process of manually cleaning and rinsing a normal cell is avoided in CFMS. Another advantage of using a flow cell is that the time for complex formation is always a constant, which may be difficult to achieve using a normal cell.

Although DCP-AES and ICP-AES can provide satisfactory analyses under many conditions, the ICP-MS is better in terms of greater sensitivity and minimal matrix interferences. However for routine analysis, for solutions with a simple matrix, the method developed using the continuous flow spectrophotometric method is satisfactory for uranium determination for concentrations as low as 0.1 ppm uranium.

**CHAPTER III****EXTRACTION OF URANIUM FROM AQUEOUS SYSTEMS USING  
COMMONLY AVAILABLE SORBENTS****3 Introduction**

A number of sorbents that are commonly available in an analytical laboratory were evaluated for their ability to extract uranium from simple aqueous solutions.

Experiments were then performed to evaluate the sorbents that were capable of extracting uranium from complex aqueous solutions containing uranium in addition to nine other competing ions. This procedure was done to determine the nature of the functional group of the sorbents that could be used for the selective extraction of uranium from an even more complex system, such as natural water (eg. sea, ocean, lakes, rivers, streams, etc.). Seawater, for example, has more than 80 elements present in solution and extracting uranium from this matrix would involve the use of a sorbent with a functional group which is highly selective for uranium.

An evaluation of these sorbents to determine the effectiveness of various functional groups in extracting uranium from simple and complex aqueous solutions will be discussed in this chapter.

### 3.1 Materials used

#### 3.1.1 Reagents used

Calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ, USA). Sodium chloride ( $\text{NaCl}$ ), ferrous ammonium sulphate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ), manganous sulphate ( $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ ), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) and nickel ammonium sulphate ( $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) were obtained from Fisher Scientific Co. (Fairlawn, NJ, USA). Anhydrous copper sulphate ( $\text{CuSO}_4$ ) and uranyl acetate ( $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) were obtained from BDH Chemicals Ltd. (Poole, England). Zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was obtained from Matheson Company Inc. (East Rutherford, NJ, USA). The above chemicals were of reagent grade and were used without further purification.

A stock solution containing 1000 ppm of each of the following metals was prepared by dissolving 5.8927 grams of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 10.5492 grams of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 2.5413 grams of  $\text{NaCl}$ , 2.5116 grams of  $\text{CuSO}_4$ , 3.3576 grams of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 7.0211 grams of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 3.4780 grams of  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ , 1.5985 grams of  $\text{Pb}(\text{NO}_3)_2$ , 6.7298 grams of  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and 1.7820 grams of  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in 1 litre of water. Solutions containing 100 and 10 ppm of each of the above metals were prepared by successive dilutions of the 1000 ppm stock solution.

### 3.1.2 Sorbents used

AG 2X8, AG 1X8, AG 50WX8, AG MP1, Bio-Rex 70 and Chelex 100 were obtained from Bio-Rad Laboratories (Richmond, CA, USA). Rexyn 101, Rexyn 102, Rexyn 201, Rexyn 203, Rexyn AG4 and Florisil were obtained from Fisher Scientific Co. (Fairlawn, NJ, USA). Amberlite IRA-400, Amberlite IRA-401, Amberlite IRC-718, Amberlite IR-120, Amberlite CG-400 I, Amberlite CG-400 II, Amberlite IR-45 and Amberlite IRC-50 were obtained from Rohm and Haas Company (Philadelphia, PA, USA). Dowex 1X4, Dowex 1X10, Dowex 2X8, Dowex 50WX8 and Dowex 21K were obtained from J. T. Baker Chemical Company (Phillipsburg, NJ, USA). Chromosorb W was obtained from Wilkens Instrument and Research Inc. (Walnut Creek, CA, USA) and Seelex A100 from Seekay Chemical Company (New York, NY, USA). Polythioether and poly- $\beta$ -diketone were obtained from Dr. Chow and Dr. Gesser respectively, from the Department of Chemistry, University of Manitoba. Some of the sorbents that were used were old and have been discontinued for production by the manufacturer.

The above sorbents that were used in this study can be broadly classified as cation exchange, anion exchange, chelating or miscellaneous sorbents as shown in Table 3.1. The sorbents were used as provided by the manufacturer (i.e. no pretreatment of the sorbent for the purpose of cleaning or otherwise was undertaken). The sorbents were used in this way as the pretreatment procedure for each sorbent would be different and would have to be determined prior to their use for that particular extraction system.



**TABLE 3.1 Classification of the sorbents used for the extraction of uranium from simple aqueous systems**

<u>Functional Group</u>	<u>Sorbents</u>
A Cation exchange resin with strongly acidic group - sulphonic acid	AG 50WX8, Dowex 50WX8 Amberlite IR-120 and Rexyn 101
B Cation exchange resins with weakly acidic group - carboxylic acid	Bio-Rex 70, Amberlite IRC-50 and Rexyn 102
C Anion exchange resins with strongly basic group - Quaternary ammonium	Amberlite CG-400 I, Amberlite CG-400 II, Amberlite IRA-400, Amberlite IRA-401, AG 1X8, AG 2X8, AG MP1, Rexyn 201, Rexyn AG4, Dowex 1X4, Dowex 1X10, Dowex 2X8 and Dowex 21K
D Anion exchange resin with weakly basic group - polyamine	Amberlite IR-45 and Rexyn 203
E Chelating resins	
- iminodiacetic acid	Chelex 100 and Amberlite IRC-718
- amine and carboxyl groups	Seelex A100
- $\beta$ -diketone	Poly- $\beta$ -diketone
F Miscellaneous Sorbents	
- thio ether	polythioether
- diatomite	Chromosorb W
- magnesia-silica gel	Florisil

### 3.1.3 Apparatus used

Measurements of pH were obtained using a Fisher Accumet™ Model 825 MP pH meter. Adjustments of pH were made using 2M HNO<sub>3</sub> or 2M KOH. Water used for making the solutions was purified by reverse osmosis. Whatman™ 541 filter paper was used for all filtering purposes.

### 3.2 Procedure

The sorbent capability for the extraction of uranium was determined using the following general procedure. Approximately one gram of the sorbent was weighed and placed into a 125 mL glass Erlenmeyer flask. After the addition of 25 mL of 10 ppm uranium solution, the flask was covered with Parafilm™. The covered flask was hand shaken every 8 hours for a total of 24 hours. The sorbent was separated from solution by filtering through a filter paper and the filtrate analyzed by ICP-AES to determine the amount of uranium left in solution. A blank extraction was conducted in a similar way by equilibrating one gram of the sorbent with 25 mL of purified water to determine if any cations were leaching from the sorbent. The amount of uranium that was actually available for extraction was determined in a similar way, without the addition of the sorbent, by taking 25 mL of 10 ppm uranium solution in the flask. After equilibrating for 24 hours the filtered solution was analyzed by ICP-AES. The amount of uranium that was actually available for extraction was determined in order to allow for any loss of uranium due to precipitation or adsorption of uranium on the flask or filter paper.

### 3.2.1 *Extraction of uranium from simple aqueous solution*

This study was undertaken to determine the sorbent capability for the uptake of uranium from simple aqueous solution, i.e. uranyl acetate solution.

A 10 ppm uranium solution was prepared by successive dilution of a 2000 ppm uranium stock solution. The 2000 ppm stock solution was prepared by dissolving 3.564 grams of uranyl acetate ( $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) in 1 litre of deionized water. The pH of the 100 ppm uranium solution was found to be 4.1, but for this study the pH of the 10 ppm uranium solution was adjusted to 7.0 by using 2M KOH. The pH of 7.0 was chosen so as to have a neutral pH, and because the pH values of most natural waters was  $7.0 \pm 3.0$ . The capability of the sorbents for the uptake of uranium from simple aqueous solution was determined by equilibrating 25 mL of 10 ppm uranium solution with one gram of the sorbent in a 125 mL Erlenmeyer flask. The flasks were covered with Parafilm™ and the covered flasks hand shaken every 8 hours for a total of 24 hours.

Cations that leached from the sorbent at pH 7.0 were determined by performing a blank extraction in a similar way by using 25 mL of water (pH was adjusted to 7.0) instead of the 10 ppm uranium solution. The amount of uranium that was actually available for extraction was determined in a similar way by placing just the 25 mL of 10 ppm uranium solution in a 125 mL Erlenmeyer flask, which was covered with Parafilm™ and shaken every 8 hours for a total of 24 hours.

The sorbents were separated from solution by filtering through a Whatman™ 541 filter paper which is suitable for retaining coarse and gelatinous precipitates. The filtered solutions were analyzed by ICP-AES.

### ***3.2.2 Extraction of uranium from complex aqueous solution***

The study was undertaken to determine the capability of the sorbents for the selective uptake of uranium from a complex solution that contained nine competing ions in addition to uranium.

The 1000, 100 and 10 ppm solutions which contained all the ten cations appeared cloudy, suggesting formation of some precipitate which may have been lead chloride or iron hydroxide. The pH of the 10 ppm solution was found to be 3.0 and when an attempt was being made to raise its pH to 7.0, it was noticed that the precipitation increased with the addition of 2M KOH. This effect suggested that the precipitate must be a hydroxide, possibly iron hydroxide.

Experiments to determine sorbent selectivity were conducted at the original pH of the 10 ppm solution (i.e. 3.0) because precipitation increased with an increase of the pH from 3.0 to 7.0. This minimized complications that might arise from occlusion of cations inside the precipitate or from the precipitate itself acting as a sorbent for some of the cations that were present in solution.

The capability of the sorbents for the selective uptake of uranium from a complex solution that contained several competing ions was determined by equilibrating 1 gram of the sorbent with 25 mL of the solution that contained 10 ppm of each of the nine ions in addition to uranium. The particular cations were chosen for our study as they are commonly present in natural water systems and also because the analysis of these ions was convenient since the ICP-AES instrument had the capability to analyze all of them simultaneously.

A blank extraction using water, instead of the 10 ppm solution, was performed in a similar way to determine if any metals were leaching out of the sorbent at pH 3.0. The concentration of the cations that was available for extraction was determined by placing 25 mL of the 10 ppm solution that contained the ten cations in a 125 mL Erlenmeyer flask. The flasks were covered with Parafilm™ and hand shaken every 8 hours for a total of 24 hours. The filtered solutions were analyzed by ICP-AES.

### 3.3 Results and discussion

One of the criteria used for the evaluation of the sorbents was percent extraction (% E) and was calculated using the equation:

$$\% E = \{I - (F - B)\} \cdot I^{-1} \times 100$$

where, I was the concentration of the metal ion of interest ( $M^{n+}$ ) that was available for

extraction, **F** was the concentration of  $M^{n+}$  that was left in solution after extraction and **B** was the concentration of the  $M^{n+}$  that leached from the sorbent when a blank extraction was performed.

ICP-AES readings that were below the detection limits were treated as zero ppm and are indicated with an asterisk (detection limits for each element are shown at the end of both Tables 3.2 and 3.3). ICP-AES software at times reported certain readings as > 'x' ppm, which meant that the concentration was beyond the linear range of the calibration graph for that metal ion and that the concentration was higher than 'x' ppm.

In Tables 3.2 and 3.3, percent extraction, at times, were reported as < 0 or > 100 and, for our evaluation of the sorbents, they were treated as 0 and 100 respectively.

Negative extraction values, i.e. less than zero, occurred when (**F-B**) was greater than both **I** and zero. This negative value for % **E** can be explained by the fact that some sorbents swell by absorbing water, and this leaves the resulting solution more concentrated in the metal ion than what was originally present before the addition of the sorbent (i.e. **F** is greater than **I**).

Similarly, percent extraction values greater than 100 may occur when **B** is larger than **F**. This happened when the concentration of  $M^{n+}$  leaching from the sorbent during the blank extraction (**B**) was higher than the concentration of  $M^{n+}$  that was left in solution

(F) during a normal analytical extraction. The problem of trace metals leaching from the sorbent can be prevented by adopting a cleaning procedure to remove trace metals from the sorbents prior to their use. The cleaning procedure might involve the use of a Soxhlet extractor and an organic solvent to remove organic or organometallic impurities. This could be followed by treating the sorbents with suitable eluting agents for inorganic species such as strong mineral acids. The cleaning procedure would be different for each sorbent and would depend on the nature of the functional group present in the sorbent as well as the physical and chemical stability of the sorbent itself.

The problems associated with swelling of the sorbent may be prevented by pre-swelling the sorbent before its use in a solution of similar ionic strength and pH as the sample solution that is to be analyzed. Although such treatments would be useful in treating real samples, the calculation of extraction efficiencies would be difficult for the present test samples due to varying amounts of remaining liquids.

### **3.3.1 Sorbent behaviour in simple aqueous solution**

Table 3.2 indicates only two sorbents (i.e. Dowex 21K and Dowex 2X8) were not efficient (i.e. < 10% E) in the extraction of uranium. Four sorbents showed reasonable extraction capability (i.e. % E was between 10 and 75), as follows:

AG MP1, Dowex 1X10, Chromosorb W and polythioether. The remaining twenty of the twenty-six sorbents that were tested showed good capability (i.e. % E > 75) for the

Table 3.2 Extraction capability of various sorbents for the separation of uranium from simple aqueous solution

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
A: Cation exchange resins with strongly acidic functionality (sulphonic acid)												
AG 50WX8	S	*0.459	0.680	1.140	0.390	0.160	0.059	*0.003	*0.036	0.013	0	100.0
	Bk	0.560	0.640	*0.960	0.390	0.220	0.048	*0.002	0.000	0.020	0	
Dowex 50WX8	S	0.650	0.741	1.160	0.360	0.164	0.069	*0.005	*0.058	0.029	*0.272	100.0
	Bk	1.075	*0.394	1.270	0.562	0.235	0.133	*0.008	*0.063	0.046	0	
Amberlite IR-120	S	0.568	0.710	1.410	0.465	0.269	0.047	*0.003	*0.068	0.024	*0.475	100.0
	Bk	0.573	0.806	1.200	0.378	0.187	0.038	*0.002	*0.009	0.011	0	
Rexyn 101	S	*0.332	0.737	1.060	0.355	0.174	0.029	*0.002	*0.034	0.017	*0.059	100.0
	Bk	*0.227	*0.331	*0.762	0.265	0.134	*0.014	*0.001	0	*0.007	0	



Table 3.2 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
B: Cation exchange resins with weakly acidic functionality (carboxylic acid)												
BIO-REX 70	S	*0.120	*0.240	> 400	0.140	0.030	0	0	0	0	0	100.0
	Bk	*0.150	*0.310	340	0.125	0.027	0	0	0	0	0	
Amberlite IRC-50	S	0.668	0.945	2.91	0.391	0.192	0.034	*0.003	*0.053	0.023	1.020	89.1
	Bk	1.300	0.960	3.32	0.610	0.252	0.098	0	*0.065	0.022	0	
Rexyn 102	S	0.550	0.765	3.18	0.500	0.308	0.056	*0.005	*0.038	0.022	*0.850	100.0
	Bk	0.670	0.712	2.58	0.430	0.184	0.034	*0.002	0	0.012	0	

Table 3.2 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
C: Anion exchange resins with strongly basic functionality (Quaternary Ammonium)												
Amberlite CG-400 I	S	0.674	0.955	28.8	0.329	0.273	*0.012	*0.003	*0.037	0.025	0.080	100.0
	Bk	0.580	0.830	19.3	0.449	0.275	*0.011	*0.002	0	0.010	0	
Amberlite CG-400 II	S	1.300	0.730	32.7	0.808	0.279	*0.018	*0.006	*0.036	0.027	0.136	100.0
	Bk	0.702	0.761	17.1	0.230	0.180	0	0	0	0.003	0	
Amberlite IRA-400	S	0.724	0.545	1.74	0.400	0.304	*0.014	*0.003	*0.044	0.018	1.200	87.1
	Bk	0.562	0.518	1.48	0.321	0.203	*0.002	0	0	0.007	0	
Amberlite IRA-401	S	1.350	1.020	1.09	0.313	0.300	*0.015	*0.016	*0.053	0.019	1.030	89.0
	Bk	1.100	1.150	1.32	0.300	0.309	*0.006	*0.014	0	0.016	0	
AG 1X8	S	0.696	*0.199	1.44	0.170	0.146	0.031	*0.004	*0.058	0.014	1.480	84.1
	Bk	*0.39	0.589	*0.69	0.300	0.162	0.020	0	*0.024	0.090	0.023	

Table 3.2 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
C: Anion exchange resins with strongly basic functionality (Quaternary Ammonium)												
AG MP1	S	0.925	0.948	2.60	0.606	0.334	2.050	*0.009	*0.105	0.038	6.300	32.5
	Bk	0.508	*0.222	2.50	0.258	0.094	0.266	0	0	0.006	0	
Rexyn 201	S	1.300	0.617	1.33	0.154	0.302	*0.001	*0.004	*0.029	0.013	*0.033	100.0
	Bk	1.090	0.533	*0.97	0.144	0.222	0	*0.002	0	0	0	
Rexyn AG-4	S	0.639	0.788	1.80	0.579	0.280	0.506	*0.003	*0.030	0.022	*0.700	100.0
	Bk	*0.490	*0.440	1.10	0.330	0.186	0.360	*0.001	0	*0.006	0	
Dowex 1X4	S	0.784	0.675	1.88	0.432	0.266	*0.019	*0.007	*0.055	0.023	1.170	87.5
	Bk	0.511	0.688	1.10	0.348	0.164	*0.010	*0.003	*0.010	*0.009	0	
Dowex 1X10	S	0.545	*0.461	1.30	0.309	47.75	0.110	*0.003	*0.070	0.017	2.970	68.2
	Bk	0.699	0.514	1.18	0.491	37.10	0.070	*0.003	*0.025	0.015	0	

Table 3.2 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
C: Anion exchange resins with strongly basic functionality (Quaternary Ammonium)												
Dowex 2X8	S	0.782	0.728	2.04	0.469	0.246	0.128	*0.009	*0.085	0.028	9.245	1.0
	BK	0.920	0.570	2.63	0.661	0.213	0.041	*0.002	*0.125	0.021	0	
Dowex 21K	S	0.863	0.684	1.67	0.512	0.352	0.545	*0.011	*0.115	0.038	13.85	< 0.0
	BK	1.085	0.770	1.71	0.615	0.307	0.176	*0.003	*0.042	0.180	0	
D: Chelating Resins												
Poly- $\beta$ -Diketone ( $\beta$ -diketone group)	S	0.870	0.570	2.85	0.445	0.256	0.056	*0.006	*0.030	0.037	*0.291	100
	BK	0.960	*0.378	3.765	0.420	0.210	0.039	*0.002	0	0.010	0	

Table 3.2 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
E: Anion exchange resins with weakly basic functionality (polyamine)												
Amberlite IR-45	S	1.730	1.410	1.76	0.342	0.185	*0.014	0.023	*0.043	0.026	*0.178	100.0
	BK	1.840	1.690	1.22	0.358	0.145	*0.010	0.022	*0.006	0.022	*0.029	
Rexyn 203	S	0.736	0.570	1.41	0.420	0.150	*0.005	*0.002	*0.014	0.019	*0.144	100.0
	BK	0.706	0.810	1.80	0.560	0.120	0	*0.002	0	0.011	0	

Table 3.2 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U	% E Uranium
F: Miscellaneous Sorbents												
Chromosorb W (diatomite)	S	0.570	0.668	14.1	0.133	0.085	*0.014	*0.003	*0.035	*0.008	4.81	48.5
	Bk	0.939	3.470	7.60	0.139	0.072	0	0	0	0	0	
Poly-thio- ether (thioether group)	S	*0.457	*0.420	1.34	0.310	0.168	0.029	*0.003	*0.027	0.019	3.11	66.7
	Bk	*0.340	*0.470	*0.95	0.340	0.180	*0.003	0	0	0	0	
Florisil (Magnesia- -silica gel)	S	1.220	11.300	215	0.079	0.030	*0.005	0	*0.008	0	0	100.0
	Bk	1.040	9.620	232	0.093	0.039	0	0	*0.013	*0.005	0	
Amberlite IRC-718	S	*0.360	0.630	> 400	0.455	0.214	0.025	0	*0.070	*0.008	*0.62	100.0
	Bk	*0.315	*0.440	> 400	0.370	0.175	*0.008	0	0	0	0	

Table 3.2 Continued

Sorbent	Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
Detection Limits	0.500	0.500	1.00	0.010	0.010	0.020	0.020	1.000	0.010	1.000
Available U Concentration	---	---	---	---	---	---	---	---	---	9.340

"S" and "Bk" are the ICP-AES analysis of the sample solution and blank solution respectively. ICP-AES readings are in ppm and are an average of two burns.

**Table 3.3 Extraction capabilities of various sorbents for the separation of uranium from complex aqueous solution**

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
A: Cation exchange resins with strongly acidic functionality (sulphonic acid)											
AG 50WX8	S	0.641	*0.465	8.24	0.385	0.390	0.589	0.482	*0.194	0.311	0
	Bk	*0.364	*0.096	5.37	0.014	0.014	*0.017	*0.003	*0.026	0.000	0
	%E	94.3	100.0	79.2	96.7	96.7	87.2	96.8	100.0	96.9	100.0
Dowex 50WX8	S	*0.430	*0.204	8.16	0.161	0.161	0.757	0.183	*0.037	0.115	0
	Bk	*0.309	*0.045	5.24	0.020	0.016	*0.002	*0.004	*0.092	0.012	0
	%E	100.0	100.0	78.8	98.7	98.7	83.6	98.8	100.0	99.0	100.0
Amberlite IR-120	S	0.771	*0.488	29.8	0.365	0.387	0.875	0.502	*0.144	0.310	0
	Bk	*0.252	*0.040	16.6	0.012	0.018	0.000	*0.002	*0.043	*0.004	*0.414
	%E	93.2	100.0	4.3	96.8	96.7	81.1	96.7	100.0	96.9	100.0
Rexyn 101	S	0.614	*0.413	7.86	0.265	0.455	0.812	0.428	*0.026	0.266	*0.067
	Bk	*0.322	*0.048	5.77	0.045	0.074	*0.007	*0.003	*0.075	0.013	0
	%E	94.6	100.0	84.8	98.0	96.7	82.4	97.2	100.0	97.5	100.0



Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
B: Anion exchange resins with strongly basic functionality (Quaternary ammonium)											
Amberlite CG-400 I	S	6.490	7.560	88.2	6.540	6.670	0.982	9.260	4.010	6.050	5.140
	Bk	*0.275	*0.095	68.7	0.036	0.046	*0.010	*0.004	*0.760	0.010	0.000
	%E	42.6	37.5	< 0.0	41.4	41.4	78.7	39.5	56.1	40.2	55.3
Amberlite CG-400 II	S	5.350	6.720	58.0	2.060	5.130	0.213	7.930	1.290	4.990	1.950
	Bk	*0.227	*0.046	42.4	0.039	0.042	0.023	*0.003	*0.074	0.011	0.000
	%E	52.6	44.5	< 0.0	81.8	55.0	95.9	48.2	85.9	50.7	83.0
Amberlite IRA-400	S	11.500	12.400	17.1	11.100	11.400	0.410	16.100	9.080	10.200	10.200
	Bk	*0.164	*0.049	4.04	0.075	0.088	0.000	*0.004	*0.081	0.016	0.000
	%E	< 0.0	< 0.0	5.4	0.7	< 0.0	91.1	< 0.0	0.7	< 0.7	11.3
Amberlite IRA-401	S	10.800	11.500	24.7	7.870	10.300	0.226	14.500	4.750	9.310	*0.094
	Bk	2.110	0.567	11.9	0.010	0.017	0.000	*0.006	*0.020	0.0	*0.782
	%E	23.1	9.6	7.2	29.2	9.0	95.1	5.2	48.0	7.8	100

Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
B: Anion exchange resins with strongly basic functionality (Quaternary ammonium)											
AG 1X8	S	11.700	12.500	18.50	11.700	11.600	1.590	16.200	10.300	10.300	9.660
	Bk	1.050	*0.154	5.83	0.200	0.099	0.144	*0.004	*0.083	0.016	0.000
	%E	5.7	< 0.0	8.2	< 0.0	< 0.0	68.7	< 0.0	< 0.0	< 0.0	16.0
AG 2X8	S	11.500	12.400	18.000	11.700	11.600	1.880	15.800	10.200	10.400	10.800
	Bk	0.538	*0.219	6.13	0.185	0.165	0.038	0.180	*0.082	0.110	*0.951
	%E	3.0	< 0.0	14.0	< 0.0	< 0.0	60.1	< 0.0	< 0.0	< 0.0	6.1
AG MP1	S	9.600	10.300	394	9.770	9.580	1.440	13.400	8.270	8.610	8.730
	Bk	*0.356	*0.365	201	0.161	0.065	1.350	*0.002	*0.011	0.000	0.000
	%E	15.0	14.9	< 0.0	13.4	15.8	98.0	12.4	9.5	14.7	24.1
Rexyn 201	S	10.400	11.100	14.10	1.890	23.100	0.185	14.400	*0.771	9.130	0.000
	Bk	0.980	*0.051	5.21	0.017	1.760	0.000	*0.002	*0.056	*0.008	0.000
	%E	16.6	8.3	35.6	83.1	< 0.0	96.0	5.9	100.0	9.6	100.0

Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
B: Anion exchange resins with strongly basic functionality (Quaternary ammonium)											
Rexyn AG4	S	11.400	12.300	17.70	11.000	11.300	2.110	15.400	9.790	10.100	1.040
	Bk	0.584	0.520	6.21	0.050	0.122	0.479	*0.006	*0.028	*0.004	*0.448
	%E	4.3	2.6	16.7	1.3	1.1	64.7	< 0.0	< 0.0	0.0	91.0
Dowex 1X4	S	11.000	11.600	17.60	10.200	10.600	0.333	14.900	7.880	9.620	9.660
	Bk	*0.413	*0.082	4.25	0.031	0.000	0.000	*0.002	*0.043	*0.006	0.000
	%E	2.6	4.1	3.2	8.4	6.2	92.8	2.6	13.8	4.7	16.0
Dowex 1X10	S	10.800	11.500	17.40	10.800	> 50.0	2.350	14.900	9.380	9.620	8.400
	Bk	0.665	*0.122	6.43	0.119	> 50.0	0.043	*0.004	*0.218	0.032	0.000
	%E	10.3	5.0	20.5	3.8	-NA-	50.1	2.6	< 0.0	5.1	27.0
Dowex 2X8	S	11.000	11.800	17.30	11.100	10.900	8.860	15.300	9.600	9.750	10.700
	Bk	0.631	*0.137	5.91	0.074	0.102	0.216	*0.006	*0.080	0.011	0.000
	%E	8.2	2.5	17.5	0.7	4.4	< 0.0	0.0	0.0	3.6	7.0

Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
B: Anion exchange resins with strongly basic functionality (Quaternary ammonium)											
Dowex 21K	S	11.100	11.700	17.10	10.700	10.600	19.100	15.000	9.650	9.690	11.400
	Bk	0.936	*0.254	5.45	0.077	0.035	17.900	*0.013	*0.091	0.016	0.000
	E	10.0	3.3	15.6	4.3	6.5	74.0	2.0	< 0.0	< 0.0	0.9
C: Cation exchange resins with weakly acidic functionality (carboxylic acid)											
Rexyn 102	S	9.190	10.400	21.60	6.380	9.290	1.030	13.100	1.060	8.280	2.410
	Bk	*0.107	*0.015	5.44	0.017	0.096	*0.010	*0.001	*0.053	*0.005	0
	%E	18.7	14.0	< 0.0	42.7	18.6	77.7	14.4	88.4	18.0	79.0

Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
D: Anion exchange resins with weakly basic functionality (polyamine)											
Amberlite IR-45	S	11.000	11.600	15.00	2.130	3.720	0.194	14.000	*0.282	6.300	*0.918
	Bk	4.800	2.220	5.87	0.047	0.052	0.000	0.048	*0.084	0.018	0.000
	%E	45.1	22.5	33.8	81.2	67.5	95.8	8.8	100.0	37.8	100.0
Rexyn 203	S	10.700	11.900	16.60	10.100	3.680	0.154	14.100	*0.293	7.730	8.740
	Bk	*0.376	*0.052	16.20	*0.008	*0.004	0.000	*0.007	0.000	0.000	0.000
	%E	5.3	1.6	97.1	9.0	67.4	96.7	7.8	100.0	23.5	24.0

Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
E: Chelating resins											
Chelex 100 (imino- diacetic acid group)	S	1.160	1.390	138.00	0.797	0.820	0.151	1.140	*0.647	0.797	1.780
	Bk	0.000	*0.017	218.00	0.000	*0.003	0.000	*0.005	0.000	0.000	0.000
	%E	89.7	88.5	> 100.0	92.8	92.7	96.7	92.5	100.0	92.1	84.5
Seelex A100 (amine with carboxylic group)	S	> 400	10.500	18.70	7.800	5.750	5.680	7.490	7.170	4.730	24.000
	Bk	> 400	1.450	8.01	0.045	0.133	0.933	0.043	*0.561	*0.009	22.600
	%E	-NA-	25.2	22.5	30.1	50.3	< 0.0	51.3	21.5	53.2	87.8
Poly- $\beta$ - diketone ( $\beta$ -diketone group)	S	10.800	11.300	19.90	9.790	10.500	7.790	14.500	8.080	9.350	7.550
	Bk	1.080	*0.066	12.90	0.438	0.076	0.034	*0.005	*0.227	*0.007	1.370
	%E	14.0	6.6	49.3	15.7	7.7	< 0.0	5.2	11.6	7.4	46.3
Amberlite IRC-718 (imino- diacetic acid)	S	1.200	1.550	> 400	1.650	1.490	0.172	3.540	*0.892	2.800	1.060
	Bk	*0.086	*0.260	> 400	0.027	0.038	0.000	0.000	0.000	0.000	*0.059
	%E	89.4	87.2	-NA-	85.4	87.1	96.3	76.9	100.0	72.3	90.8

Table 3.3 Continued

Sorbent		Ca	Mg	Na	Cu	Zn	Fe	Mn	Pb	Ni	U
F: Miscellaneous sorbents											
Chromosorb W (diatomite)	S	10.300	12.000	29.20	9.220	9.980	0.105	13.900	2.370	9.050	5.400
	Bk	*0.241	0.512	73.20	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	%E	8.8	5.1	> 100.0	16.9	11.7	97.7	9.1	74.1	10.4	53.0
Florisil (Magnesia silica gel)	S	1.240	20.200	222.00	0.481	0.364	0.121	0.175	*0.248	0.163	0.000
	Bk	2.420	38.000	331.00	0.025	0.033	0.000	*0.001	*0.070	0.011	0.000
	%E	> 100.0	> 100.0	> 100.0	95.9	97.1	97.4	98.9	100.0	98.5	100.0
Concentration available		11.300	12.100	13.80	11.100	11.300	4.620	15.300	9.140	10.100	11.500
Detection limits		0.500	0.500	1.00	0.010	0.010	0.020	0.020	1.000	0.010	1.000

"S" and "Bk" are the ICP-AES Analysis of the sample solution and blank solution respectively. ICP-AES readings are in ppm and are an average of two burns.

extraction of uranium.

From the above results it can be seen that most of the sorbents tested were capable of extracting uranium when the matrix was a simple aqueous solution. The sorbents that showed greater than 75 percent extraction included all of the cation exchangers and chelating sorbents that were tested, but not the anion exchangers and miscellaneous sorbents.

### ***3.3.2 Sorbent behaviour in complex aqueous solution***

When the sorbents were used with a uranium solution that had other cations present, the sorbent behaviour was different as shown in Table 3.3. Three sorbents showed less than 10 percent extraction and they were AG 2X8, Dowex 2X8 and Dowex 21K. Nine sorbents had extraction values between 10 and 75 percent extraction. The remaining fourteen of the twenty-six sorbents tested showed good capability (i.e. % E > 75) in extracting uranium from a complex matrix.

A comparison of Table 3.2 and Table 3.3 shows that 76 percent of the sorbents tested were capable of extracting uranium from a simple aqueous matrix, but this dropped to 53 percent when the matrix was a more complex solution. It can be concluded from the above that when the matrix becomes even more complex, for example seawater, the number of sorbents that would be capable of extracting uranium would be even fewer in number.



On closer examination of Table 3.3, it was observed that a large proportion of cation exchange sorbents were capable of extracting uranium and also the other competing ions that were present in solution. In the extraction of uranium from seawater these sorbents would quickly reach capacity if they do not show selectivity towards uranium. The chelating sorbents Chelex 100 and Amberlite IRC-718, like the cation exchange sorbents, did not show any selectivity towards uranium.

The chelating sorbents, poly- $\beta$ -diketone and Seelex A100, showed some selectivity towards the uptake of uranium from complex aqueous solutions. Although Seelex A100 appears to show selectivity, it lacked physical stability and a significant proportion of it was soluble in water. Among the chelating sorbents that were tested, only poly- $\beta$ -diketone displayed good selectivity and physical stability for the uptake of uranium from complex solutions. The low % extraction (i.e. % E = 46.3) can be improved by either increasing the amount of poly- $\beta$ -diketone or by incorporating a larger number of  $\beta$ -diketone functional groups on the sorbent. The preparation of a  $\beta$ -diketone sorbent will be discussed in Chapter IV.

Tables 3.2 and 3.3 show that the concentrations of cations that were available for extraction were around 10 ppm or higher. The higher values obtained may have been caused to a small extent by impurities in the salts used for making up the solutions. Another possible minor source of error could arise from the successive volumetric dilutions of the stock solution. The latter problem can be prevented by diluting the

stock solution by weight instead of by volume. Since only relative changes in concentration of the metal ion were used for the evaluation of the sorbents (i.e. concentrations before and after the addition of the sorbent) the above errors did not affect overall results. In Table 3.3, the concentration of Fe that was available for extraction was found to be 4.62 ppm. This was a considerable difference from the 10 ppm that was supposed to be in solution. This drop in concentration leads us to the conclusion that the precipitation or cloudiness that was observed during the preparation of the stock solution was due to the formation of iron hydroxide.

The relative selectivities of sorbents that were evaluated for the various cations are given in Table 3.4. The selectivity was based on the extraction values that were obtained from Table 3.3. Cations with extraction values below 10 percent were not included in the above series. Table 3.4 would give greater information to the analyst as far as choice of sorbent availability and the selectivity of the sorbent when working with relatively simple solutions.

### **3.4 Conclusion**

The results of this survey show that when the experimental system was a simple aqueous solution (i.e. uranyl acetate solution) many sorbents were capable of extracting uranium. In the presence of competing ions, the number of sorbents that were capable of extracting uranium decreased considerably, and only one sorbent, i.e. poly- $\beta$ -diketone, had displayed good selectivity towards uranium and had good

**Table 3.4 Relative selectivities of sorbents based on percent extraction for various cations**

**A: Cation exchange resins that have a strongly acidic functionality (sulphonic acid)**

1. AG 50WX8:  $\text{UO}_2^{2+}, \text{Pb}^{2+}, \text{Mg}^{2+} > \text{Mn}^{2+}, \text{Ca}^{2+}, \text{Cu}^{2+},$   
 $\text{Zn}^{2+}, \text{Ni}^{2+}, > \text{Fe}^{2+}, > \text{Na}^+$
2. Dowex 50WX8:  $\text{UO}_2^{2+}, \text{Pb}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}, > \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+},$   
 $> \text{Fe}^{2+}, > \text{Na}^+$
3. Amberlite:  $\text{UO}_2^{2+}, \text{Pb}^{2+}, \text{Mg}^{2+}, > \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Ca}^{2+}, > \text{Fe}^{2+}$   
IR-120
4. Rexyn 101:  $\text{UO}_2^{2+}, \text{Pb}^{2+}, \text{Mg}^{2+}, > \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Ca}^{2+}, > \text{Fe}^{2+},$   
 $\text{Na}^+$

**B: Cation exchange resins that have a weakly acidic functionality (carboxylic acid)**

1. Rexyn 102:  $\text{Pb}^{2+}, > \text{UO}_2^{2+}, \text{Fe}^{2+}, \gg \text{Cu}^{2+}, \gg \text{Ca}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+},$   
 $\text{Mg}^{2+}$

**C: Anion exchange resins that have a strongly basic functionality (Quaternary Ammonium)**

1. Amberlite CG-400 I:  $\text{Fe}^{2+} \gg \text{UO}_2^{2+}, \text{Pb}^{2+}, \gg \text{Ca}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, > \text{Mn}^{2+},$   
 $\text{Mg}^{2+}$
2. Amberlite CG-400 II:  $\text{Fe}^{2+}, > \text{Pb}^{2+}, \text{UO}_2^{2+}, \text{Cu}^{2+}, > \text{Zn}^{2+}, \text{Ca}^{2+}, \text{Ni}^{2+}, > \text{Mn}^{2+},$   
 $\text{Mg}^{2+}$
3. Amberlite IRA-400:  $\text{Fe}^{2+}, \gg \text{UO}_2^{2+}$
4. Amberlite IRA-401:  $\text{UO}_2^{2+}, > \text{Fe}^{2+}, \gg \text{Pb}^{2+}, > \text{Cu}^{2+}, \text{Ca}^{2+}$
5. AG 1X8:  $\text{Fe}^{2+}, \gg \text{UO}_2^{2+}$
6. AG 2X8:  $\text{Fe}^{2+}, \gg \text{Na}^+$
7. AG MP-1:  $\text{Fe}^{2+} \gg \text{UO}_2^{2+} > \text{Zn}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}$

Table 3.4 Continued

8. Rexyn 201:  $\text{UO}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $> \text{Fe}^{2+}$ ,  $> \text{Cu}^{2+} > \text{Na}^+$ ,  $> \text{Ca}^{2+}$
9. Rexyn AG4:  $\text{UO}_2^{2+}$ ,  $>> \text{Fe}^{2+}$ ,  $>> \text{Na}^+$
10. Dowex 1X4:  $\text{Fe}^{2+} >> \text{UO}_2^{2+}$ ,  $\text{Pb}^{2+}$
11. Dowex 1X10:  $\text{Fe}^{2+} >> \text{UO}_2^{2+}$ ,  $\text{Na}^+$ ,  $> \text{Ca}^{2+}$
12. Dowex 2X8:  $\text{Na}^+$
13. Dowex 21K:  $\text{Fe}^{2+} >> \text{Na}^+$ ,  $\text{Ca}^{2+}$

D: Anion exchange resins that have a weakly basic functionality (Polyamines)

1. Amberlite IR-45:  $\text{UO}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $> \text{Fe}^{2+} > \text{Cu}^{2+} >> \text{Zn}^{2+} >> \text{Ca}^{2+} > \text{Ni}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$
2. Rexyn 203:  $\text{Pb}^{2+} > \text{Fe}^{2+}$ ,  $\text{Na}^+ >> \text{Zn}^{2+}$ ,  $>> \text{UO}_2^{2+}$ ,  $\text{Ni}^{2+}$

E: Chelating resins

1. Chelex 100:  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $> \text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $> \text{Ca}^{2+}$ ,  
(iminodiacetic acid group)  $\text{Mg}^{2+}$ ,  $\text{UO}_2^{2+}$
2. Poly- $\beta$ -diketone:  $\text{UO}_2^{2+}$ ,  $\text{Na}^+$ ,  $>> \text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$   
( $\beta$ -diketone group)
3. Amberlite IRC-718:  $\text{Pb}^{2+} > \text{Fe}^{2+}$ ,  $\text{UO}_2^{2+} > \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+} > \text{Mn}^{2+}$ ,  
(iminodiacetic acid)  $\text{Ni}^{2+}$

F: Miscellaneous Sorbents

1. Chromosorb-W:  $\text{Na}^+$ ,  $\text{Fe}^{2+} >> \text{Pb}^{2+} >> \text{UO}_2^{2+} >> \text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$   
(diatomite)
2. Florisil:  $\text{UO}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+ > \text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  
(magnesia silica gel)  $\text{Cu}^{2+}$

physical stability under the conditions tested. Although the poly- $\beta$ -diketone displayed good selectivity it had a low extraction (i.e. 46.3%); the percent extraction can be improved by using larger amounts of the sorbent or by increasing the number of  $\beta$ -diketone groups on the sorbent.

## CHAPTER IV

PREPARATION AND EVALUATION OF SOME NEW SORBENTS FOR  
THE SORPTION OF URANIUM**4 Introduction**

Commonly available instrumental techniques are unable to directly determine trace uranium levels in samples with a complex matrix. Separation techniques (such as solvent extraction or column extraction) must be employed to preconcentrate and separate uranium from the matrix to obtain accurate and reproducible analytical measurements.

During the past three decades, the use of column extractions for trace metal preconcentration has far exceeded the use of solvent extraction in most analytical laboratories. However, the survey of commonly available sorbents, as shown in Chapter III, revealed the lack of sorbents for the selective extraction of uranium.

The need to develop sorbents for the selective uptake of uranium is of importance not only in analytical chemistry but also for a number of other applications, for example, in the nuclear industry they could be used for the manufacture and reprocessing of high grade fuel rods. The sorbents would play a vital role in the clean-up procedures for spills involving uranium in the nuclear industry and other radiochemical facilities. Sorbents, with the capability to selectively sorb uranium, would replace the existing

ion exchangers that are used in the uranium mining industry for the production and refining of uranium metal from its ores. These sorbents can be used for the removal of uranium from uranium mine tailings and as a filter for removing uranium from natural ground water to make the water potable in locations close to uranium deposits.

Ideally the sorbent should have high porosity, good mechanical and chemical stability, be relatively inexpensive and simple to make if it is to be used for analytical, environmental or industrial purposes. The preparation and evaluation of three sorbents, with the above characteristics, for the preconcentration of uranium will be discussed in this chapter.

#### **4.1 Reagents used**

Polyvinylalcohol (average molecular weight of 115,000 and 3,000), 1-benzoylacetone, N-2-thiazoly-acetoacetamide, 4,4,4-trifluoro-1-phenyl-1,3-butanedione, phenylphosphonic acid, benzyl cyanide, stearyl nitrile and acrylonitrile were obtained from Aldrich Co. (WI, USA). Chromium trioxide, acetylacetone, hydroxylamine-hydrochloride and N,N-dimethylformamide were obtained from Fisher Scientific Co., (NJ, USA). Phthalonitrile and N-butyranitrile were obtained from Eastman Kodak Co. (NY, USA). The above chemicals were of reagent grade and were used without further purification. Hypol™ FHP 2002 prepolymer, used in the production of various foams, was a sample provided by W. R. Grace and Co., (MA, USA). Commercially available polyester and polyether foams were obtained from Canlab (Winnipeg,

Canada) and Zellers department stores (Winnipeg, Canada) respectively. Industrial polyacrylonitrile fibres were obtained from Woolco department stores (Winnipeg, Canada) and polyacrylonitrile (Orlon™) fabric was obtained from E. I. DuPont de Nemours and Co. Inc., (DE, USA). The "Instant Ocean™" that was used to make artificial seawater was obtained from Aquarium System Inc., (OH, USA).

#### 4.2 Apparatus used

All water used was first purified by reverse osmosis followed by passage through a Barnstead Nanopure II™ system. Measurements of pH were obtained using a Fisher Accumet™ model 825 MP pH meter. Whatman No. 541™ filter paper was used for all filtering purposes. Infrared measurements, were obtained using a FT-IR instrument (Bomem Inc., Model M-100, Quebec, Canada) which was equipped with an ATR cell (Spectra-Tech Inc., CT, USA). Foam pieces were ground to a powder in a stainless steel container on a Waring™ blender (Dynamics Corporation of America, CT, USA). Similarly polyacrylonitrile (Orlon™) fibres were ground to a powder using a Wiley™ mill (Thomas Scientific Apparatus, PA, USA). Sample solutions were shaken either with a Burrell Wrist-Action Shaker (Burrell Corp., PA, USA) for solutions at 4°C and 22°C or a Dubnoff Metabolic Shaking Incubator (Precision Scientific, IL, USA) for solutions at 40°C and 70°C.



### 4.3 Polyvinylalcohol conversion to poly- $\beta$ -diketone

Poly- $\beta$ -diketone (P $\beta$ DK) was described in Chapter III as an effective sorbent for the selective extraction of uranium from aqueous solutions. The synthesis of P $\beta$ DK from polyvinylalcohol (PVA), using various methods, will be described in this section.

Poly- $\beta$ -diketone, as a functional group for the selective extraction of uranium, has been reported extensively by workers in Japan and many European countries.<sup>74,76,177,178</sup> Japanese and Europeans have been concerned mainly with the profitable extraction of uranium from seawater with the goal of using the recovered uranium as a fuel for their nuclear plants.<sup>3,17,18,155,156,164</sup>  $\beta$ -diketone has been shown to be effective in extracting uranium from seawater with good selectivity.<sup>74</sup> Djamali and Lieser<sup>76</sup> synthesized polystyrene with 1,3-diketone as the anchor group which was capable of extracting uranium. Tabushi *et al.*<sup>178</sup> have synthesized a macrocyclic hexaketone and a cyclic tetraketone which were also effective in the selective extraction of uranium. Marmor and Kidane<sup>177</sup> prepared a poly- $\beta$ -diketone resin by the controlled oxidation of polyvinyl alcohol with chromic acid.

These resins are not available commercially and attempts to synthesize the macrocyclic poly- $\beta$ -diketone in our laboratory failed although the synthesis was performed according to the procedures outlined in the literature. The controlled oxidation of polyvinyl alcohol with chromic acid<sup>177</sup> was attempted and this resulted in a poor yield of a very fine powder of poly- $\beta$ -diketone (P $\beta$ DK).

Chromic acid was prepared by dissolving 28.5 grams of  $\text{CrO}_3$  in 500 mL of deionized water, to which 175 mL of concentrated  $\text{H}_2\text{SO}_4$  was added with constant stirring. This chromic acid was added slowly to a freshly prepared mixture of 25 grams of PVA (MW 3000) and 375 mL of deionized water. Care was taken to see that the temperature of the resulting solution never exceeded  $60^\circ\text{C}$  during the addition of chromic acid. The temperature of the solution was raised to  $90^\circ\text{C}$  for 24 hours, followed by filtration through a Buchner funnel with No. 541 Whatman™ filter paper. The brown product was dried under vacuum in the presence of Drierite™ for 24 hours. The final product was a fine powder which, when packed into a column, resulted in considerable back pressure.

In the above procedure, we observed that PVA dissolved immediately forming a solution rather than the slurry which was observed by Marmor and Kidane.<sup>177</sup> The formation of a solution, instead of a slurry, resulted in a final product that was a fine powder. Several methods were then attempted to increase the particle size and one such method was to add PVA (MW 3000) directly to the chromic acid solution, but this did not produce larger sized P $\beta$ DK material.

The lack of information on the molecular weight of PVA used by Marmor and Kidane<sup>177</sup> in their publication, led us to attempt the synthesis with a higher molecular weight PVA (i.e. MW 115,000). The assumption made in the use of MW 115,000 (PVA) was that it would have a smaller solubility compared to MW 3000 (PVA) and

this smaller solubility would produce a slurry instead of a solution. Although the use of PVA (MW 115,000) resulted in a slurry, the addition of chromic acid converted the slurry into a solution producing finely divided P $\beta$ DK material.

The use of a salting agent such as NaCl in the chromic acid to decrease the solubility of PVA (MW 115,000) was suggested by Dr. Charlton of this Department. Twenty grams of PVA (MW 115,000) was added to 100 mL of 10% H<sub>2</sub>SO<sub>4</sub> which was previously saturated with NaCl solid. To the resulting slurry, 100 mL of 20% (wt/vol) CrO<sub>3</sub> in deionized water was added slowly with constant stirring using a magnetic stirrer. The temperature of the above mixture was kept below 25°C and this was done by carefully controlling the rate of addition of CrO<sub>3</sub> solution. This resulted in larger sized P $\beta$ DK which started to dissolve when left in chromic acid solution for more than 15 minutes.

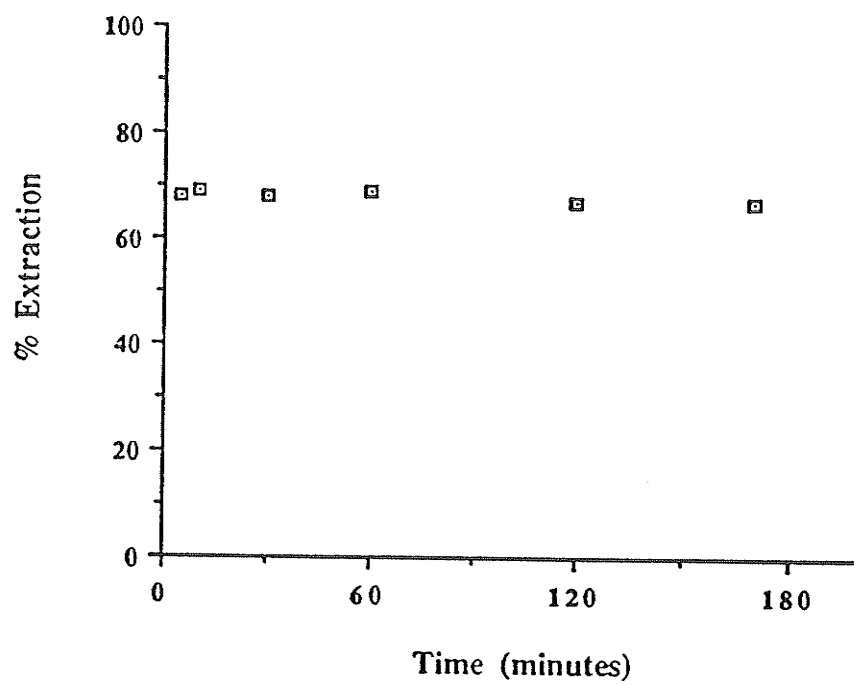
When the procedure was modified by drastically reducing the concentration of H<sub>2</sub>SO<sub>4</sub> and CrO<sub>3</sub>, the resulting P $\beta$ DK formed was of larger particle size. The method used 400 mL of 5% CrO<sub>3</sub> with 5 mL of concentrated H<sub>2</sub>SO<sub>4</sub> which was added to 10 grams of PVA (MW 115,000) with constant stirring for 10 minutes. The resulting brown crystalline product was washed with deionized water to remove any unreacted Cr<sup>6+</sup> and then rinsed with acetone and later dried under vacuum in the presence of Drierite™ for 24 hours.

The extraction efficiencies of the above P $\beta$ DK materials were determined by equilibrating one gram of P $\beta$ DK with 25 mL of 10 ppm uranium solution in a covered beaker with constant stirring for 24 hours. The solutions were filtered and analyzed by ICP-AES. The results showed an 83% extraction by P $\beta$ DK made by the modified procedure (i.e. reduced concentration of H<sub>2</sub>SO<sub>4</sub> and CrO<sub>3</sub>), compared with 54% by P $\beta$ DK made by the salting out procedure and 34% by untreated PVA (MW 115,000).

#### 4.3.1 *Time study*

Although P $\beta$ DK, made by the modified procedure, showed a good capability in extracting uranium from a simple aqueous solution it was of importance to determine if P $\beta$ DK was capable of sorbing uranium from a bicarbonate solution. The purpose of using a bicarbonate solution was to simulate seawater in its simplest form. The determination of the time required for equilibration was of importance if one was interested in using P $\beta$ DK as a column material. To determine the capability of P $\beta$ DK in sorbing uranium from a bicarbonate solution, and also to determine the effect of equilibrium time on percent extraction, the following experiment was performed. Two hundred mL of a 10 ppm uranium solution (which contained 200 ppm of sodium bicarbonate) were added to a sample of 50 grams of P $\beta$ DK in a 500 mL beaker. The solution was stirred using a magnetic stirrer. At different times, 5 mL of solution was removed and filtered prior to analysis by ICP-AES.

Figure 4.1 shows the poly- $\beta$ -diketone was capable of sorbing uranium from the



**Figure 4.1** The effect of time of contact on the percent extraction of uranium by PβDK resin

bicarbonate solution and that the % extraction did not increase after five minutes of contact.

#### 4.3.2 *Column studies*

The usefulness of this material was evaluated by packing it into a Seastar™ columns. These columns were made with Teflon™ and were obtained from Seastar™ Instruments Ltd., B.C., Canada. Twenty litres of a solution containing 30 ppb uranium and 200 ppm sodium bicarbonate was pumped through the column at 100 mL.min<sup>-1</sup>. The bicarbonate concentration was chosen to partially simulate the seawater concentration. The uranium was eluted with 100 mL of 3M HCl and analyzed by ICP-AES which showed a 63% extraction, assuming complete elution.

Although PβDK was found to be effective in extracting uranium, it presented problems due to the presence of unreacted PVA. After reusing the PβDK a few times, it formed a gel-like substance which would eventually crack, resulting in bleeding from the column. In an attempt to prevent crumbling of PβDK, it was mixed with sodium chloride in the ratio 10:1 (wt) and pelletized under hot conditions. It was thought that when this pellet was placed in water the sodium chloride present in the matrix would dissolve, leaving porous PβDK. However, the pellet collapsed after standing in water.

An ideal sorbent should have high porosity, good mechanical (i.e physical) and chemical stability. Mechanical stability is important for a sorbent if it is to be used as

a column material. To prevent column bleed, the column material should withstand some pressure without collapsing into a fine powder. A fine powder increases the back pressure exerted by the column, thereby requiring the need for a high power performance pump to move liquid through the column. As P $\beta$ DK lacked mechanical stability, further work on the direct conversion of PVA to P $\beta$ DK was discontinued. However, the incorporation of  $\beta$ -diketone group into a matrix with good mechanical and chemical stability could prove to be useful. One such matrix is polyurethane foam which would offer several advantages such as good porosity, mechanical and chemical stability, easily available, relatively inexpensive and simple to make.

The use of polyurethane foams for the extraction, recovery and preconcentration of various inorganic and organic species from aqueous, non-aqueous and gaseous mixtures has received considerable attention during the past two decades. A review of literature devoted to polyurethane-based polymeric sorbents in separation chemistry, was documented by Moody and Thomas<sup>260</sup> and Braun et al.<sup>261</sup> Polyurethane foams have been shown to be inert and stable, but they degrade when heated between 180 and 200°C. The polyurethane foams remain unaltered, apart from swelling reversibly, when treated with water, 6M HCl, 4M H<sub>2</sub>SO<sub>4</sub>, 2M HNO<sub>3</sub>, NH<sub>4</sub>OH, NaOH or CH<sub>3</sub>COOH. These foams decompose in concentrated HNO<sub>3</sub> and dissolve in concentrated H<sub>2</sub>SO<sub>4</sub>. Polyurethane foams are also stable in organic solvents such as light petroleum, benzene, carbon tetrachloride, chloroform, diethylether, acetone and alcohols.

Polyurethanes constitute one of the few polymers that are highly elastomeric and show good biocompatibility and have been used in the making of many biomedical implant devices. The long term stability of polyurethanes in biomedical environments is currently being debated, especially in the use of polyurethanes for extended implant applications, as some studies have shown that polyurethane foams undergo some degradation.<sup>262,263,264</sup> Although the long term stability of polyurethanes in biomedical implant applications is being debated, polyurethane foam in analytical chemistry has been considered to be sufficiently inert and stable<sup>260,261</sup> for use as a sorbent material.

#### **4.4 Incorporation of polyvinylalcohol into Hypol™ polyurethane foam**

Since the PβDK lacked mechanical stability, it was decided to incorporate PVA into the matrix of the polyurethane foam by imbedding the PVA during the foaming process. The PVA in the foam would then be converted into PβDK by controlled oxidation with chromic acid as given by Marmor and Kidane.<sup>177</sup>

PVA-imbedded polyurethane foam was prepared by mixing equal weights of Hypol™ prepolymers and an aqueous solution of 5% (wt) or 10% (wt) PVA (M.W. 3000). Hypol™ prepolymers, which are derived from toluene diisocyanate, react with active hydrogen-containing compounds (i.e H<sub>2</sub>O, ROH etc.) to form polyurethane foams that are both elastomeric and hydrophilic in nature. The foams can be prepared by mixing equal weights of Hypol™ prepolymers and water or other active hydrogen-containing compounds. Additives may be suspended or dissolved in either or both of the organic



and aqueous layer.<sup>265</sup>

A PVA of molecular weight 3000 was chosen as it was easily soluble in the aqueous phase, compared to PVA with higher molecular weight, i.e. 115,000. The basic method of synthesis was to mix the Hypol™ prepolymer with an equal weight of aqueous solution of PVA followed by rapid stirring of the mixture for 15 seconds with a glass rod. A blank foam was made in a similar way by mixing water with Hypol™ prepolymer. The procedure for grinding and cleaning the foam was the same as the one given later for  $\beta$ -diketone-embedded polyurethane foams. An oxidizing solution for the controlled oxidation of PVA was prepared by dissolving 7 grams of  $\text{CrO}_3$  in 125 mL of deionized water. Thirty-five mL of concentrated  $\text{H}_2\text{SO}_4$  was added slowly to the  $\text{CrO}_3$  solution with constant stirring. Three grams each of the blank foam, 5% PVA foam and 10% PVA foam were added to separate 50 mL portions of the oxidizing solution; the oxidation was done to oxidize the PVA in the foam to form a  $\text{P}\beta\text{DK}$  foam. On addition of the chromic acid solution, all of the foams were converted to a thick liquid in about 5 minutes.

The PVA foams and the blank foams produced were not stable at the conditions that were used for the oxidation of PVA. Other oxidizing reagents, such as  $\text{H}_2\text{O}_2$  or a more dilute chromic acid solution, may produce better results. Rather than incorporating PVA into the foam matrix and then converting it into a  $\beta$ -diketone (a two step synthesis), it was decided to incorporate a reagent with

$\beta$ -diketone as the functional group directly into the foam matrix. The single step method in the making of the foam with  $\beta$ -diketone group is simpler and is described in the next section.

## **4.5 Preparation and evaluation of a $\beta$ -diketone-imbedded polyurethane foam**

### **4.5.1 Introduction**

Polyurethane foams have been used as supports for various extractants; for example, foams treated with dithiazone or diethyldithiocarbamate or sulphide treated foams have been used for the sorption of mercury,<sup>266-268</sup> ethanediol-treated foams for antimony,<sup>269</sup> and pyridylazonaphthol-treated foams for the sorption of zinc, copper and mercury.<sup>270</sup> Copper and cadmium were extracted using polyurethane treated with benzoylacetone.<sup>271</sup> Polyurethane foam, when coated with a long chain tertiary amine, was effective in extracting uranium<sup>214</sup> from acidic solutions with pH values between 1 and 3. Gesser and Gupta<sup>272</sup> have shown that uranyl nitrate can be extracted by polyurethane foam from aqueous acidic solutions in the presence of salting agents. Extraction of uranium from aqueous solutions using polyurethane foams that had been loaded with various organic extractants have been described earlier in Chapter I (i.e. 1.4.11).

The preparation of a  $\beta$ -diketone-imbedded polyurethane foam and the evaluation of its

ability to extract uranium from aqueous solutions with a wide range of temperature and pH values will be discussed in this section.

#### **4.5.2 Procedure**

Hypol™ foams are commonly foamed using approximately equal weights of Hypol™ prepolymer and water. Additives that contain  $\beta$ -diketones may be suspended or dissolved in either or both of the organic and aqueous layer. In a preliminary study, different  $\beta$ -diketones (acetylacetone, N-2,thiazolylacetoacetamide, 1-benzoylacetone and 4,4,4-trifluoro-1-phenyl-1,3-butanedione) were used with varying amounts (1, 5 and 10% by weight) in the prepolymer matrix in an attempt to incorporate them into the Hypol™ foam matrix. The procedure for incorporation was similar to the procedure used for the preparation of the  $\beta$ -diketone foam, which is described later in this section. Of the various  $\beta$ -diketones studied only the foam with 5% (wt/wt) 1-benzoylacetone showed good foam formation and also exhibited the ability to extract uranium from aqueous solution. The incorporation of acetylacetone and 4,4,4-trifluoro-1-phenyl-1,3-butanedione resulted in the formation of a solid plastic instead of a foam. N-2,thiazolylacetoacetamide formed a foam which was unable to extract uranium from aqueous solution.

The Hypol™ foam produced by the incorporation of 5% (wt/wt) of 1-benzoylacetone into the foam matrix during the foaming process will be called " $\beta$ -diketone foam" throughout the remainder of this thesis.  $\beta$ -diketone foam was prepared by mixing

equal weights of Hypol™ prepolymer containing 5% (wt) of 1-benzoylacetone and water. The basic method was to mix Hypol™ prepolymer with 1-benzoylacetone solid to form a clear viscous solution. An equal weight of water was then added to the viscous polymer solution followed by rapidly stirring the mixture for 15 seconds by using a glass rod.

The mixture initially became cloudy and then rose to ten times the original volume by releasing small bubbles of carbon dioxide. The resulting  $\beta$ -diketone foam became tack-free within five minutes and was air dried in a fumehood for eight hours. The dried  $\beta$ -diketone foam was then cut into small pieces. These pieces were frozen in liquid nitrogen and then ground into a fine powder in a stainless steel container on a Waring™ blender. Freezing was necessary to make the foam brittle and therefore easier to grind. Any pieces of unground foam were discarded.

Powdering of the foam was necessary to reach equilibrium more quickly between the foam and the uranium solution, and also to ensure more reproducible results. The powdered foams were first cleaned by washing with water followed by acetone. This washing process should remove any foam impurities that are soluble in water or acetone. The powdered foams were initially soaked in water for four hours and the resulting slurry was then filtered under vacuum through a Whatman™ No. 541 filter paper using a Buchner funnel. The foam was recovered from the filter paper and the complete procedure, soaking and filtering was repeated two more times. The foam

was then washed, in a similar way, with acetone. The clean, powdered foam was then left to dry under vacuum for four hours to remove traces of acetone vapour. Blank foam was prepared in a similar manner without the addition of 1-benzoylacetone. The colour of the clean, dry  $\beta$ -diketone foam was cream yellow compared to the blank foam which was white.

The extraction capability was tested by adding 25 mL of 10 ppm uranium solution to a 60 mL screw top Nalgene™ plastic bottle together with approximately  $0.200 \pm 0.003$  grams of dried powdered foam. The capped bottles were shaken for five hours in an automatic shaker and the filtered solutions were then analyzed by CFSM.

#### ***4.5.3 Characterization of the $\beta$ -diketone-embedded polyurethane foam***

The extraction characteristics of the  $\beta$ -diketone foam were studied by equilibrating the foam with uranium solutions at different temperatures and pH values. The pH of the uranium solutions was adjusted with 2M HCl or 2M NaOH solution and the pH values were monitored with a pH meter. Uranium solutions with pH values between 1.4 and 11.0 and at different temperatures (i.e. between 4°C and 70°C) were used to study the extraction characteristics of the  $\beta$ -diketone foam.

Uranium solutions were equilibrated to the required temperatures before adding them to the plastic bottles containing the foam. Shaking of solutions at room temperature (22°C) and at thermostatically-controlled cold room temperature (4°C) was done using

a Burrell Wrist Action Shaker. Similar experiments at 40°C and 70°C were performed with a Dubnoff Metabolic Shaking Incubator equipped with a variable temperature-controlled water bath. Temperature measurements were within  $\pm 2^\circ\text{C}$ .

% Extraction was calculated as

$$\% E = (I - F) I^{-1} \cdot 100$$

Where % E is percent extraction, F is the concentration of uranium left in solution after extraction and I is the concentration of uranium originally available. F is the concentration of uranium in the solution that was left back after the extraction and after the foam pieces had been filtered.

The concentration of available uranium, rather than the initial concentration, was used to take into account any precipitation of uranium species which is known to occur at  $\text{pH} > 2$ . The precipitate is not visible to the naked eye; however, Feldman<sup>273</sup> *et al.* had observed the precipitation of uranyl nitrate at  $\text{pH} > 4.5$  by centrifuging the solution. I is the concentration of uranium in the solution that was subjected to the identical filtration, pH and temperature conditions as the foam sample solution, but without the presence of any foam. The values for I and F, used in the calculation of % E, were the averages obtained from experiments that were performed in triplicate at a particular pH and temperature.

The uncertainty or error involved in % E was calculated<sup>274</sup> using the following formula:

$$\% \text{ Uncertainty} = I^{-2} \cdot [I^2 B^2 + F^2 A^2]^{1/2} \cdot 100$$

where B is the standard deviation of F, and A is the standard deviation of I.

#### 4.5.4 Results and discussion

The  $\beta$ -diketone foam exhibits a high extraction between pH = 3 and pH = 8 and the extraction decreases at either end of the pH range, as shown in Figures 4.2 and 4.3. The drop in extraction can be explained by the fact that uranium in aqueous solution exists as a number of species depending on the pH of the solution. For uranium solutions acidified with 2M HCl, the species formed in aqueous medium are  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_2\text{Cl}^+$  at pH values below 3. Under very basic conditions (i.e. pH values above 10) species such as  $\text{UO}_2(\text{OH})_3^-$  are formed due to the hydrolysis of the uranyl ion<sup>275</sup> and these species may not be as extractable by this foam.

Sary and Hladky<sup>276</sup> undertook a systematic investigation of the solvent extraction of thirty metals using various solvents such as acetylacetone, benzoylacetone and dibenzoylmethane in benzene. Included in their study was the extraction of uranium by benzoylacetone and their results are given in Figure 4.4. The extraction profile reported by Sary and Hladky<sup>276</sup> was similar to the  $\beta$ -diketone foam profile at 22°C,

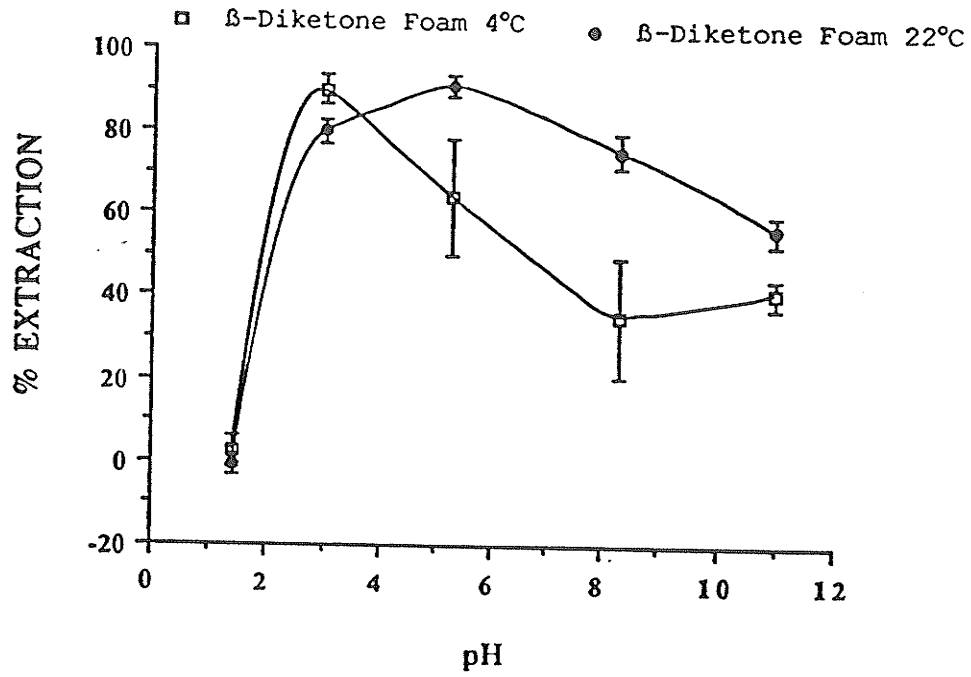


Figure 4.2 Extraction capability of  $\beta$ -diketone foam at 4°C and 22°C



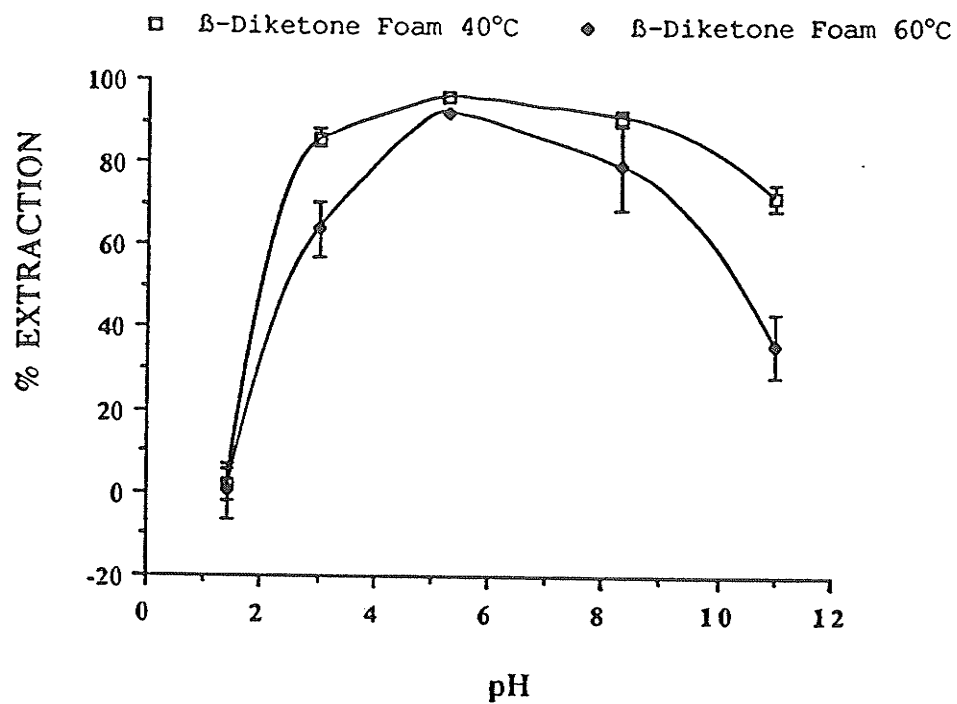


Figure 4.3 Extraction capability of  $\beta$ -diketone foam at 40°C and 60°C

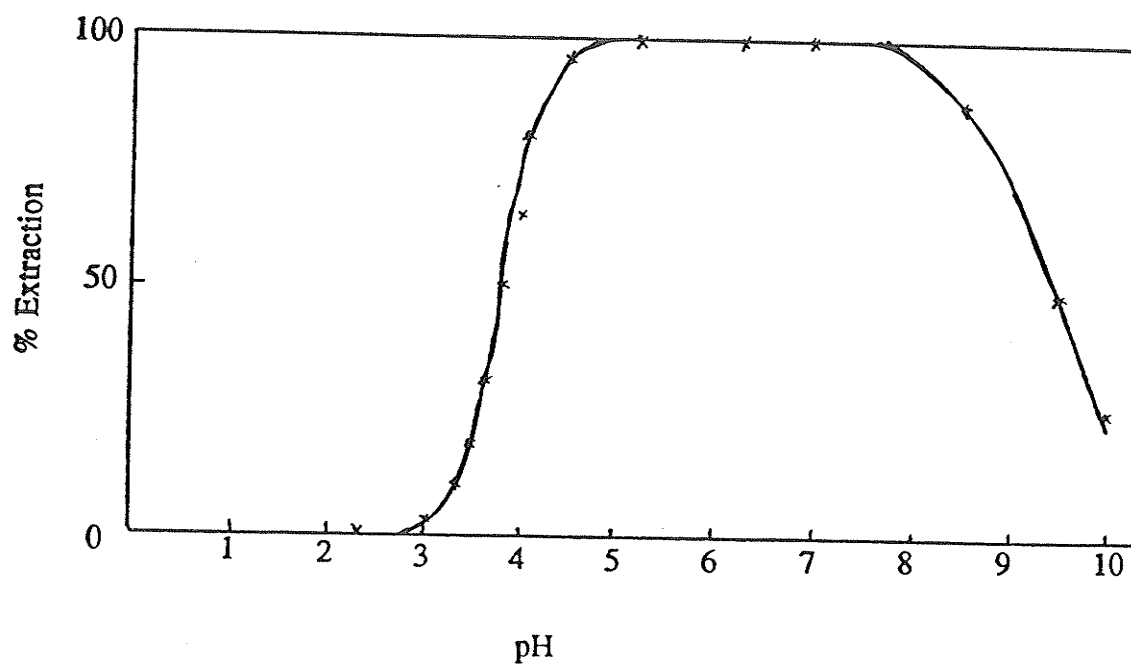


Figure 4.4 Effect of pH on the solvent extraction of uranium by 0.10 M benzoylacetone in benzene<sup>276</sup>

suggesting that the  $\beta$ -diketone foam's ability in sorbing uranium involves a solvent extraction type of mechanism. On comparing the extraction efficiency by solvent extraction and that of  $\beta$ -diketone foam, it can be seen that the solvent extraction performs slightly better than the  $\beta$ -diketone foam between  $\text{pH} = 4.5$  and  $\text{pH} = 7.5$ . However, at other  $\text{pH}$  values the  $\beta$ -diketone foam is better than the solvent extraction in sorbing uranium. This difference in extraction profiles can be attributed to the different methods involved, i.e. solvent extraction vs. sorption by a solid sorbent.

Furthermore, between  $\text{pH} = 3$  and  $\text{pH} = 8$ , it can be seen in Figures 4.2 and 4.3 that the % extraction generally increases with an increase in temperature from  $4^\circ\text{C}$  to  $40^\circ\text{C}$ , followed by a drop at  $60^\circ\text{C}$ . This drop may be attributed to the instability of the  $\beta$ -diketone foam at high temperatures. The decrease in extraction efficiency at the lower end of the  $\text{pH}$  range suggests the use of a solution with  $\text{pH} \leq 1$  as a possible eluting solution to desorb uranium from the foam. For maximum extraction, one may have to perform the experiments at different temperatures depending on the  $\text{pH}$ .

Figures 4.2 and 4.3 show that the ideal temperature for the extraction of uranium is at  $40^\circ\text{C}$ .

Blank foams (i.e without the inclusion of 1-benzoylacetone) showed little capability in extracting uranium from aqueous solutions in comparison to the  $\beta$ -diketone foam. In general,  $\beta$ -diketone foams showed superior extractability of uranium over blank foam at all values of  $\text{pH}$  and temperatures tested as shown in Figures 4.5 to 4.8.

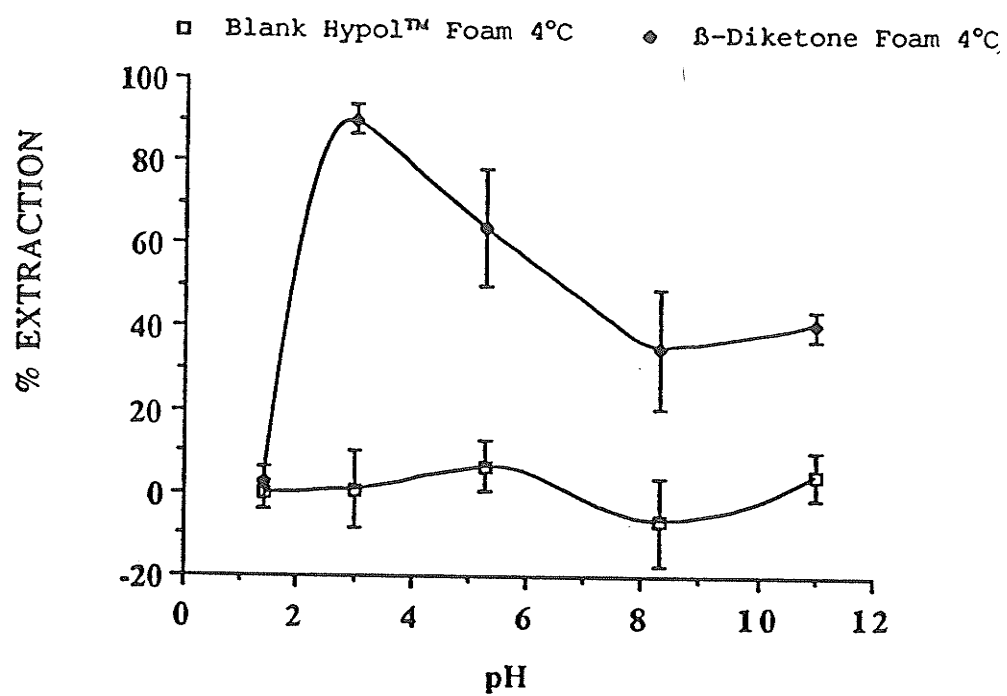


Figure 4.5 Comparison of the extraction capabilities of  $\beta$ -diketone foam and blank Hypol™ foam at 4°C

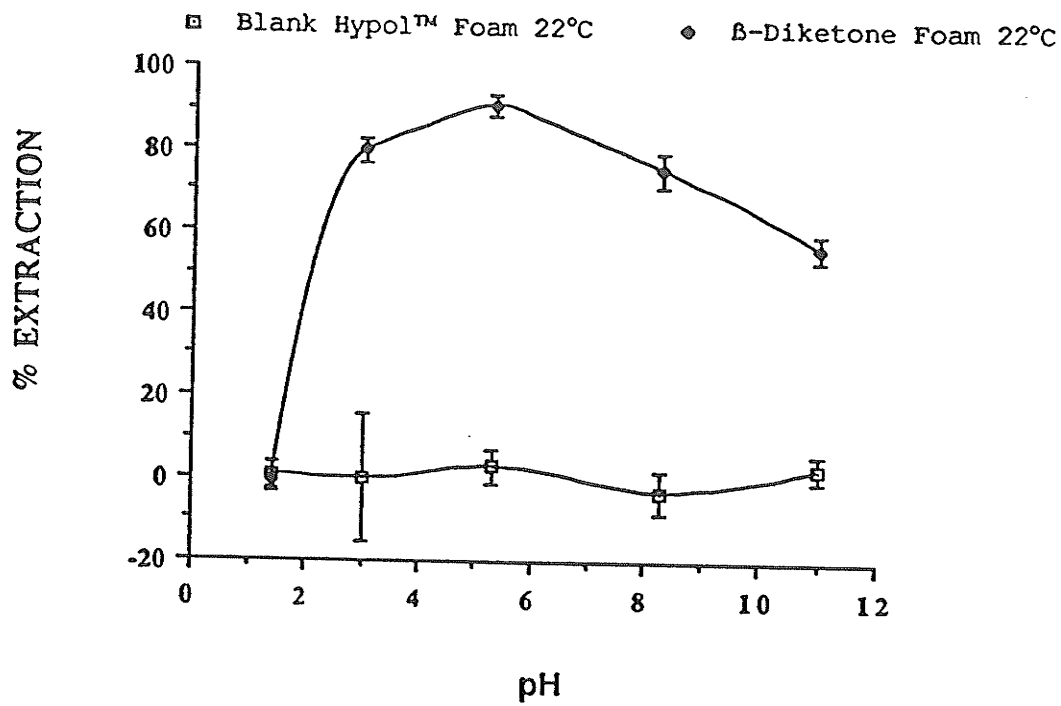


Figure 4.6 Comparison of the extraction capabilities of  $\beta$ -diketone foam and blank Hypol™ foam at 22°C

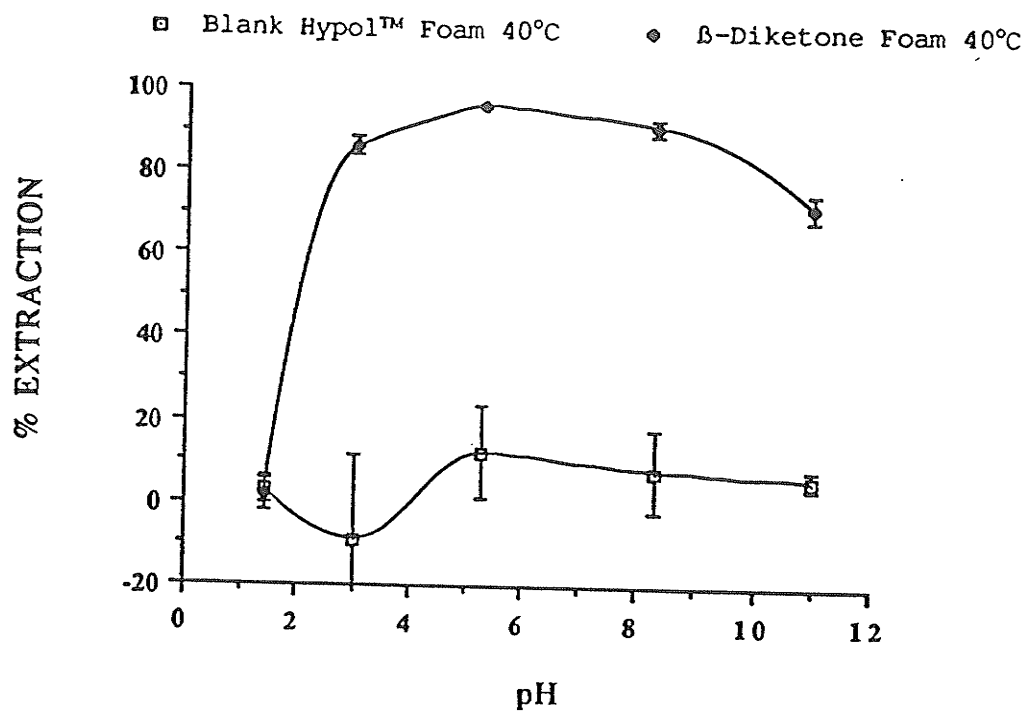


Figure 4.7 Comparison of the extraction capabilities of  $\beta$ -diketone foam and blank Hypol™ foam at 40°C

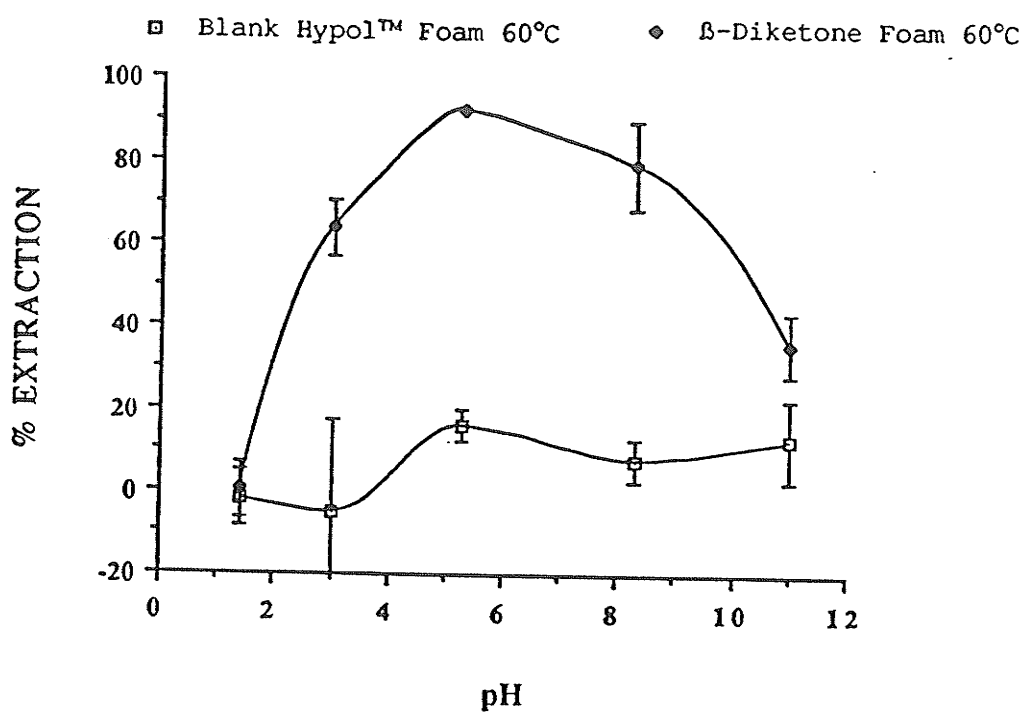


Figure 4.8 Comparison of the extraction capabilities of  $\beta$ -diketone foam and blank Hypol™ foam at 60°C

Gesser and Ahmed<sup>214</sup> have reported that Adogen-impregnated polyurethane foam is capable of extracting uranium from acidic solutions whose pH values range from pH = 1 to pH = 3. The  $\beta$ -diketone foam synthesized in this work was shown to extract uranium from aqueous solutions whose pH values range from pH = 3 to pH = 10. Both foams (i.e. Adogen-impregnated and  $\beta$ -diketone foams) complement each other by extending the ability of modified foams to extract uranium from aqueous solutions with a wide range of pH values.

#### 4.5.5 Conclusion

1-Benzoylacetone was imbedded into the matrix of the polyurethane foam during the fabrication of the foam. The resulting  $\beta$ -diketone foam is capable of extracting uranium from aqueous solution whose pH ranges between pH = 3 and pH = 10.

The  $\beta$ -diketone foam would be a good sorbent for the sorption of uranium from natural waters as the pH of most natural waters are usually in the range of pH =  $7 \pm 3$ . The  $\beta$ -diketone foam is simple to make, relatively inexpensive, has high porosity and has good chemical and mechanical stability. The above qualities make the  $\beta$ -diketone foam a promising sorbent for the separation and preconcentration of uranium for both analytical and large scale industrial applications.



## 4.6 Preparation and evaluation of a phosphonic acid-imbedded polyurethane foam

### 4.6.1 Introduction

Chelating polymeric materials (e.g. Chelite P and Duolite ES 467, Serva Chemicals, Germany) that have phosphonic acid functional groups, have shown a remarkable extraction efficiency for uranium and certain trace metals from artificial seawater in studies that were undertaken in our laboratory as shown in Chapter V. These polymeric materials have recently been introduced into the market and have rarely been used in analytical chemistry, and are relatively expensive at the present time. A number of papers have been published<sup>185,186,188-192,277,278</sup> describing the synthesis and/or evaluation of sorbents with phosphonic acid for the sorption of uranium from seawater. The synthesis of these sorbents usually is a multi-step process, which is both tedious and difficult to undertake.

Due to the success achieved in the preparation of a  $\beta$ -diketone foam, as shown in the previous section, a similar attempt was made to incorporate the phosphonic acid group into Hypol™ foam. The preparation of a phosphonic acid-imbedded polyurethane foam and the evaluation of its ability to extract uranium from artificial seawater and from aqueous solution (with relatively simple matrix) with a wide range of pH and temperature values will be discussed in this section.

#### 4.6.2 Procedure

The foams were prepared by mixing 10 mL of Hypol™ prepolymer with various amounts of water in a 150 mL glass beaker, with a glass rod. Phenylphosphonic acid and/or a surfactant (Neutral™) were added to the aqueous layer. The preparation of the foams was carried out at three pH values, i.e. 1, 7 and 13 (i.e. the aqueous layer pH values were adjusted to 1, 7, and 13). A solution of pH = 1 was obtained by simply dissolving phenylphosphonic acid; pH = 7 and pH = 13 solutions were obtained by the addition of 2M NaOH. The resultant phosphonic acid-imbudded foams were dried in the fumehood and ground to a fine powder in the presence of liquid nitrogen. The powdered foams were washed with water and acetone and then air dried. The details of the preparation of the phosphonic acid foam and the cleaning procedure involved are similar to the  $\beta$ -diketone foam as described in the previous section (i.e. 4.5.2).

The above three foams (i.e. phosphonic acid-imbudded foams that were made at pH = 1, pH = 7 and pH = 13) were evaluated for their ability to extract uranium from artificial seawater. Artificial seawater was prepared by dissolving 750 grams of a synthetic salt mixture "Instant Ocean™" (Aquarium System Inc., Ohio, U.S.A.)<sup>279</sup> in deionized water to make 20 litres of artificial seawater. Problems associated with differences in the batches of seawater made were avoided by mixing 20 bags of Instant Ocean™ to make a uniform salt mixture. Laboratory air was bubbled through the seawater solution to adjust the pH to 8.4 which is that of natural seawater. The

solution was then decanted to remove any undissolved particles and organic residues. The resulting solution was then spiked with a known amount of uranium and equilibrated for at least five hours before use. The chemical composition of the unspiked seawater provided by the manufacturer is given in Table 4.1.

Several experiments were performed to study the effects of changing the ratio of the prepolymer to the aqueous layer, the effect of using a vacuum during the foaming process, the effect of a surfactant and the effect of the presence of phenylphosphonic acid and its concentration in the aqueous layer. Artificial seawater sample solutions (25 mL) containing 16.5 ppm of uranium were equilibrated with 0.5 grams of phosphonic acid foam, and the filtered solutions were analyzed by DCP-AES. The uranium concentration of 16.5 ppm was chosen to make the analysis by DCP-AES more convenient. The results obtained and extraction capabilities of these foams for the sorption of uranium from seawater are shown in Table 4.2. Commercially available polyether and polyester foams along with blank foams (Hypol™) were also evaluated and were unable to extract uranium under the same conditions.

When the ratio of the polymer to aqueous layer was 1 : 0.5, the result was a strong but hydrophobic foam. When the ratio was 1 : 2, the foam was weak in mechanical strength but hydrophilic in nature. The optimal foam, which is both hydrophilic and strong, was obtained when the ratio was 1 : 1.

Table 4.1 Chemical composition of "Instant Ocean"<sup>279</sup>

<u>Component</u>	<u>% By Weight</u>
NaCl	65.226
MgSO <sub>4</sub> .7H <sub>2</sub> O	16.307
MgCl <sub>2</sub> .6H <sub>2</sub> O	12.762
CaCl <sub>2</sub>	3.261
KCl	1.737
NaHCO <sub>3</sub>	0.4963
KBr	0.07206
H <sub>3</sub> BO <sub>3</sub>	0.06214
SrCl <sub>2</sub> .6H <sub>2</sub> O	0.04689
MnSO <sub>4</sub> .H <sub>2</sub> O	0.009379
Na <sub>2</sub> HPO <sub>4</sub> .7H <sub>2</sub> O	0.009379
LiCl	0.002343
Na <sub>2</sub> MoO <sub>4</sub> .2H <sub>2</sub> O	0.002343
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .5H <sub>2</sub> O	0.002343
Ca(C <sub>6</sub> H <sub>11</sub> O <sub>7</sub> ) <sub>2</sub> .H <sub>2</sub> O	0.001669
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .18H <sub>2</sub> O	0.001202
RbCl	0.000405
ZnSO <sub>4</sub> .7H <sub>2</sub> O	0.0002563
KI	0.0002403
EDTA.NaFe	0.0001936

Table 4.2 Evaluation of various types of polyurethane foams, with and without phosphonic acid

Expt.No.	Ratio of		Fumehood	Vacuum	Surfac- tant 1 mL	Phenyl Phosph- onic acid	pH of Aqueous Solution	wt of Foam (grams)	%E
	Polymer	Water							
1	1	0.5	x	---	---	---	6.8	0.506	0
2	1	0.5	---	x	---	---	6.8	0.506	0
3	1	0.5	x	---	x	---	6.8	0.507	5
4	1	0.5	---	x	x	---	6.8	0.504	0
5	1	1	x	---	---	---	6.8	0.505	0
6	1	1	---	x	---	---	6.8	0.508	0
7	1	1	x	---	x	---	6.8	0.504	0
8	1	1	---	x	x	---	6.8	0.506	0
9	1	2	x	---	---	---	6.8	0.502	0
10	1	2	---	x	---	---	6.8	0.502	0
11	1	2	x	---	x	---	6.8	0.504	0
12	1	2	---	x	x	---	6.8	0.506	0

Table 4.2 Continued

Expt. No.	Ratio of		Fumehood	Vacuum	Surfac- tant 1 mL	Phenyl Phosph- onic acid	pH of Aqueous Solution	wt of Foam (grams)	%E
	Polymer	Water							
13	1	1	x	---	---	5%	0.95	0.503	91
14	1	1	---	x	---	5%	0.95	0.505	83
15	1	1	x	---	x	5%	0.95	0.508	87
16	1	1	---	x	x	5%	0.95	0.507	85
17	1	1	x	---	---	10%	0.95	0.503	63
18	1	1	---	x	---	10%	0.95	0.507	50
19	1	1	x	---	x	10%	0.95	0.504	68
20	1	1	---	x	x	10%	0.95	0.507	59
21	1	1	x	---	---	5%	7.0	0.506	17
22	1	1	---	x	---	5%	7.0	0.508	16
23	1	1	x	---	x	5%	7.0	0.507	13
24	1	1	---	x	x	5%	7.0	0.504	19

Table 4.2 Continued

Expt. No.	Ratio of		Fumehood	Vacuum	Surfactant 1 mL	Phenyl Phosphonic acid	pH of Aqueous Solution	wt of Foam (grams)	%E
	Polymer	Water							
25	1	1	x	---	---	10%	7	0.503	5
26	1	1	---	x	---	10%	7	0.502	39
27	1	1	x	---	x	10%	7	0.503	73
28	1	1	---	x	x	10%	7	0.504	38
29	1	1	x	---	---	5%	13.0	0.504	0
30	1	1	---	x	---	5%	13.0	0.507	0
31	1	1	x	---	x	5%	13.0	0.504	0
32	1	1	---	x	x	5%	13.0	0.508	2
33	1	1	x	---	---	10%	13.0	0.503	3
34	1	1	---	x	---	10%	13.0	0.508	0
35	1	1	x	---	x	10%	13.0	0.504	0
36	1	1	---	x	x	10%	13.0	0.504	0

The foam produced using 5% (wt/wt) phosphonic acid in the aqueous layer at pH = 1 showed the best percent extraction of uranium from seawater. When the concentration of phosphonic acid was changed to 10% and when the pH of the aqueous layer was increased from pH = 1 to pH = 7 or 13, the percent extraction decreased. The use of a surfactant or foaming under vacuum showed no appreciable effect. The Hypol™ foam produced by incorporating 5% (wt/wt) of phenyl phosphonic acid into Hypol™ foam matrix during the foaming process will be called "phosphonic acid foam" for future references in this thesis.

The extraction capability of phosphonic acid foam for uranium was studied at different pH values and temperatures. Phosphonic acid foam was prepared by mixing equal weights of the Hypol™ prepolymer and a 5% (wt) aqueous solution of phenyl phosphonic acid. The mixture (polymer + aqueous layer) became cloudy and then rose to ten times its original volume. The resulting phosphonic acid foam became tack-free within five minutes.

The procedures for powdering and cleaning of the foam and evaluating the extraction capability of this foam are as given for the  $\beta$ -diketone foam. The colour of the dry and clean phosphonic acid foam was light brown compared to the blank foam, which was white.



### 4.6.3 Results and discussion

Phosphonic acid foam exhibits good extraction capability for the sorption of uranium between pH = 5.3 and pH = 8.2 and the extraction decreases at either end of the pH range as shown in Figures 4.9 and 4.10.

The drop in extraction efficiency at either end of the pH range can be explained by the formation of  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_2\text{Cl}^+$  at pH values below 3, and  $\text{UO}_2(\text{OH})_3^-$  at pH values above 10; these species may not be as extractable by the phosphonic acid foam.

Furthermore, between pH = 3 and pH = 8, it can be seen in Figures 4.9 and 4.10 that the extraction generally increased with an increase in temperature from 4°C to 70°C.

The extraction of uranium from aqueous solutions whose pH is between 3 and 8 would be best at 70°C for this foam. The decrease in extraction efficiency at either end of the pH range suggests the use of a solution with pH less than 1 or greater than 11 as a possible eluting solution to desorb uranium from the foam.

In general, phosphonic acid foam showed superior extractability of uranium over blank foams at pH values between 3 and 8 at all temperatures tested as shown in Figures 4.11 to 4.14.

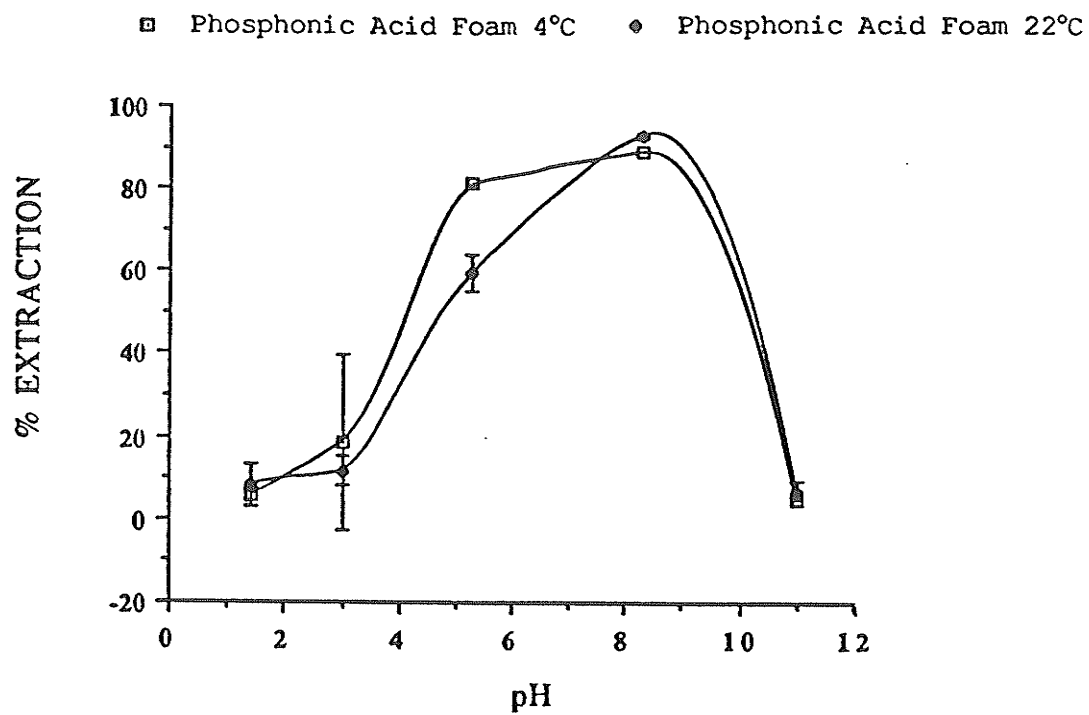


Figure 4.9 Extraction capability of phosphonic acid foam at 4°C and 22°C

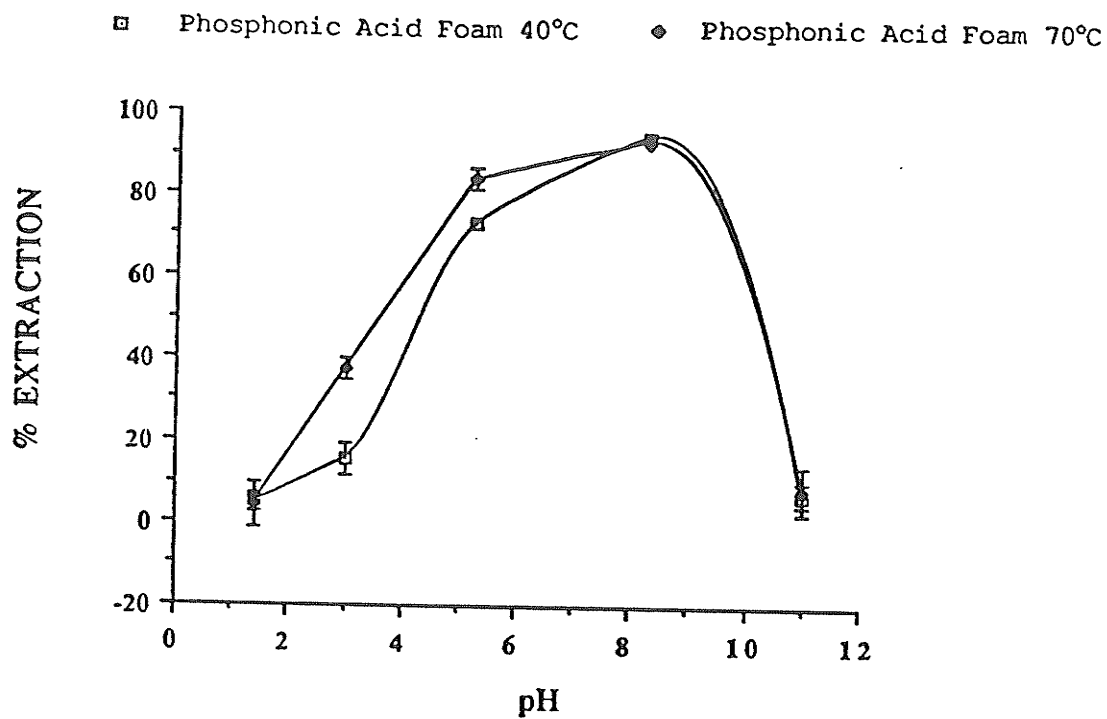
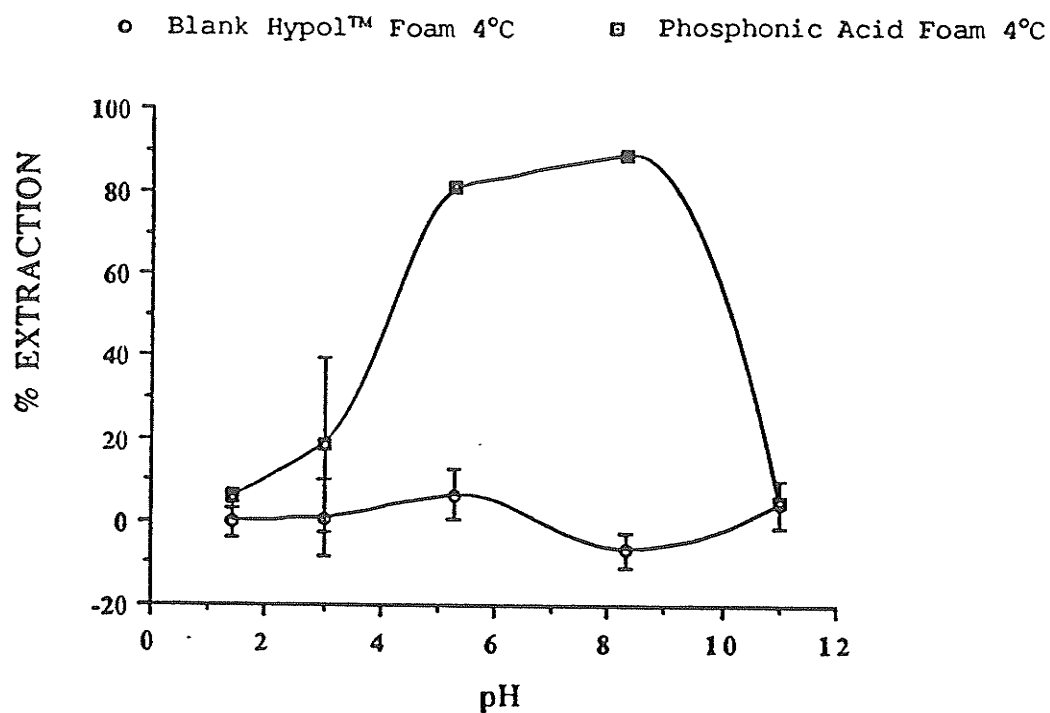


Figure 4.10 Extraction capability of phosphonic acid foam at 40°C and 70°C



**Figure 4.11** Comparison of the extraction capabilities of phosphonic acid foam and blank Hypol™ foam at 4°C

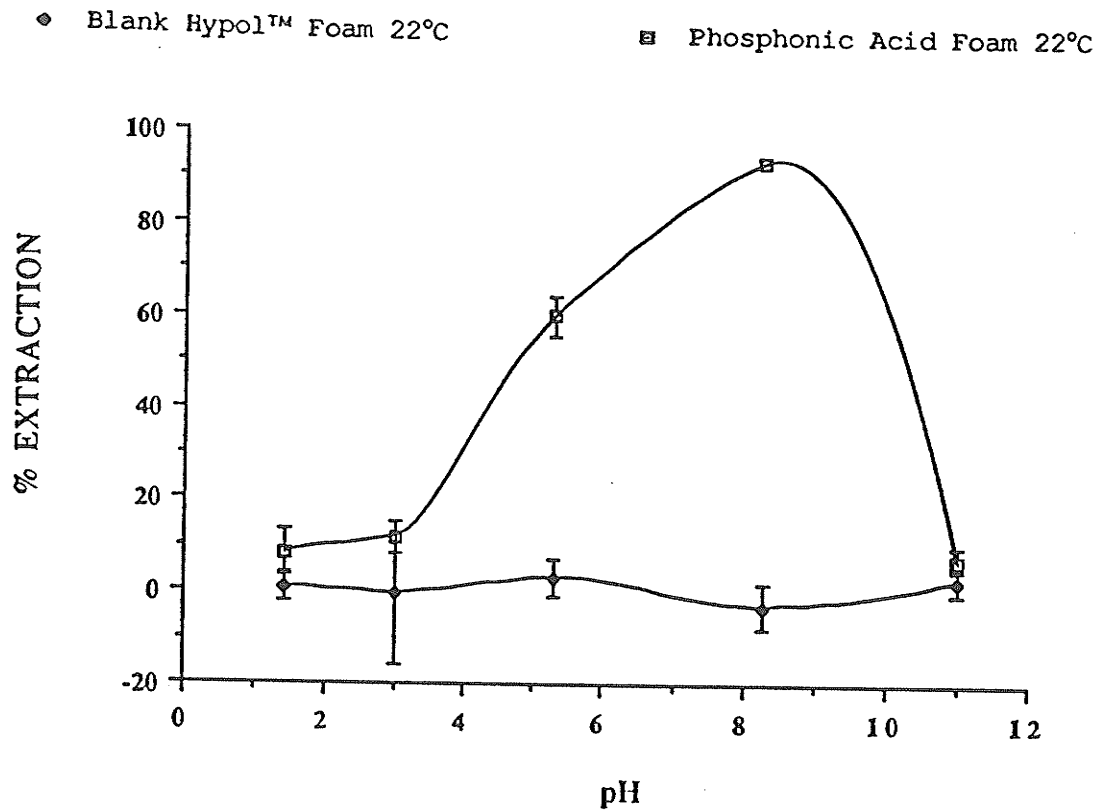


Figure 4.12 Comparison of the extraction capabilities of phosphonic acid foam and blank Hypol™ foam at 22°C

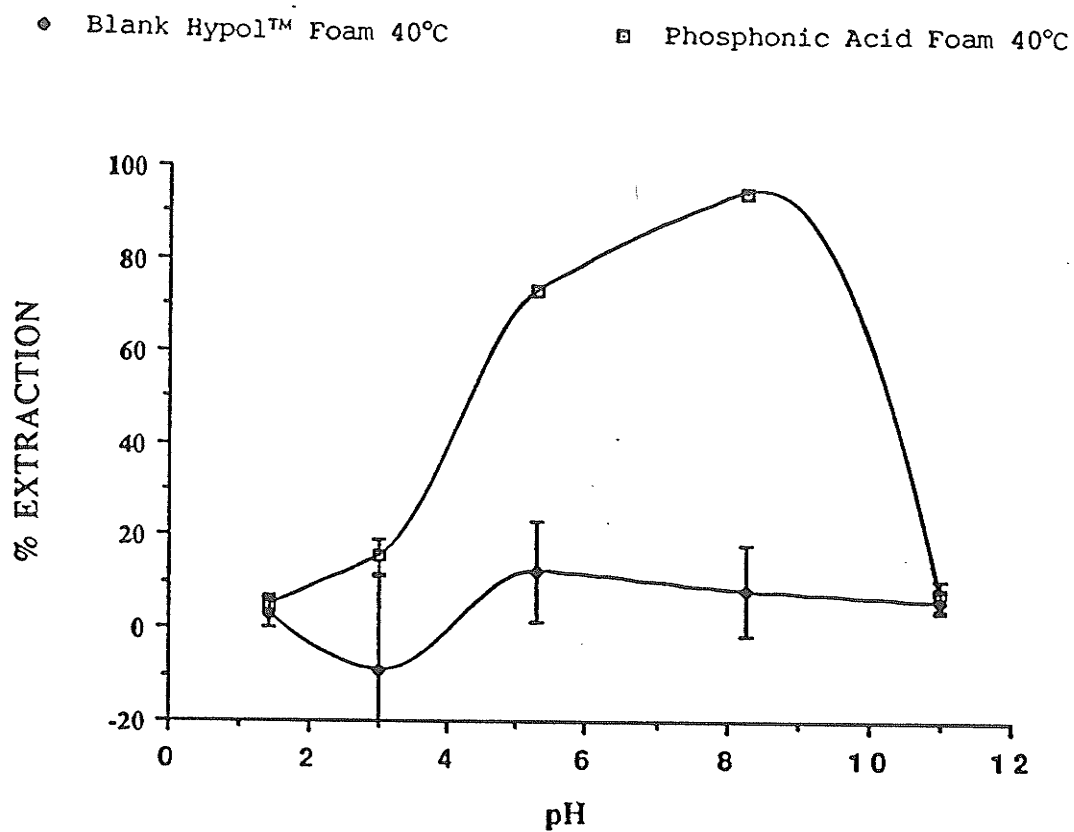


Figure 4.13 Comparison of the extraction capabilities of phosphonic acid foam and blank Hypol™ foam at 40°C

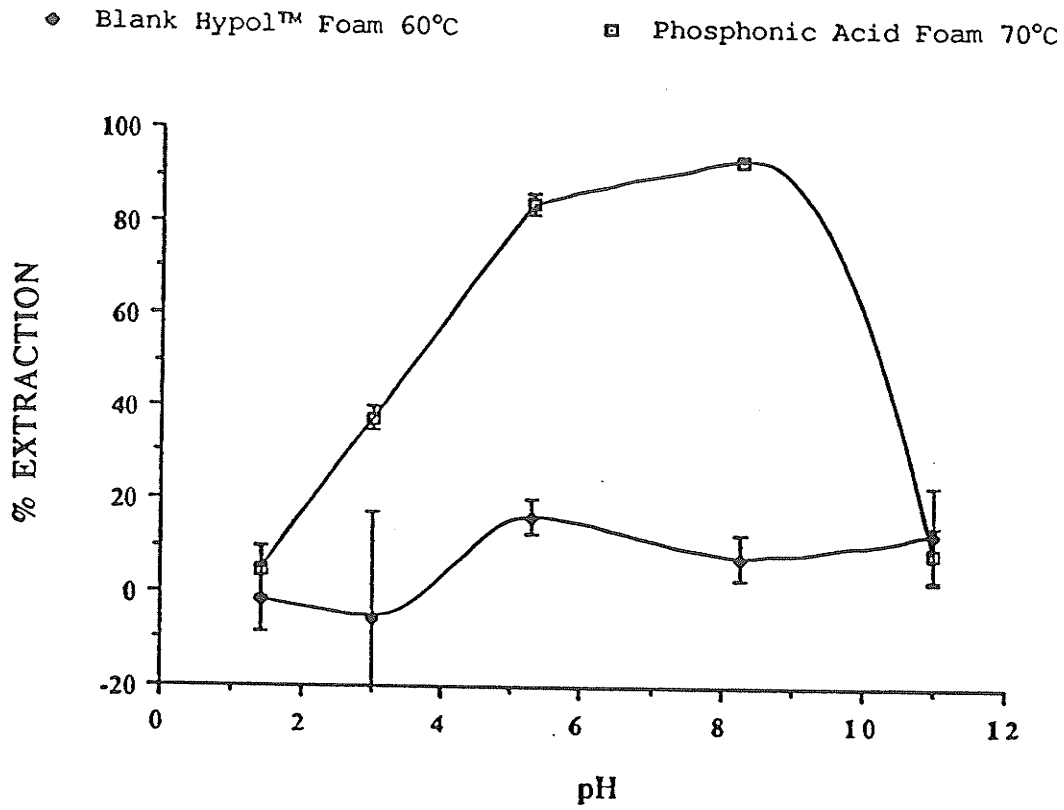


Figure 4.14 Comparison of the extraction capabilities of phosphonic acid foam and blank Hypol™ foam at 70°C

#### 4.6.4 Conclusion

Phenylphosphonic acid was imbedded into the matrix of the polyurethane foam during the fabrication of the foam. The resulting phosphonic acid foam is capable of extracting uranium from aqueous solution whose pH ranges between pH = 5 and pH = 8. The phosphonic acid foams produced by mixing equal amounts of prepolymer and aqueous layer with 5% phosphonic acid (wt/wt) exhibited the best extraction capability in sorbing uranium from artificial seawater. The phosphonic acid foam is simple to make, relatively inexpensive, has high porosity and has good chemical and mechanical stability. The above qualities would render the phosphonic acid foams to be used as a good sorbent for the preconcentration of uranium from solutions whose pH range is  $7.0 \pm 1.5$ . On comparing the  $\beta$ -diketone foam and phosphonic acid foam, it can be seen that  $\beta$ -diketone foam is capable of sorbing uranium from a solution with a wider range of pH (i.e. between pH = 3 and pH = 10) but is unable to stand temperatures greater than 40°C without showing a decrease in its extraction ability. Phosphonic acid foam on the other hand is only capable of sorbing uranium from solutions with pH values between 5 and 8; however, it is stable and performs best at 70°C.

At higher temperatures (i.e. 70°C) the choice of sorbent for preconcentrating uranium from solution with pH values  $7.5 \pm 1.5$  would be the phosphonic acid foams and at lower temperatures (i.e. less than 70°C) the sorbent of choice would be the  $\beta$ -diketone foam. In conclusion, the above foams are simple to make and also relatively



inexpensive. These foams have shown good chemical and mechanical stability along with high porosity, thus making them good sorbents for column packing and for industrial applications.

#### 4.7 Preparation and evaluation of amidoximated fabric

##### 4.7.1 Introduction

A number of papers have been published for the synthesis of macroreticular resins with amidoxime groups<sup>80-138</sup> because of their use in the extraction of uranium from seawater, as shown in Chapter I. The papers describing the synthesis of a sorbent with an amidoxime group, for the most part, involve the incorporation of a nitrile group into a polymer matrix, followed by the conversion of the nitrile group into an amidoxime group by treatment with a solution of hydroxylamine in methanol.

Egawa *et al.*<sup>83,84</sup> prepared a macroreticular chelating resin containing amidoxime by reacting acrylonitrile-divinyl benzene co-polymer beads with hydroxylamine.

Sugasuka *et al.*<sup>85</sup> synthesized a number of polyacrylamidoxime resins from various co-polymers of acrylonitrile and cross-linking agents. Work on fibres has generated wide interest in the last decade with improvements being made with respect to flow rate through the column and the mechanical stability of the fibre. Fibres have been made by radiation-induced graft polymerization of acrylonitrile into polymeric fibres, followed by amidoximation<sup>88,89</sup>. Amidoximation was attained by treating the

polyacrylonitrile fibre with hydroxylamine in methanol<sup>85</sup>.

In a previous section of this chapter it was shown that we have been successful in incorporating functional groups that were attached to a benzene ring into the polyurethane foam matrix during the foaming process; therefore an attempt was made to do the same with an amidoxime group. As phenyl amidoxime was not commercially available, the direct method of incorporating a reagent with an amidoxime group into the foam matrix could not be done without the preliminary synthesis of this reagent. Instead, if one was able to incorporate a nitrile ( $-C\equiv N$ ) group into the foam, the product then can be subjected to amidoximation by treating with hydroxylamine in methanol solution.

Several attempts were made to incorporate various compounds, such as benzylnitrile, styrylnitrile, phthalonitrile, acrylonitrile and N-butyranitrile, into Hypol™ foam during the foaming process. The procedure for incorporation and cleaning was similar to that of  $\beta$ -diketone foam, where 5% (wt/wt) of the above compounds were added to the Hypol™ prepolymer, with constant stirring, to form a viscous solution. An equal weight of water was then added to the viscous polymer solution followed by a rapid stirring of the mixture for 15 seconds. The clean, dry, powdered foams were subjected to amidoximation by treating with a solution of hydroxylamine in methanol. The resulting foams (i.e. after amidoximation) were unable to extract uranium from aqueous solutions.

FT-IR (ATR) analysis of these foams, before amidoximation, revealed the absence of an absorption band around  $2250\text{ cm}^{-1}$ , which is the characteristic absorption band for the  $-\text{C}\equiv\text{N}$  group. The absence of an absorption band at  $2250\text{ cm}^{-1}$  led us to believe that the  $-\text{C}\equiv\text{N}$  groups of the above compounds were reacting with the Hypol™ prepolymer. Further experiments to incorporate amidoxime into the foam matrix during the fabrication of the foam were discontinued due to the reaction between the nitrile-containing compounds and the Hypol™ prepolymers.

In another experiment, commercially available foams were coated with nitrile containing compounds. This was done with an intention to convert the nitrile groups into amidoxime groups to produce a foam with amidoxime groups on the surface of the foam. Industrial fibres made of polyacrolein, that were obtained from Dr. Gesser, were dissolved in dimethyl formamide (DMF) in order to coat commercially available polyurethane foam (Dispo™). Polyester foam plugs and polyether foam plugs were soaked in a 3%(wt/vol) polyacrolein in DMF for 4 hours. The squeezed and dried foams were subjected to amidoximation. The polyether plugs were discarded as they were unable to regain their original shapes after squeezing. When the polyacrolein coated polyester plugs were subjected to amidoximation the polyacrolein layer fell off the foam as a fine powder.

Work with amidoxime and polyurethane foams was discontinued as attempts to incorporate nitrile groups on to the foam proved to be unsuccessful or the conversion

of these nitrile groups into amidoxime groups, while still being on the foam, proved to be unsuccessful. The above unsuccessful attempts to produce an amidoxime containing polyurethane foam led us to seek commercially and commonly available material with nitrile groups and also with good porosity, good mechanical and chemical stability. Such a material could then be treated with hydroxylamine solution to produce an amidoxime-containing sorbent.

It was of interest to us to determine if the nitrile groups of commonly available materials, such as polyacrylonitrile (eg. Orlon™) could be converted to have amidoxime groups. The successful conversion of nitrile groups of a polyacrylonitrile fabric into amidoxime groups would result in a modified polyacrylonitrile fabric with amidoxime groups, which would then be evaluated for the preconcentration of uranium from aqueous solutions.

Orlon™ is the trade mark for an acrylic fibre that was first introduced into the market in 1950 by E. I. DuPont de Nemours and Co. Inc.. Chemically the polymer contains at least 85 percent by weight of acrylonitrile moieties. The fabric is readily available, inexpensive and shows good chemical and physical/mechanical stability.<sup>280</sup> Orlon™ fabric was obtained from Prof. King of Department of Textile and Clothing of this University to study its amidoximation properties. Preliminary experiments showed that after amidoximation, the modified Orlon was capable of extracting uranium from aqueous solutions. The Orlon™ fabric, which remained flexible throughout the

process of amidoximation, changed colour from white to yellow. During amidoximation it was noticed that the cloth pieces became entangled with one another while stirring, which resulted in uneven reaction. The large knots that resulted due to entanglement were not of uniform colour. The problem of entanglement of the Orlon™ fabric pieces can be avoided if the Orlon™ fabric could be ground to fine powder before subjecting it to hydroxylamine solution. The procedure used for the powdering of foams, i.e. freezing with liquid nitrogen and grinding with a blender, proved to be unsuccessful for Orlon™ fabric. An alternative method was to grind the Orlon™ fabric with a Wiley™ Mill (a mechanical fabric grinder) to a fine powder prior to amidoximation. When subjected to amidoximation, the fibres now formed were uniformly yellow in colour. These yellow fibres will be called "modified Orlon" through the remainder of this thesis.

#### **4.7.2 Procedure**

Modified Orlon fibres were prepared by treating 30 grams of ground Orlon™ fabric with 1 litre of amidoximating reagent. This reagent was freshly prepared by dissolving 40 grams of hydroxylamine hydrochloride in a 50% (vol/vol) mixture of methanol and water. This solution was adjusted to pH 7.0 by using 2M KOH solution, and made up to 1 litre to give the amidoximating reagent. The mixture of Orlon™ fibres and amidoximating reagent was heated at 40°C with constant stirring under reflux for 12 hours. The fibres changed from white to yellow during the process. After cooling, the mixture was filtered through a Buchner funnel fitted with a

Whatman 541<sup>TM</sup> filter paper. The modified Orlon fibres were removed from the filter paper, soaked in 500 mL of water for four hours, and the resulting slurry then filtered under vacuum through the Buchner funnel. The fibres were recovered from the filter paper and the complete washing procedure of soaking and filtering was repeated two more times. The fibres were then washed three more times using the same procedure, except for the use of acetone in place of water. This washing procedure should remove impurities that are soluble in water or acetone and any unreacted reagents from the modified Orlon fibres. The clean, powdered fibres were left to dry under vacuum for four hours to remove traces of acetone. Blank Orlon<sup>TM</sup> fibres, without the addition of hydroxylamine hydrochloride, were prepared in a similar manner to serve as a blank.

The extraction capability of modified Orlon was determined by adding 25 mL of 10 ppm uranium solution to a 60 mL screw top Nalgene<sup>TM</sup> plastic bottle, together with approximately  $0.200 \pm 0.003$  grams of dried powdered fibres. The capped bottles were shaken for five hours in an automatic shaker. The filtered solutions were then analyzed by CFSM to determine the uranium uptake by the fibres. The extraction capabilities of these fibres for uranium at different temperatures and pH values were studied and the analysis method and the calculation of % extraction for the evaluation of these fibres were the same as given for  $\beta$ -diketone foams.

The extraction characteristics of modified Orlon and blank Orlon<sup>TM</sup> fibres were studied

by equilibrating the fibres with uranium solutions at different temperatures and pH values. The pH values of the uranium solutions were adjusted with 2M HCl or 2M NaOH solution and the pH values were monitored with a pH meter.

Uranium solutions were equilibrated to the required temperatures before adding them to the plastic bottles containing the fibres. Shaking of solutions at room temperature (22°C) and at thermostatically-controlled cold room temperatures (4°C) was done using a Burrell Wrist Action Shaker. Similar experiments at 40°C and 70°C were performed with a Dubnoff Metabolic Shaking Incubator equipped with a variable temperature-controlled water bath. Temperature measurements were within  $\pm 2^\circ\text{C}$ .

#### 4.7.3 *Results and discussion*

In Figure 4.15 it can be seen that modified Orlon at 4°C exhibits a high percent extraction between pH = 3 and pH = 8 and that the extraction decreases at either end of the pH range. The decrease in percent extraction can be explained by the formation of  $\text{UO}_2\text{Cl}_2$ ,  $\text{UO}_2\text{Cl}^+$  at pH values below 3 and  $\text{UO}_2(\text{OH})_3^-$  at pH values above 10; these species may not be as extractable by this modified Orlon. At higher temperatures, and between pH = 3 and pH = 5, it can be seen in Figure 4.15 and 4.16 that the percent extraction decreases or remains constant with an increase in temperature. This occurs because the amidoxime group is unstable at higher temperatures.<sup>220</sup> At pH = 1.4 and 11 the percent extraction increases with temperatures which may be due to the acid/base hydrolysis product of the amidoxime group that are present at that pH.

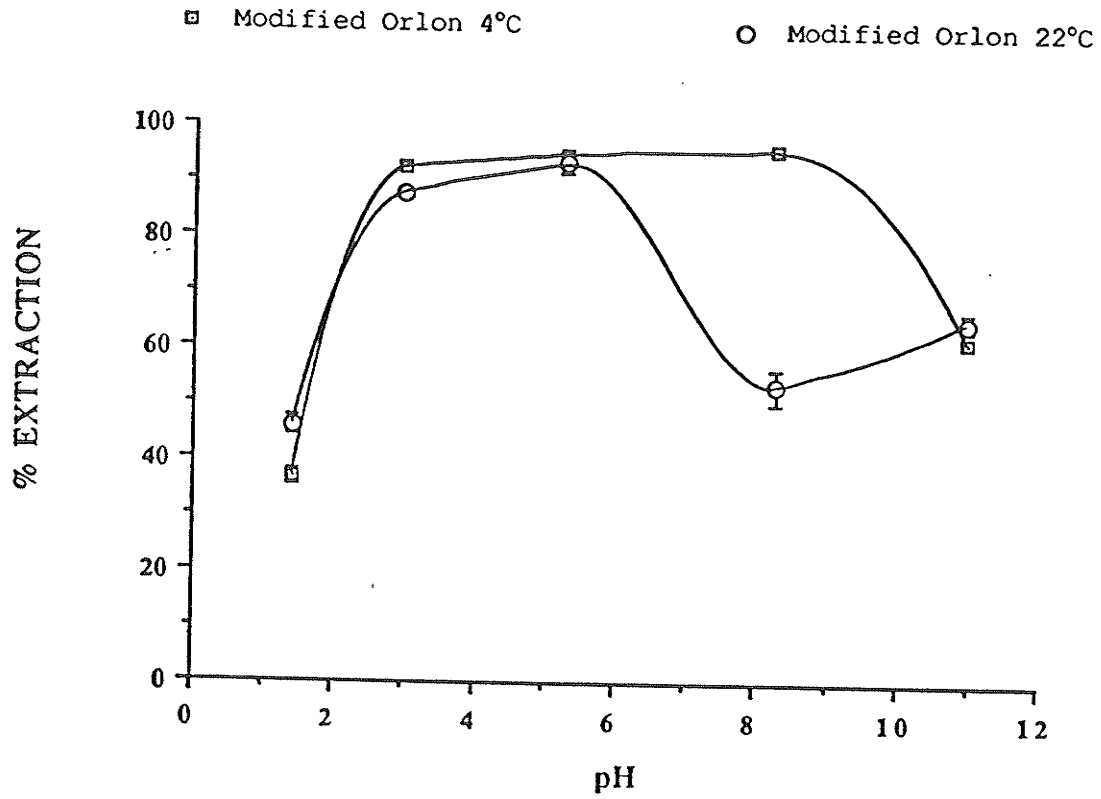


Figure 4.15 Extraction capability of modified Orlon at 4°C and 22°C



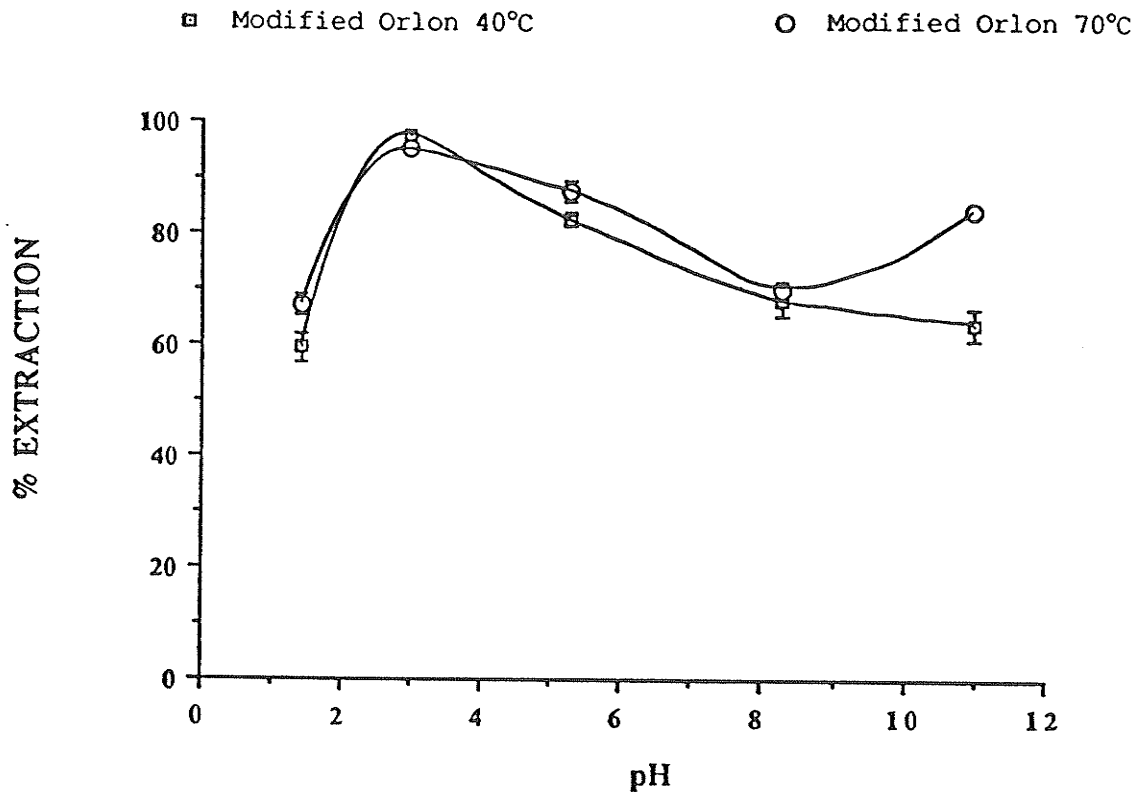


Figure 4.16 Extraction capability of modified Orlon at 40°C and 70°C

At lower pH values acid hydrolysis of the amidoxime group takes place, while at higher pH values base hydrolysis occurs.<sup>281</sup> At pH = 8, the percent extraction drops as the temperature increases from 4°C to 22°C and then it increases as the temperature rises from 22°C to 70°C. The anomaly in the extraction profile at pH = 8 at 22°C was not reported earlier and it is our opinion that the initial decrease in percent extraction that was observed between 4°C and 22°C was due to the base hydrolysis of the amidoxime group, and the increase in percent extraction that was observed between 22°C and 70°C was due to the hydrolysed amidoxime group.

In Figures 4.15 and 4.16 it can be seen that to obtain maximum extraction one may want to perform the experiments at different temperatures. For example, at pH = 1 and 11 the ideal extraction temperature would be 70°C, while at pH = 5.3 and 8.3 the ideal temperature would be 4°C and at pH = 3 the ideal temperature would be 40°C. Experiments beyond 70°C were not undertaken as it proved to be difficult to maintain the temperature of the shaking waterbath due to vaporization of water.

Modified Orlon fibres showed better extraction capability over the wide range of pH and temperature values compared to blank Orlon™ fibres (i.e. without amidoxime transformation) as shown in Figures 4.17 to 4.20. In Figure 4.17 it can be seen that the uncertainty in the percent extraction by blank Orlon™ fibres at pH = 5.3 was very high. Repeated experiments showed inconsistent results suggesting that the blank Orlon™ fibres may be acting as nucleation sites for the precipitation of uranium.

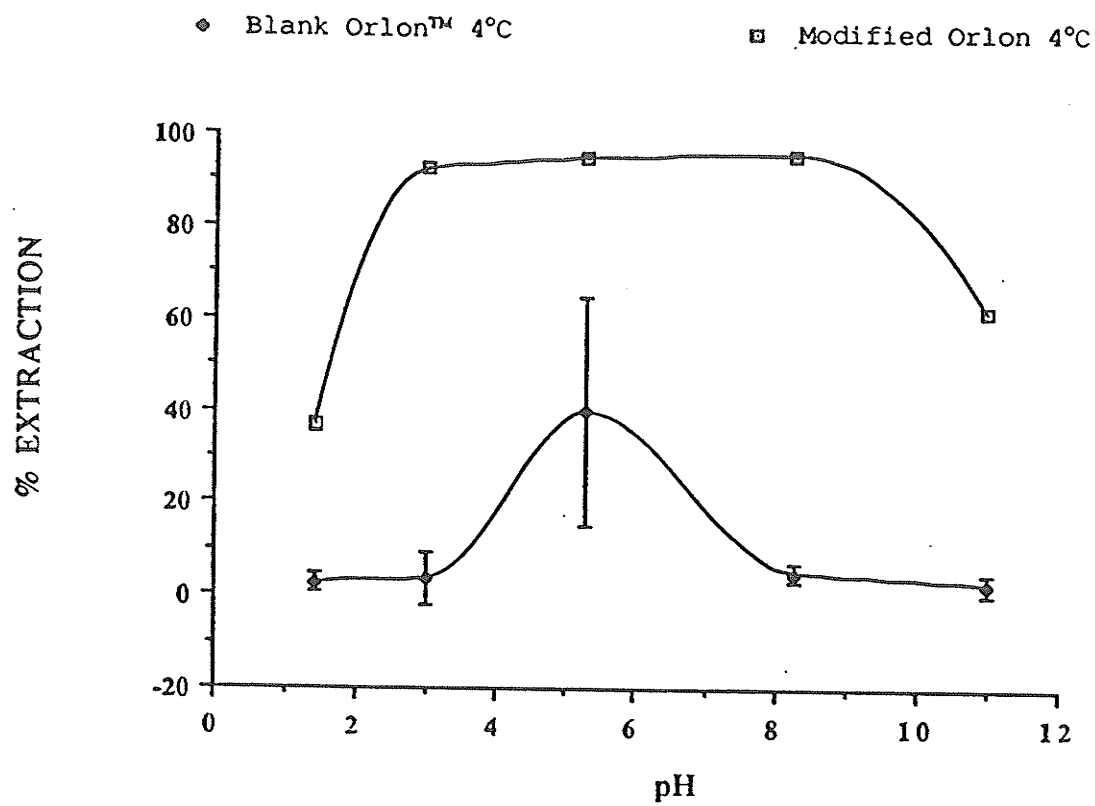


Figure 4.17 Comparison of the extraction capabilities of modified Orlon and blank Orlon™ at 4°C

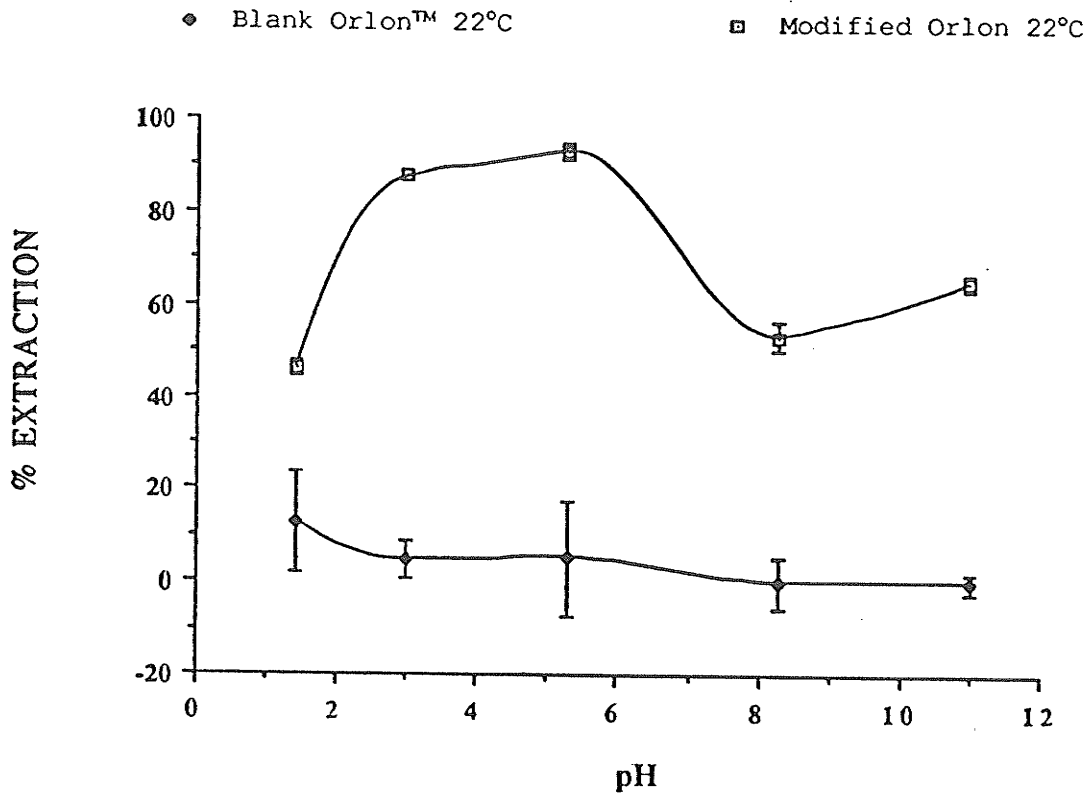


Figure 4.18 Comparison of the extraction capabilities of modified Orlon and blank Orlon™ at 22°C

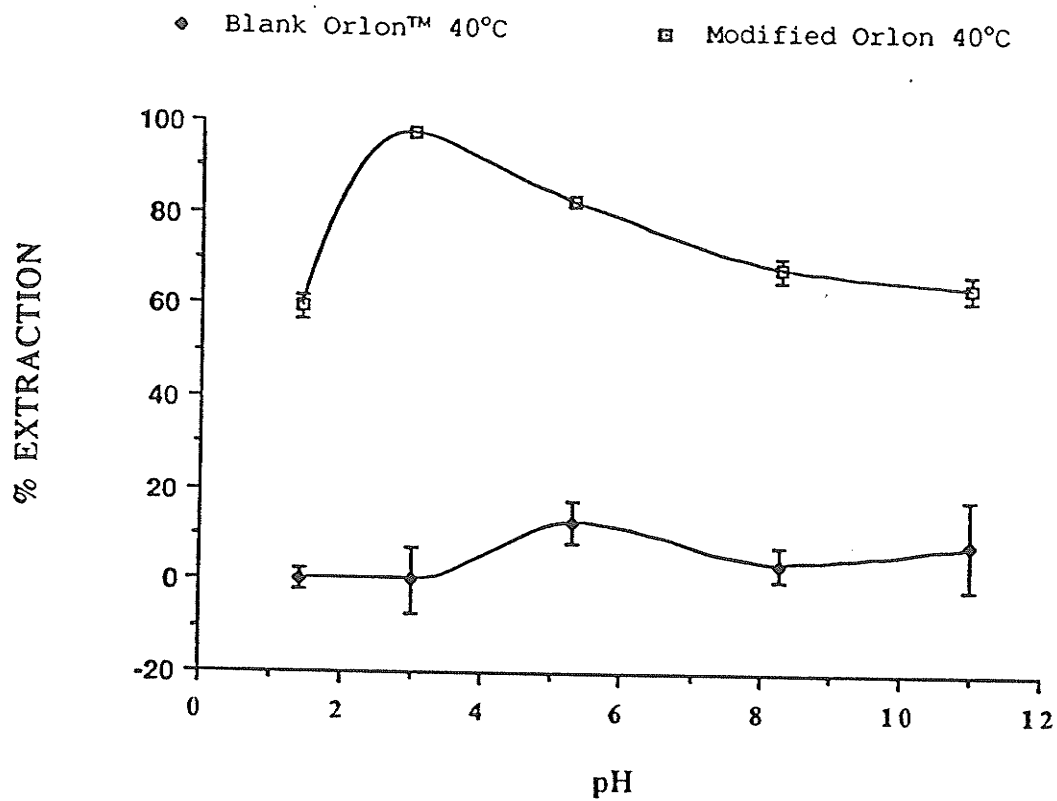


Figure 4.19 Comparison of the extraction capabilities of modified Orlon and blank Orlon™ at 40°C

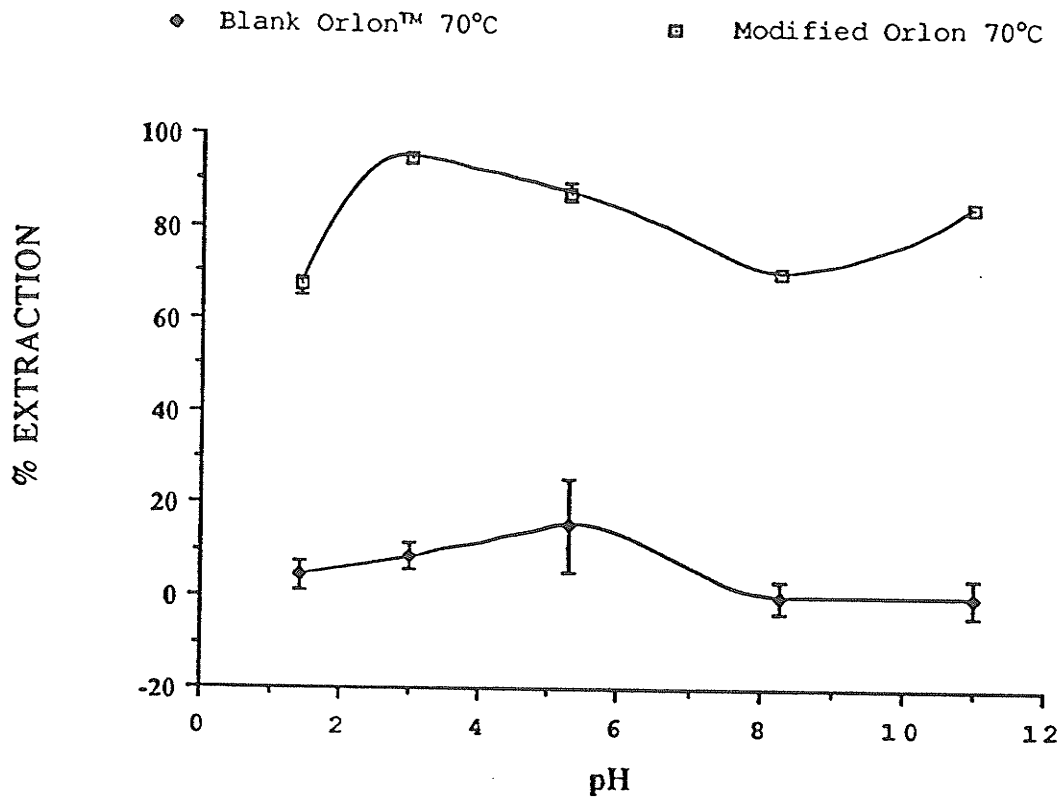


Figure 4.20 Comparison of the extraction capabilities of modified Orlon and blank Orlon™ at 70°C

#### 4.7.4 Conclusion

Orlon™ fabric was successfully amidoximated by converting the  $-C\equiv N$  groups of the Orlon™ fibre into amidoxime groups which are capable of extracting uranium from aqueous solution whose pH ranges between 1.4 and 11. The modified Orlon fabric appears to retain all physical qualities of the Orlon™ fabric, i.e. flexibility, strength etc., thereby making large scale industrial use possible. Alternatively, the ground-up fibres could be packed into a column for analytical purposes. The modified Orlon fibres would be a good sorbent for the sorption of uranium from natural waters as the pH values of natural waters are usually in the range of  $pH = 7 \pm 3$ . These fibres are unique in their ability to extract uranium at low temperature (i.e.  $4^{\circ}C$ ) making it an ideal sorbent for the preconcentration of uranium from natural water systems during the colder months.

The modified Orlon fabric is simple to make, relatively inexpensive and has good chemical and mechanical stability. The porosity of the fabric is good and it can easily be controlled by changing the weaving pattern during the production of the Orlon™ fabric. The above qualities would render the modified Orlon fabric as a promising sorbent for the preconcentration of uranium for both analytical and industrial purposes.

#### 4.8 Conclusion

A  $\beta$ -diketone foam, a phosphonic acid foam, and modified Orlon fibres were developed in our laboratory which are capable of extracting uranium from solutions at

a wide range of pH and temperature.

$\beta$ -diketone foam and modified Orlon were found to be useful for sorbing uranium from solutions with pH values between 3 and 8, whereas phosphonic acid foam was useful only between 5 and 8. Information such as the choice of sorbent for the sorption of uranium at a particular temperature or pH can be obtained by comparing the extraction profiles of  $\beta$ -diketone foam, phosphonic acid foam, and modified Orlon as shown in Figures 4.21 to 4.24.

The choice of sorbent at 4°C would be the modified Orlon over the whole range of pH that was evaluated as shown in Figure 4.21. Similarly, at 22°C the choice of sorbent would be modified Orlon over the range of pH that was evaluated, except at pH = 8 where the choice of sorbent would be phosphonic acid foam, as shown in Figure 4.22. At 40°C, the choice of sorbent at pH = 1 and 3 would be modified Orlon and at pH = 5 and 11 it would be  $\beta$ -diketone foam and at pH = 8 it would be phosphonic acid foam as shown in Figure 4.23. Similarly at higher temperatures, it can be seen from Figure 4.24 that the choice of sorbent at pH = 1, 3 and 11 would be modified Orlon and at pH = 5 it would be  $\beta$ -diketone foam and pH = 8 it would be phosphonic acid foam.



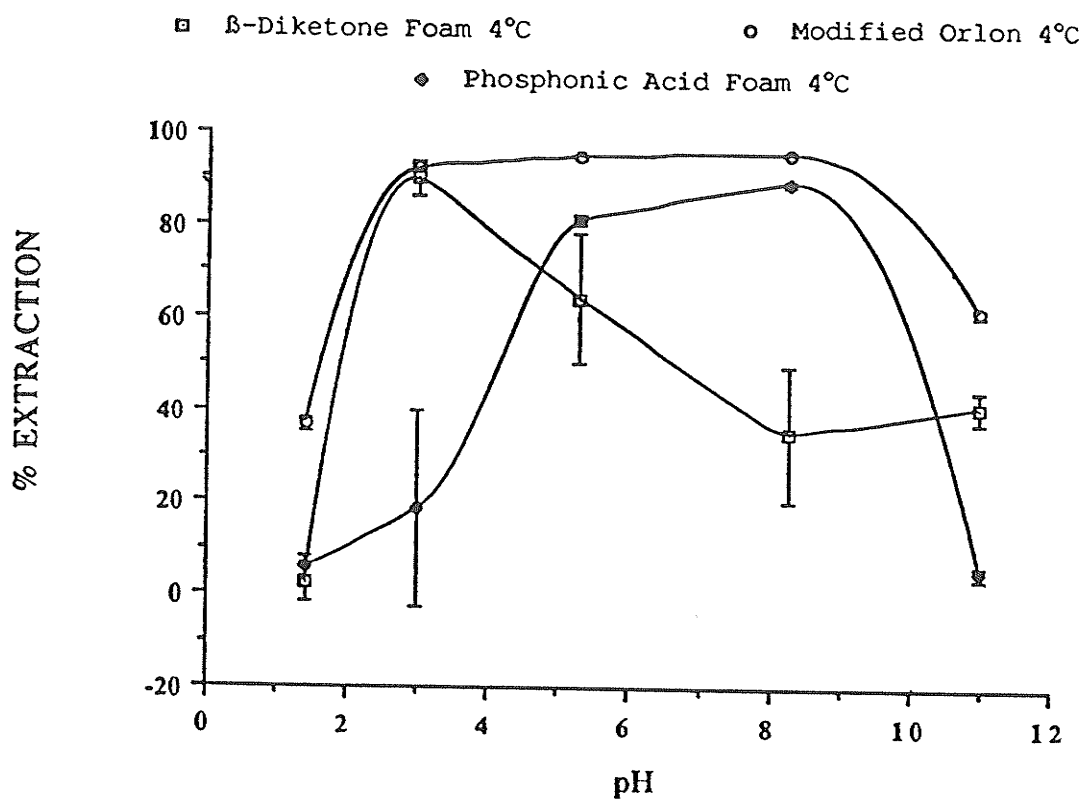


Figure 4.21 Comparison of the extraction profiles of  $\beta$ -diketone foam, phosphonic acid foam and modified Orlon at 4°C

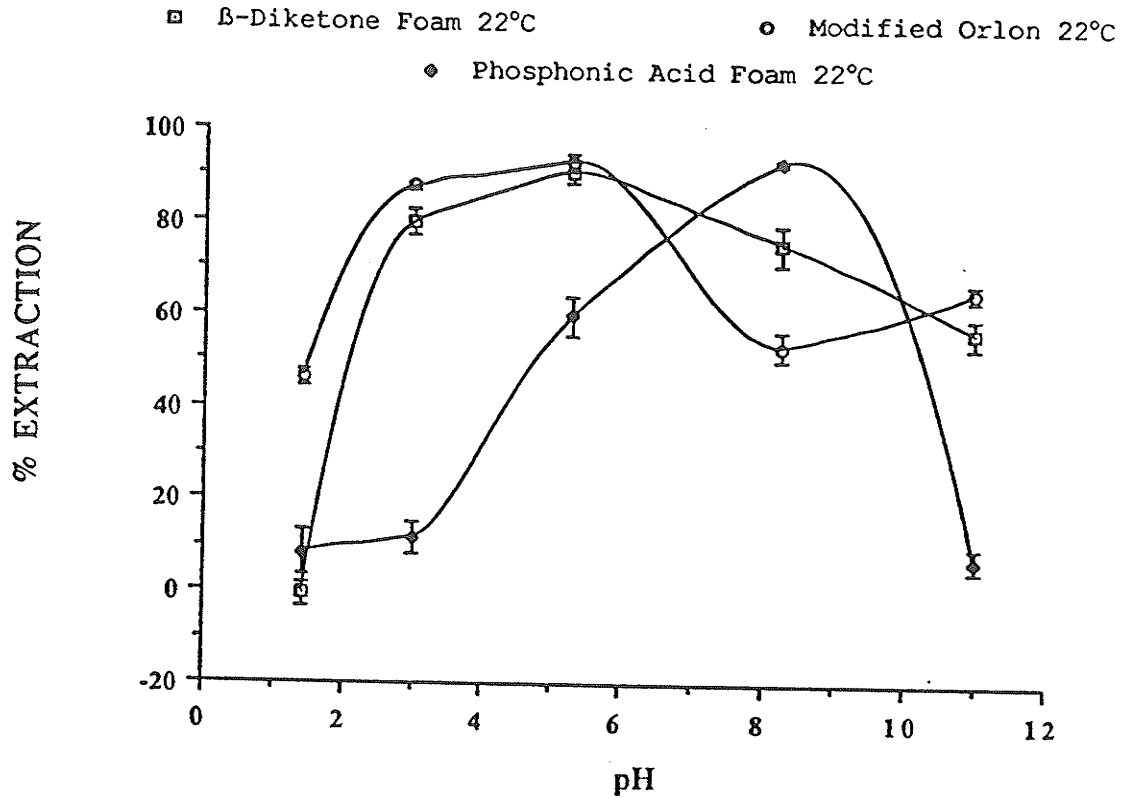


Figure 4.22 Comparison of the extraction profiles of  $\beta$ -diketone foam, phosphonic acid foam and modified Orlon at 22°C

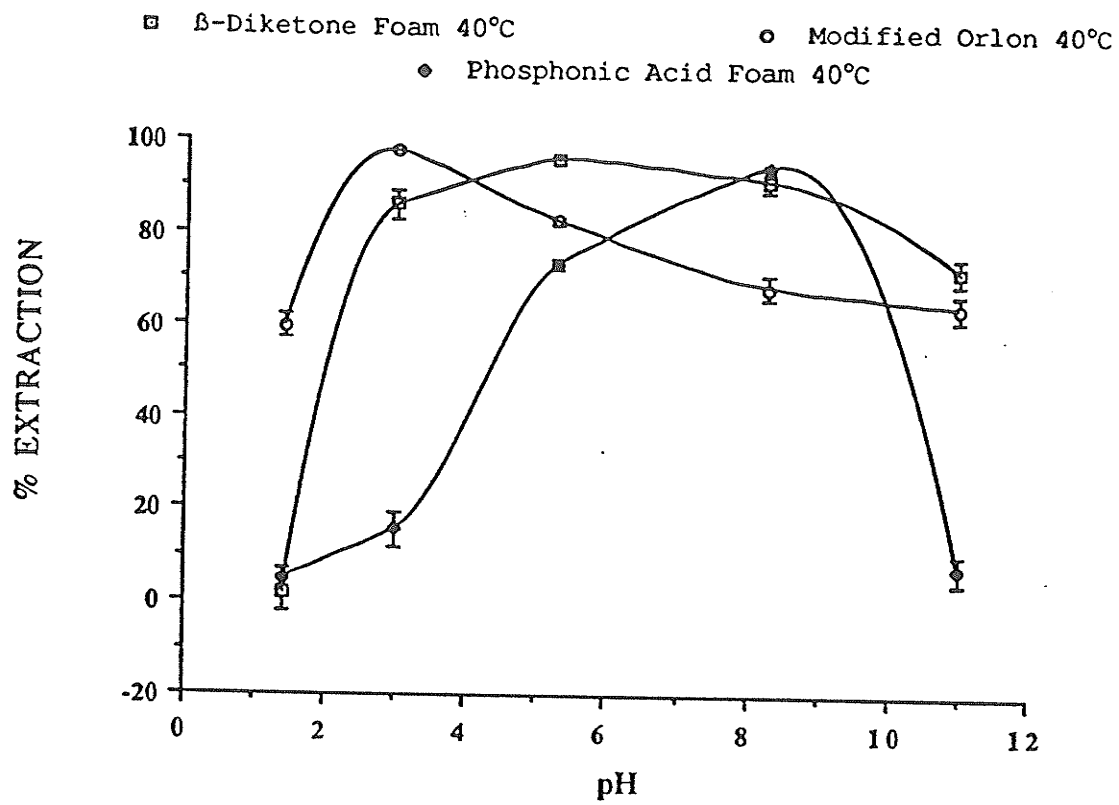


Figure 4.23 Comparison of the extraction profiles of  $\beta$ -diketone foam, phosphonic acid foam and modified Orlon at 40°C

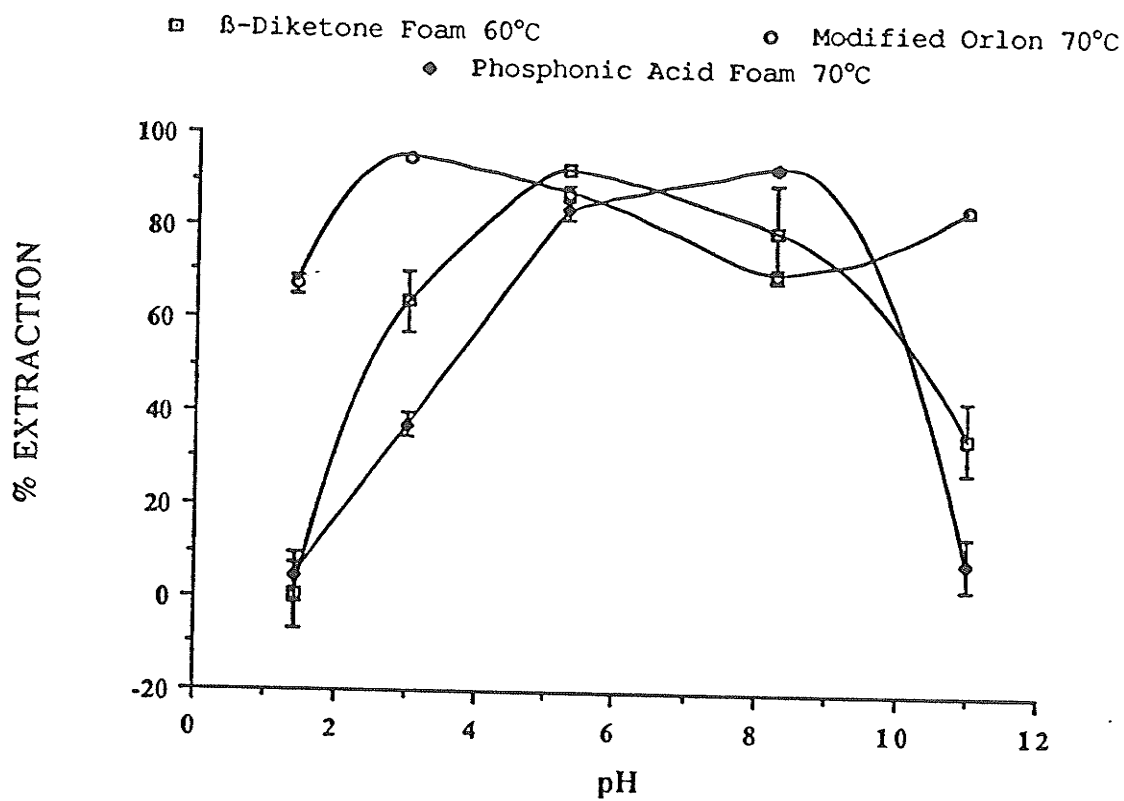


Figure 4.24 Comparison of the extraction profiles of  $\beta$ -diketone foam, phosphonic acid foam and modified Orlon at temperatures above 60°C

The above sorbents were relatively inexpensive and simple to make. They had good porosity along with good chemical and mechanical stability thereby rendering them as useful sorbents for the sorption of uranium for preconcentration purposes. The three sorbents that were developed in our laboratory, i.e.  $\beta$ -diketone foam, phosphonic acid foam and modified Orlon can be packed into a column for use in analytical chemistry. These sorbents can now be used for a number of industrial applications including the nuclear industry. These sorbents may play a vital role in the clean-up procedures for spills involving uranium in industry and other radiochemical facilities and in the uranium mining and refining industry. These sorbents could be used for the removal of uranium from uranium mine tailings.

## CHAPTER V

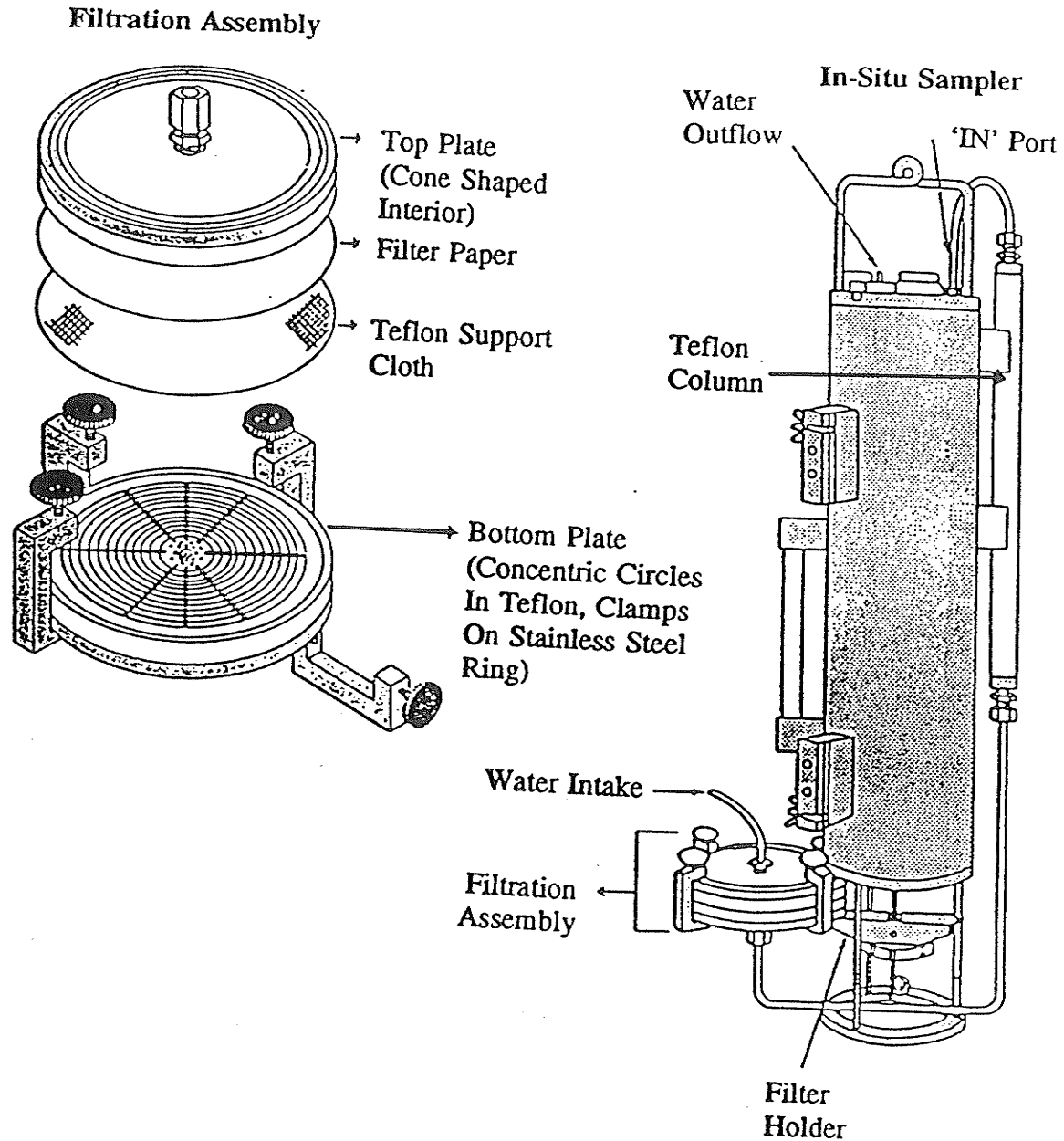
COMMERCIAL RESINS FOR THE UPTAKE OF URANIUM  
FROM SEAWATER**5 Introduction**

Functional groups such as diketone, phosphonic acid and amidoxime, when present in a solvent or sorbent, were capable of extracting uranium from aqueous solutions, as shown in Chapters I and IV. The evaluation of commercially available resins containing these functional groups for the extraction of uranium from seawater was undertaken to compare their performance with the widely used Chelex 100 resin. This work was part of a project (Natural Sciences and Engineering Research Council's University Industry Grant CRD-8510) whose objectives were to develop and test chelating polymeric materials specifically for use with the Seastar™ In-situ Water Sampler for the extraction of uranium and other radionuclides from sea and fresh water media.

The Seastar™ In-situ Water Sampler was designed by Seastar™ Instruments Ltd., Sidney, British Columbia, Canada. This sampler<sup>282</sup> is capable of sampling large volumes, which is an advantage if one is interested in trace and ultra-trace analysis. The sampler is microprocessor-controlled, which adds flexibility in the mode of sampling, and it has 12 different sampling modes. It has a precise control of flow rates and sample volume and has three choices of pump speeds, i.e. 50, 100 and

150 mL.min<sup>-1</sup>. The sampling choices vary from continuous pumping to pumping for an hour twice each day for several days. The sampler can be submerged for days or weeks, and the attachments on the side of the sampler allow for electrical connections and activation by a messenger, or to be moored with a float and anchor. The sampler can start or stop at preprogrammed times. It uses a 142 mm diameter filter unit which is useful for particulate/colloidal matter analysis. The sampler, along with the filter unit, is shown in Figure 5.1. This unit is operational down to a depth of 300 meters and is capable of operating at temperatures between -40 and +70°C. The unit is self-contained and is powered by 20 D cell batteries, which provide up to 100 hours of continuous pumping. The pump and flow meter are downstream of the extraction column, thereby eliminating contamination problems. Water to be sampled is drawn in from the bottom into the extraction column (a Teflon™ tube) containing the sorbent material.

As part of this project, experiments by Dr. Kantipuly, Ms. LeBlanc and Mr. Chan of our laboratory have shown that Chelex 100, Duolite ES 467, 8-Hydroxyquinoline and Chelite N were capable of extracting uranium from artificial seawater, as shown in Table 5.1. These resins are stable in seawater and in eluting agents such as 0.2M Na<sub>2</sub>CO<sub>3</sub>, 0.2M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, 2M HNO<sub>3</sub>, 2M HCl and 1 : 1 HCl and HNO<sub>3</sub> solutions. Results in Table 5.1 show that all the resins showed a decrease in the absorption capability as the temperature was lowered from 22 ± 2°C to 3 ± 1°C, except for Chelex 100. The absorption capability at 4°C was of importance and of interest to us



**Figure 5.1** Diagram of the Seastar™ In-situ Water Sampler with filtration assembly



Table 5.1 Evaluation of commercially available resins for the sorption of uranium from artificial seawater

Resin	Sample Composition	Sample Volume (L)	Concentration of Species in ppm			pH	Flow Rate (ml.min <sup>-1</sup> )	Temp. °C	U Conc. (ng.ml <sup>-1</sup> )	% U Recovered
			Cl <sup>-</sup>	Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>					
Chelex -100	U + H <sub>2</sub> O	20	---	---	---	---	75	22 ± 2	50.0	66.2
	"	20	---	---	---	---	75	"	50.0	97.1
	"	20	---	---	---	---	75	"	50.0	94.6
	U + NaHCO <sub>3</sub>	20	---	57	150	8.0	75	"	50.0	88.5
	U + NaCl	20	16610	10770	---	7.0	75	"	50.0	77.6
	U + NaCl + NaHCO <sub>3</sub>	20	16520	10770	150	8.0	75	"	50.0	92.7
	U + seawater	20	See Instant ocean composition			8.4	75	"	5.0	52.1
	"	20				8.0	75	2 ± 2	25.0	52.0
Duolite -ES 467	U + NaCl + NaHCO <sub>3</sub>	20	16610	10800	150	7.5	50	23 ± 2	5.0	102.0
	"	20	16610	10800	150	7.5	50	23 ± 2	5.0	99.5
	"	20	16610	10800	150	7.5	50	22 ± 2	5.0	100.2
	"	20	16610	10800	150	7.8	75	22 ± 2	5.0	99.2
	U + NaCl	21	17260	10900	---	7.0	50	22 ± 2	50.0	100.0
	U + seawater	22	See Instant Ocean Composition			8.4	75	22 ± 2	4.5	96.7
	"	20				8.4	75	4 ± 2	4.0	63.0
	"	20				8.4	200	4 ± 2	5.0	26.0
	"	20				8.2	200	22 ± 2	10.0	106.0

Table 5.1 Continued

Resin	Sample Composition	Sample Volume (L)	Concentration of Species In ppm			pH	Flow Rate (ml.min <sup>-1</sup> )	Temp ± 2 °C	U Conc. (ng.ml <sup>-1</sup> )	% U Recovered
			Cl <sup>-</sup>	Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>					
8-hydroxy-quinoline	H <sub>2</sub> O	18	---	---	---	6.2	200	22	9	70.0
	U + NaCl	20	16610	10770	---	7.6	50	20	20	87.5
	U + NaCl + NaHCO <sub>3</sub>	20	16520	10770	150	7.8	50	20	20	82.5
	U + seawater	20	See Instant ocean composition			8.4	75	22	5	51.0
Chelite-N	U + seawater	20	See Instant ocean composition			8.4	75	22	5	80.0
	"	20	"			8.4	75	3	25	41.0
	"	20	"			8.4	200	3	25	34.0

for monitoring of trace metals in natural waters during the winter months. When the atmospheric temperature falls well below the freezing temperature, only the upper layers of the natural water freeze. At lower depths, the water remains at 4°C as a liquid, as it has a maximum density at this temperature. Experiments were done to determine if the uranium uptake by these resins would improve at cold room temperatures ( $3 \pm 1^\circ\text{C}$ ) when a dual column method was used. Mann *et al.*<sup>283,284</sup> used a dual column method to successfully extract cesium, radium and some transuranic elements from seawater. The method involves two tandem columns, I and II, and the extraction efficiency is given by  $E = 1 - B \cdot A^{-1}$ , where **A** and **B** are the respective contents of the two columns. The concentration of the component in seawater **X** is given by  $X = A \cdot (EV)^{-1}$ , where **V** is the volume of seawater pumped through the columns.

The evaluation of commercial resins by the Dual Column method (using artificial seawater) along with the evaluation of the commercial resins with actual seawater using the Seastar™ In-situ Water Sampler will be discussed in this chapter.

### 5.1 Reagents used

Chelex 100 was obtained from Bio-Rad Laboratories (CA, U.S.A.), Chelite P, Chelite N, Duolite ES 467 and Duolite ES 346 from Serva Feinbiochemica G.m.b.H. and Co. (Heidelberg, Germany) and 8-hydroxyquinoline from Seastar Instruments Ltd. (British Columbia, Canada).

## 5.2 Apparatus used

Evaluation of sorbents for the uptake of trace metals in actual seawater was done with the use of a Seastar™ In-situ Water Sampler which was designed by Seastar Instruments Ltd. (British Columbia, Canada). Glass columns with adjustable height were obtained from Bio-Rad Laboratories (CA, U.S.A.) and Teflon™ columns from Seastar Instruments Ltd. (British Columbia, Canada). Whatman No. 541™ filter paper was used for most filtering purposes. A polycarbonate membrane filter obtained from Nuclepore™ Corporation (CA, U.S.A.) was used with the Seastar™ In-situ Water Sampler to collect particulate matter in seawater.

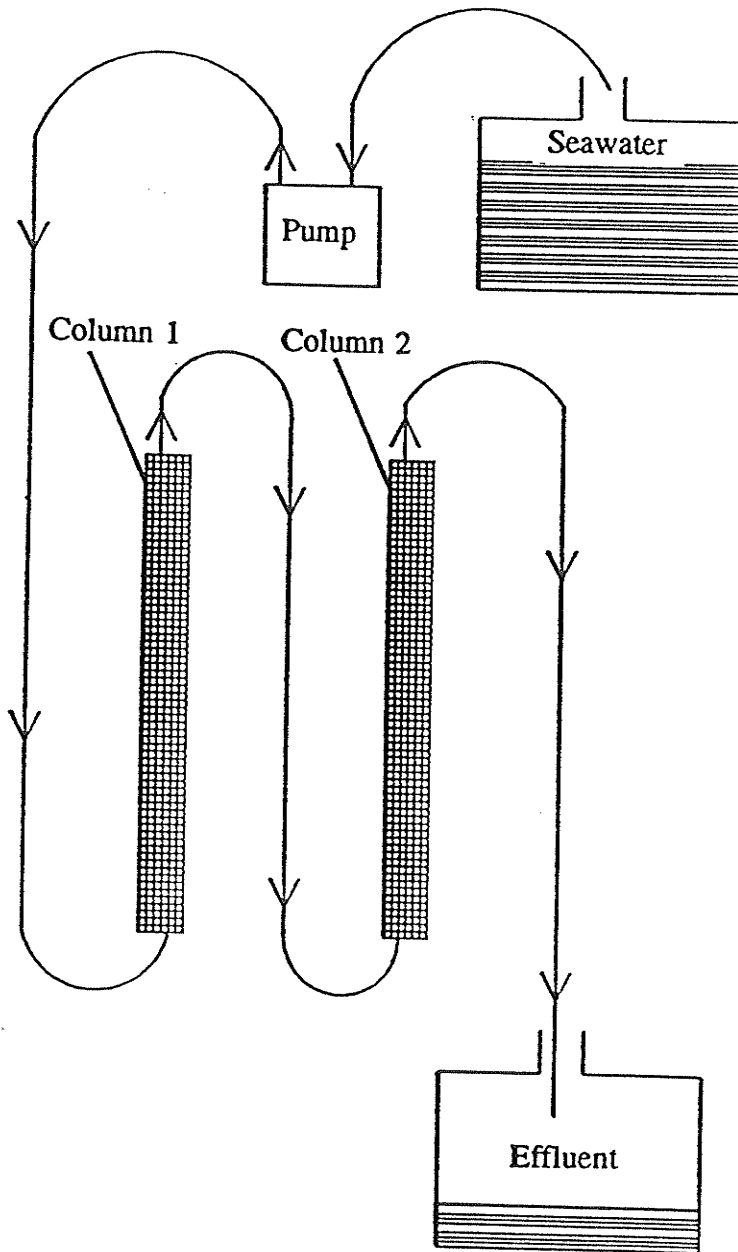
## 5.3 Procedure

Chelex 100, Chelite N, Chelite P, Duolite ES 467 and Duolite ES 346 resins were evaluated for their capability to extract uranium from seawater. Chelex 100 has an iminodiacetic acid functional group attached to a styrene-divinylbenzene copolymer matrix, Duolite ES 467 has an aminophosphonic acid group attached to a polystyrene matrix and Chelite P has a aminomethylphosphonic acid group attached to a styrene-divinylbenzene matrix. Duolite ES 346 is a polyacrylate with amidoxime group and Chelite N is a cross-linked macroporous polymer with amidoxime group. Duolite and Chelite resins are European-made resins that have rarely been used in the preconcentration of trace metals, as they were only recently introduced to the North American market.

The dual column method uses two Teflon™ columns and the system is shown in Figure 5.2. The solutions were pumped from the bottom to the top of the column to simulate the requirements for use with the Seastar™ In-situ Sampler. Another condition required by the sampler was that the solution flow rate through the column be high, i.e. at least  $100 \text{ mL}\cdot\text{min}^{-1}$ . Columns I and II were both packed with 51 grams of the dry resin. The 51 grams of dry resin was chosen as it occupied 80% of the volume of the column after pretreatment and the remaining volume was filled with liquid to accommodate any swelling of the resins. The two resins tested with the dual column system were Duolite ES 467 and Chelite N.

Synthetic seawater was prepared as described in Chapter IV and spiked with  $500 \mu\text{g}$  of uranium to give a final uranium concentration of 25 ppb. The concentration of 25 ppb uranium was chosen to make the DCP-AES analysis more convenient. The sample solution was equilibrated in the cold room ( $3 \pm 1^\circ\text{C}$ ) for 20 hours prior to pumping through the columns at a flow rate of  $75 \text{ mL}\cdot\text{min}^{-1}$ . Uranium from the columns was eluted and analyzed by DCP-AES. Duolite ES 467 was eluted with  $0.25\text{M Na}_2\text{CO}_3$  and Chelite N by  $1\text{M HCl}/0.1\text{M HNO}_3$  solution.

With Duolite ES 467 as the chelating material, the respective recoveries from Columns I and II were 23.8 and 18.6 % while with Chelite N they were 47.0 and 22.0%. These results were not reproducible when the experiments were repeated as shown in Table 5.2. To determine the cause of this problem, 50 grams of Chelite N was packed into a



**Figure 5.2** Diagram of a dual column extraction system

**TABLE 5.2** Reproducibility of three dual column experiments using Teflon™ columns

<b>Experiment Number</b>	<b>% Extraction</b>		<b>Total % Extraction by both columns</b>
	<b>Column I</b>	<b>Column II</b>	
1	23.8	18.6	42.4
2	20.6	34.6	55.3
3	3.5	29.5	33.0

glass column (Bio-Rad adjustable height column) and the seawater was pumped from the bottom. Glass columns were chosen in order to observe the flow as the Teflon™ columns were not transparent. After an hour of pumping at  $75 \text{ mL}\cdot\text{min}^{-1}$ , a movement of resin material was observed which resulted in channelling of the solution flow. To avoid this problem the solution was passed from top to bottom of the column, which resulted in a stable bed. When the dual column method of extraction was repeated thrice, with pumping from the top, more complete extraction resulted, but the reproducibility was not improved, as shown in Table 5.3. On closer or continued observation through a glass column system, it was observed that the seawater, on contact with the resin material, released bubbles (most probably carbon dioxide gas, as artificial seawater had 200 ppm of bicarbonate ion) which collected at the top of the column. These bubbles eventually (i.e. after 5 - 6 hours) displaced the liquid, either in the first or the second column, resulting in channelling. The displacement of the liquid above the column materials was not reproducible, because at times the bubbles were forced out of the column from the bottom, resulting in erratic results for the extraction of uranium.

Experiments were done to determine if these problems existed with single column experiments and when preliminary experiments were done, the displacement of the liquid layer above the column material was noted when the volume of liquid above the column material was equal to the volume of the bed; on adjusting the plunger of the adjustable glass column so as to accommodate three bed volumes of liquid above the



**TABLE 5.3** Reproducibility of three dual column experiments using adjustable glass columns

Experiment Number	% Extraction		Total % Extraction by both Columns
	Column I	Column II	
1	78.4	10.6	89.1
2	38.4	23.4	61.7
3	69.9	2.4	72.3

bed, the problem was solved. The bubbles were not able to completely displace the liquid layer above the column material. Experiments were then performed to see if uranium extractions by Chelite N, Duolite ES 346 and Duolite ES 467 were reproducible when they were subjected to ten sorption/desorption cycles.

### *5.3.1 Stability of various resins*

An earlier study with amidoxime-based resins showed a 5% decrease in their ability to extract uranium from seawater<sup>81</sup> for every sorption/desorption cycle. To observe if the commercial resins are stable over ten sorption/desorption cycles, the following experiments were conducted. The resins chosen were Duolite ES 467, Chelite N and Duolite ES 346. The resins were packed into an adjustable glass column (Bio Rad) with a bed diameter of 1.5 cm and a bed height of 9 cm. One litre of artificial seawater, which was spiked with 500 µg of uranium, was pumped through the column at a flow rate of 75 mL.min<sup>-1</sup> at 22°C. The pH of the artificial seawater was determined to be 8.5. To help prevent channelling, artificial seawater was pumped in from the top of the column with three bed volumes of liquid above the sorbent.

Chelite N and Duolite ES 346, both amidoxime-based resins, were eluted with 1M HCl. Two 50 mL fractions were collected and analyzed by DCP-AES for Chelite N, and ICP-AES for Duolite ES 346. After desorption with 1M HCl, 250 mL of deionized water and 250 mL of 2M NaOH followed by 500 mL of deionized water were pumped through the column at 75 mL.min<sup>-1</sup>. Duolite ES 467, a phosphonic acid

based resin, was eluted with 0.25M  $\text{Na}_2\text{CO}_3$  solution and the analysis was done by DCP-AES. After desorbing uranium with 0.25M  $\text{Na}_2\text{CO}_3$ , 100 mL of deionized water, 200 mL of 2M HCl, 100 mL of deionized water, 200 mL of 2M NaOH and finally 500 mL of deionized water were passed through the column at  $75 \text{ mL}\cdot\text{min}^{-1}$ . The above conditions for sorption and elution were optimised by members of this project from our laboratory.

The results are shown in Figure 5.3 and it can be seen that the Chelite N, Duolite ES 346 and Duolite ES 467 do not show any decrease in their ability to extract uranium. The difference in the procedure as reported by K. Schwochau *et al.*<sup>81</sup> and our procedure was that, in our procedure the resins were rinsed with water before elution with acid. The possible explanation for the loss of 5% efficiency for every cycle as reported could be due to the heat produced at the site of neutralization.

When similar experiments with dual consecutive columns were attempted, it proved too difficult to adjust the plunger height when two columns were involved. At the same time it was reported by Carmen and Kunin<sup>285</sup> that the second column showed greater extraction than the first column. They observed the dissociation of uranyl carbonate in the first column, which enabled the second column to extract the dissociated species, which confirms that the tandem column method by Mann *et al.*<sup>283,284</sup> will not work with this system. One may wish to use longer columns for extraction at  $4^\circ\text{C}$ . As longer columns were not compatible with the

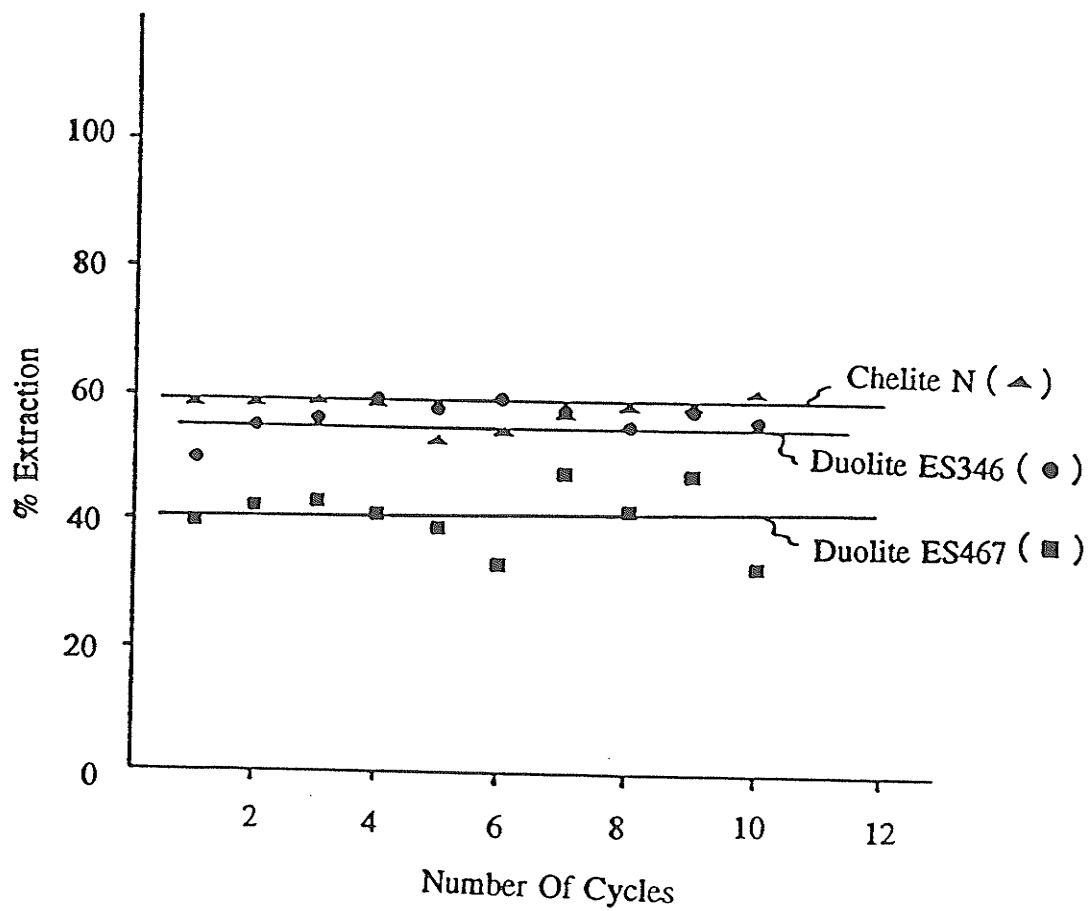


Figure 5.3 Repetitive extraction capability of uranium using various commercially available resins

Seastar™ In-situ sampler design, experiments to improve extraction at 4°C were discontinued.

### *5.3.2 Four column gravity flow system*

Problems due to channelling because of gas formation at the top of the column, or channelling when pumped from the bottom of the column, due to movement of resin material, were solved by the development of a four column gravity flow system as shown in Figure 5.4. This is a simple system that does not require a pump as the flow of solution through the resin was achieved by gravity. The air or gas that may be released when seawater comes in contact with the resin escapes into the atmosphere. The column was never allowed to dry due to the design of the drain tube and the flow of liquid was from the top to the bottom of the column. This system has an added advantage of having a multi-column capability with uniform or easily controlled flow rates. This system can be used for both extraction and elution and it can be left unattended. The flow rates at the beginning and end are uniform as it operates at constant pressure. The four column gravity flow system was designed for studying resin pretreatment procedures on the effect of flow rates that must be determined for the resins before evaluating them with actual seawater.

The effect of flow rates on extraction capability of Chelite N was evaluated to see if problems associated with pumping were solved by passing 1 litre of artificial seawater containing 25 ppm uranium through the column at different flow rates. The columns

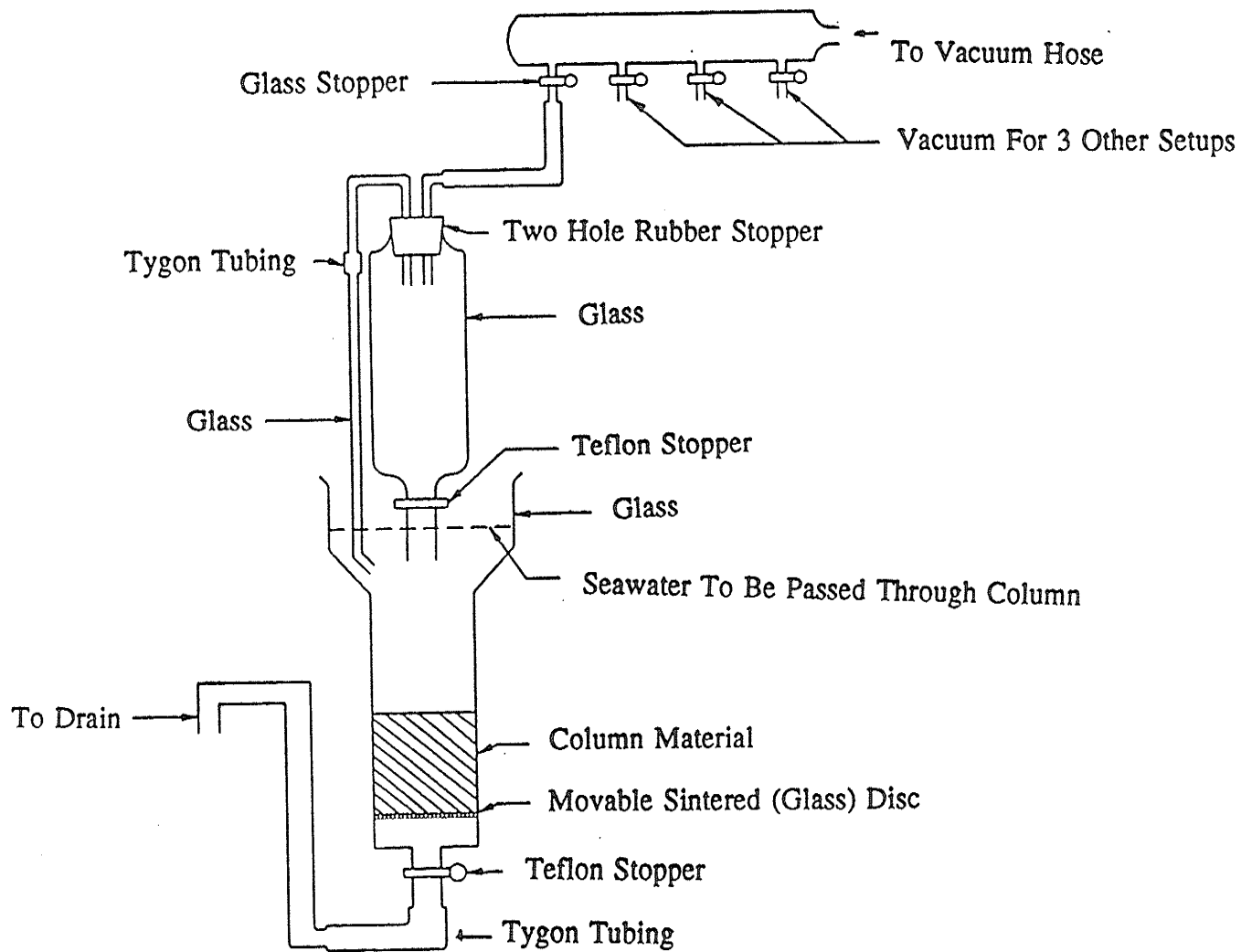


Figure 5.4 Diagram of four column gravity flow system

were then eluted with 1M HCl and the analysis was performed by DCP-AES. The extraction increased from 61.5 to 101.5% as the flow rate was decreased from 68 mL.min<sup>-1</sup> to 15 mL.min<sup>-1</sup>. At 32 mL.min<sup>-1</sup> the extraction was 85.9%. For complete extraction slower flow rates would be an advantage, but the time for extraction could be excessive for large volumes of solution. When Duolite ES 346 was packed and the extraction performed in a similar manner the % extraction increased from 69.5 to 79.0 as the flow rate decreased from 62 mL.min<sup>-1</sup> to 32 mL.min<sup>-1</sup>.

### *5.3.3 Pretreatment of resins*

The four column gravity flow system was used to evaluate various pretreatment procedures for the resins for use in the extraction of uranium from seawater. The pretreatment procedures are important, as resins swell differently when placed in different media. The resins perform better when they have been equilibrated with a solution of ionic strength similar to the solution to be analyzed.<sup>220</sup> In the following sections various pretreatment procedures to convert the resin to the sodium form along with preswelling will be discussed.

### *5.3.4 Effect of NaOH pretreatment of resins*

A sodium hydroxide pretreatment was evaluated for Chelite N and Duolite ES 467. The following solutions were passed through the columns: 250 mL of deionized water; 250 mL of 2M NaOH; 250 mL of deionized water; 1 litre of artificial seawater

spiked with 500  $\mu\text{g}$  of uranium; 250 mL of deionized water. This resulted in swelling of the resin, which decreased the flow rate significantly. Resins which were not pretreated with 2M NaOH showed a maximum flow rate of 68  $\text{mL}\cdot\text{min}^{-1}$ . The flow rate dropped to 12  $\text{mL}\cdot\text{min}^{-1}$  when the resins were pretreated with NaOH. The significant decrease in flow rate due to swelling with pretreatment with 2M NaOH suggests improved pretreatment techniques must be employed for use with the sampler.

#### *5.3.5 Effect of 1M sodium acetate*

A similar procedure (i.e. NaOH pretreatment) was followed, but with the replacement of 2M NaOH by 1M sodium acetate, and the flow rate was checked after every 250 mL of artificial seawater passed through the column. The flow rate was constant for Duolite ES 467 and Duolite ES 346 but reduced from 40  $\text{mL}\cdot\text{min}^{-1}$  after the first 250 mL to 36  $\text{mL}\cdot\text{min}^{-1}$  after 750 mL for Chelite N. A more marked change was observed for Chelite P, where the flow rate after 250 mL mark was 44  $\text{mL}\cdot\text{min}^{-1}$ , after 500 mL it was 40  $\text{mL}\cdot\text{min}^{-1}$  and after 750 mL it was 13.6  $\text{mL}\cdot\text{min}^{-1}$ . Chelite series of resins show greater swelling than Duolite series with 1M sodium acetate solution.

#### *5.3.6 Effect of 3.5% NaCl*

When the procedure was repeated with 3.5% NaCl solution, the resulting flow rates were more constant/uniform than when using either 1M NaOH or 1M sodium acetate solution. The value for Chelite N after 250 mL seawater passage only changed from



38 mL.min<sup>-1</sup> to 36 mL.min<sup>-1</sup> at 750 mL. Similarly, for Chelite P the rate changed from 36 to 34 mL.min<sup>-1</sup> and Duolite ES 467 started off with 36 mL.min<sup>-1</sup> at 250 mL and then dropped slightly to 34 mL.min<sup>-1</sup> for 500 and 750 mL.

### ***5.3.7 Preswelling with unspiked seawater***

As mentioned earlier, the resins perform better when preswelled with a solution of similar ionic strength to the sample solution and hence the pretreatment with unspiked seawater was attempted. The column material was first washed with 250 mL deionized water then with 250 mL 1M NaOH and finally with 250 mL deionized water in a beaker. The resins were then placed in a 500 mL beaker with 250 mL of unspiked seawater for 20 minutes and then slowly packed into the column. The flow rates for all four column materials were constant. This confirms that these resin must be pretreated with a solution of similar ionic strength to that to be analyzed in order to prevent swelling of the resin material.

### **5.4 Actual seawater testing at Patricia Bay**

The site that was used for testing the commercial resins for the uptake of trace metals from seawater was located in Patricia Bay, Victoria, British Columbia. (48° 39.2'N latitude and 123° 26.9' W longitude). Patricia Bay is part of the Saanich inlet, which is 24 km in length and is located at the southeastern end of Vancouver Island. Saanich inlet does not possess a significant source of fresh water at its head or anywhere along its length. The site used for the evaluation of the commercial resins

is shown in Figures 5.5 and 5.6.

Possible man-made contamination of the bay could have resulted from a "Kraft" papermill which is located in the town of Crofton at a distance of 10 to 12 nautical miles northwest of the bay where the spent effluent is released into the inlet waters. Seepage of septic tanks and sewers and dumpsites along the coastline could also contribute to the pollution of the bay waters.

In this experiment, the sampler was on sampling mode "8" which would pump for thirty minutes and then stop for thirty minutes; this process was repeated for a 24 hour time period. The delay time for pumping chosen was ten minutes, to enable lowering of the sampler into the water and to stabilize any swinging motion of the sampler. The flow rate was maintained at  $100 \text{ mL}\cdot\text{min}^{-1}$  and the filter unit contained a Nuclepore™ polycarbonate membrane filter with a nominal pore size of  $0.4 \mu\text{m}$ .

The column materials chosen for testing were Chelite N, Chelite P, Chelex 100, Duolite ES 346 and Duolite ES 467. The structure and functional groups are given in Figure 5.7. These resins were chosen as they had proved to be efficient for the extraction of uranium from artificial seawater during preliminary laboratory experiments as described earlier.

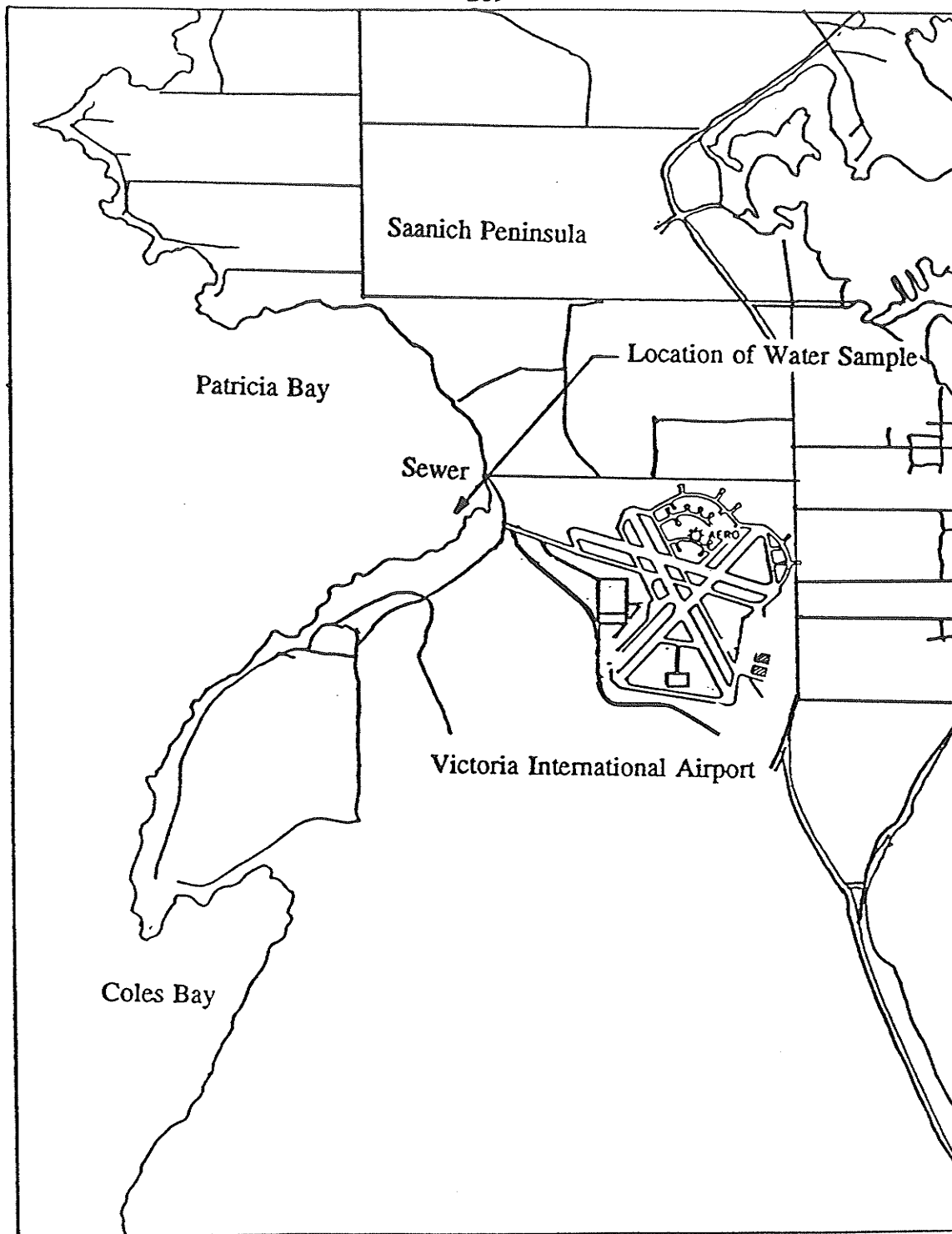


Figure 5.5 Map of the site at which actual seawater was sampled

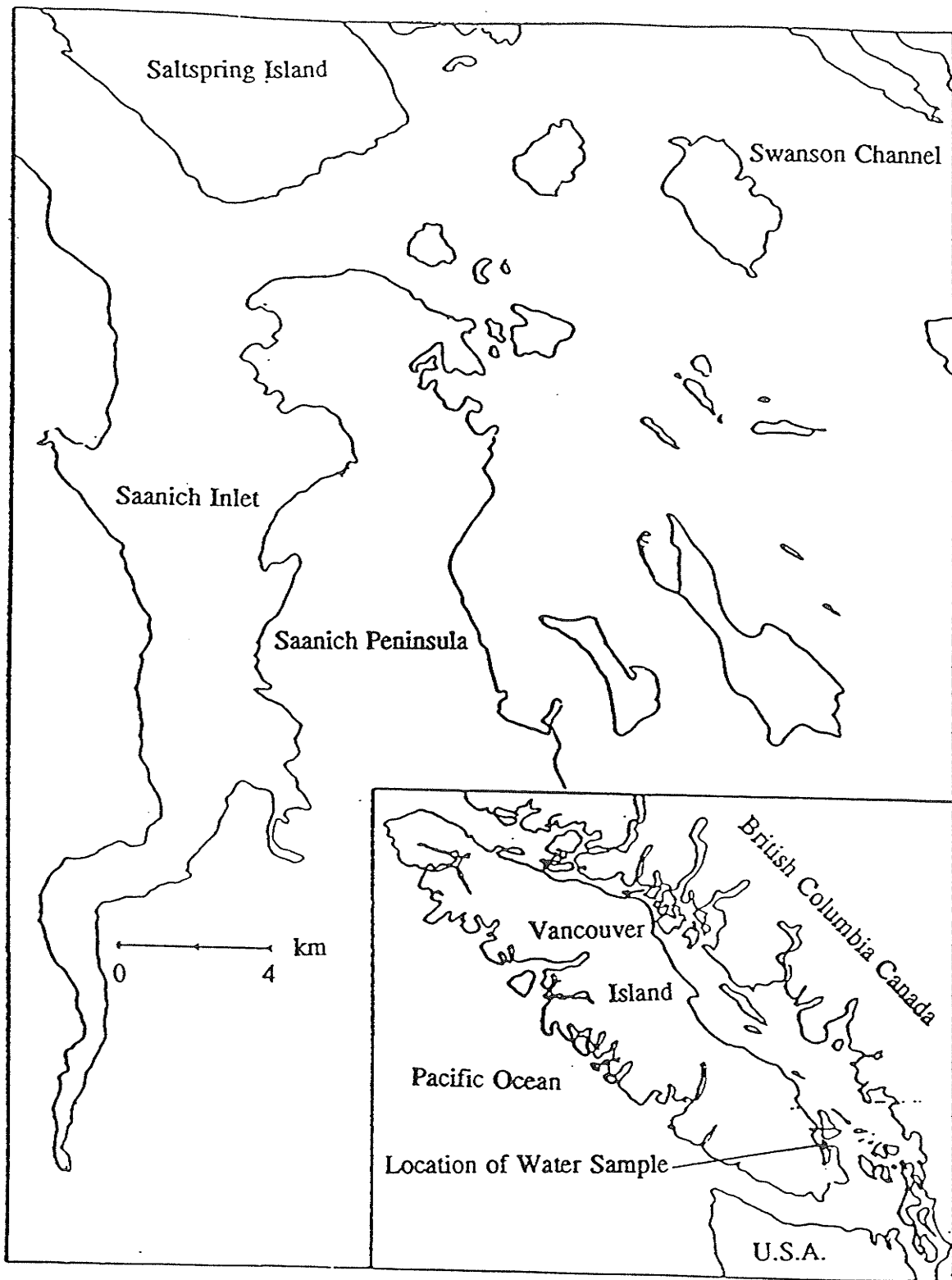


Figure 5.6 Enlarged map of the Saanich Inlet site

RESINS	FUNCTIONAL GROUP	STRUCTURE
CHELITE N DUOLITE ES 346	AMIDOXIME	$\begin{array}{c} \text{NOH} \\ \diagup \\ \text{R}-\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$
DUOLITE ES 467	AMINO PHOSPHONIC ACID	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{NH}-\text{P}-\text{OH} \\   \\ \text{OH} \end{array}$
CHELITE P	AMINO METHYL PHOSPHONIC ACID	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{NH}-\text{CH}_2-\text{P}-\text{OH} \\   \\ \text{OH} \end{array}$
CHELEX 100	IMINODIACETIC ACID	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2-\text{C}-\text{OH} \\ \diagup \\ \text{R}-\text{N} \\ \diagdown \\ \text{CH}_2-\text{C}-\text{OH} \\ \parallel \\ \text{O} \end{array}$

Figure 5.7 Functional groups of the resins used for the actual seawater sampling

The washing procedure for each of the five resins was carried out by taking 200 mL of the resin in a 2 litre beaker to which 1 litre of deionized water was added. A magnetic stirrer was used to gently stir the slurry for ten minutes after which the supernatant liquid was decanted. This step was done to remove any water soluble impurities that might have been present in these commercial resins. This washing step was repeated with the addition of 1 litre of 1M HCl in order to remove any trace metals that may have been present in these resins. This acid wash was followed by rinsing the resin with four 250 mL portions of deionized water to remove residual HCl that may have been present in the resins. With each portion, the resins were equilibrated with deionized water for ten minutes and the supernatant liquid was decanted. The resins were then converted to their sodium form by equilibrating them with 1 litre of 1M NaOH solution for ten minutes. The supernatant liquid was decanted and the resins were left to equilibrate with 1 litre of deionized water for 12 hours. The supernatant liquid was decanted, and the resins were equilibrated with 1 litre of 3.5% NaCl solution for 30 minutes. The last step was done to equilibrate the resins with a solution that could be similar to seawater, which would prevent the resin from swelling when packed into a column. Even though earlier experiments had showed a uniform flow rate when the resins were preswelled with artificial seawater, this was not attempted as artificial seawater contained a large number of trace metals which would be taken up by the resins, and this would interfere with our actual seawater experimental results.

During the above process of cleaning and converting the resin to the sodium form, two resins, namely Duolite ES 467 and Chelite P showed degradation; a fine yellow powder was noticed in the supernatant liquid. These two resins were then passed through a 210  $\mu\text{m}$  Teflon™ sieve to remove the fine powder.

Two columns of each resin were prepared by taking 80 mL of the wet slurry and packing it into Teflon™ columns. The columns were connected to the In-situ Water Sampler, along with the filter assembly used to collect colloidal/particulate matter. The two samplers were placed at either side of a concrete dock belonging to the Government of Canada, Institute of Ocean Sciences. The two samplers were lowered to a depth of  $5 \pm 1$  metres from the surface of water by a nylon rope. The total depth of the water at this location was 7 metres. The depth of  $5 \pm 1$  metres was chosen to take into account the changes in the height of surface water due to tide change. The two samplers were placed 7 metres apart and about 500 metres from shore.

Information obtained from Dr. Jeffery Thompson of Ocean Chemistry Division, Institute of Ocean Sciences (a Government of Canada facility in Sydney, B.C.) showed that the average salinity of surface water in this vicinity was 29.5% and that the water was rich in organics.<sup>286</sup>

The seawater sampling was done in May 1988 and the time of pumping, temperature and pH measurements of seawater before and after pumping, the volume of water pumped and the atmospheric conditions at the time of pumping are given in Table 5.4.

Table 5.4 Seawater sampling conditions

Date of Sampling	Time	Resin Type	Sampler Serial No.	Water Temp in °C initial/final	Water pH initial/final	Volume of seawater (L)	Atmospheric Conditions
12-May-88	12:45 P.M.	Chelite N	83006	15.4/15.1	7.4/7.1	68.82	rain
12-May-88	12:45 P.M.	Chelite N	84003	15.4/15.1	7.4/7.1	69.69	rain
16-May-88	11:15 A.M.	Chelex 100	83006	13.0/12.7	7.0/7.2	60.21	overcast
16-May-88	11:15 A.M.	Chelex 100	84003	13.0/12.7	7.0/7.2	59.08	overcast
17-May-88	12:25 P.M.	Chelite P	83006	12.7/11.1	7.2/6.5	69.90	rain
17-May-88	12:25 P.M.	Chelite P	84003	12.7/11.1	7.2/6.5	69.77	rain
24-May-88	09:20 A.M.	Duolite ES467	83006	12.8/14.1	6.8/6.8	63.62	sunshine
24-May-88	09:20 A.M.	Duolite ES467	84003	12.8/14.1	6.8/6.8	66.07	sunshine
25-May-88	10:55 A.M.	Duolite ES346	83006	14.1/13.5	6.8/6.5	69.47	sunshine
25-May-88	10:55 A.M.	Duolite ES346	84003	14.1/13.5	6.8/6.5	69.72	sunshine



Measurements of pH on site were done with pH paper strips. Once sampling was completed, the columns were removed from the samplers, capped and sealed in a bag for later elution and analysis. The Nuclepore™ filters, which contained any particulate matter, were folded inwards and stored in clean Nalgene™ bottles for subsequent wet ashing and analysis.

The columns and filter membranes were transported to the University of Manitoba for analysis. The material for each column was emptied into an individual glass column as described previously in the "four column gravity flow system". The resins were eluted at  $1 \text{ mL}\cdot\text{min}^{-1}$  using a mixture of 2M HCl and 2M HNO<sub>3</sub>. Eight 50 mL fractions were collected in 60 mL Nalgene™ bottles. The resins were then removed from the columns, emptied into beakers, and the resins were equilibrated for 30 minutes with 50 mL of the eluting mixture, using constant stirring with a magnetic stirrer. The supernatant liquid was decanted to form the ninth fraction, and a tenth fraction was obtained by repeating the last elution step. The ninth and tenth fractions were obtained in this fashion to recover final traces of any metals that might still be on the column. The total uranium recovery was obtained by taking five mL from each of the ten fractions, mixing them together in a 60 mL Nalgene™ bottle, and analyzing by ICP-AES and ICP-MS. A 50 mL sample of the eluting mixture was also analyzed as a blank to determine if any trace metals were present in it.

The filter membranes were wet-ashed by placing the filters, along with any residues,

into 150 mL Teflon™ beakers, which were heated on a hot plate at 90°C. The wet ashing procedure used 15 mL of concentrated HNO<sub>3</sub> and 15 mL of deionized water. When the solution was near boiling, 30% H<sub>2</sub>O<sub>2</sub> solution was added drop-wise and the heating continued to near dryness. The total volume of H<sub>2</sub>O<sub>2</sub> solution used was 10 mL. This procedure was repeated three more times. The residue was taken up in 0.3% HNO<sub>3</sub> solution and filtered using a Whatman™ 541 filter paper and made up to 50 mL. An unused filter membrane was also wet ashed in a similar fashion as a blank.

## 5.5 Results and discussion

When the extraction studies were performed with artificial seawater in our laboratory the Chelite N, Chelite P, Duolite ES 467, Duolite ES 346 and Chelex 100 resins were found to be capable of extracting uranium. As can be seen from Table 5.5, resins containing amidoxime groups, i.e. Chelite N and Duolite ES 346, were capable of extracting uranium from seawater and the others, namely Chelite P, Duolite ES 467 and Chelex 100, showed no ability in extracting uranium. The major difference between the artificial seawater and actual seawater is the presence of organics in actual seawater which may cause a difference in extraction capability for uranium.

In Table 5.5 it can be seen that Chelite N and Duolite ES 467 in comparison to other resins shows better extraction capability for Fe, Cu and Zn. Likewise,

Table 5.5 Results of the actual seawater experiment using commercially available resins

Expt. No.	Element	CHELEX 100 (ppb)	DUOLITE ES 467 (ppb)	CHELITE P (ppb)	DUOLITE ES 346 (ppb)	CHELITE N (ppb)	PUBLISHED <sup>287</sup> CONCENTRATION (ppb)
1	Si	18.0	12.7	29.8	19.9	5.7	300.0
2	Ti	1.0	1.0	1.0	0.4	0.4	1.0
3	Al	9.0	14.0	6.9	4.3	6.1	10.0
4	Fe	9.0	15.0	7.0	11.0	16.7	10.0
5	Mn	2.0	3.0	2.3	1.0	1.0	2.0
6	Mg	6370.0	10700.0	9670.0	3090.0	2480.0	1350000.0
7	Ca	6000.0	5000.0	5000.0	1200.0	1100.0	400000.0
8	K	500.0	300.0	400.0	400.0	300.0	380000.0
9	P	40.0	30.0	30.0	20.0	20.0	70.0
10	S	531.0	527.0	507.0	343.0	238.0	885000.0
11	Ba	1.0	1.0	1.0	1.0	1.0	30.0
12	Co	1.2	1.3	1.1	0.5	0.5	0.5

Table 5.5 Continued

Expt. No.	Element	CHELEX 100 (ppb)	DUOLITE ES 467 (ppb)	CHELITE P (ppb)	DUOLITE ES 346 (ppb)	CHELITE N (ppb)	PUBLISHED <sup>287</sup> CONCENTRATION (ppb)
13	Cr	1.55	2.30	2.06	1.02	0.78	0.05
14	Cu	3.0	3.4	2.0	2.2	3.5	3.0
15	Ni	2.4	2.4	2.3	1.3	1.2	2.0
16	Sr	30.5	38.9	32.7	11.4	9.4	8000.0
17	V	0.4	0.4	0.4	0.2	0.3	2.0
18	Zn	4.5	5.3	3.6	4.0	5.4	10.0
19	Zr*	0.0	0.1	0.0	0.0	0.0	ND
20	Hf*	0.0	0.1	0.0	0.0	0.0	ND
21	Ta*	0.0	0.0	0.0	0.0	0.0	ND
22	Th*	0.00	0.03	0.00	0.03	0.12	0.05
23	U*	0.0	0.0	0.0	2.0	2.0	3.0

Elements denoted with an astericks were analyzed by ICP-MS and the rest of the elements were analyzed by ICP-AES. Sampling of seawater was done using the Seastar™ In-situ Water Sampler.

Duolite ES 346 and Chelate N for U, Chelate P for Si and Mg, Duolite ES 467 for Mn, Cr, Sr and Al and Chelex 100 for Ca, K and P showed better extractions. For the extraction of V or S one may wish to use either Chelex 100 or Duolite ES 467; similarly Chelex 100 or Duolite ES 467 or Chelate P for Ti, Co and Ni.

In the recent past several papers<sup>41-45</sup> have been published in which Chelex 100 was used for the preconcentration of trace metals from seawater. Our study has shown that newly available commercial resins such as the Duolite and the Chelate series are better able to perform this function of preconcentration of trace metals from seawater.

The average concentration of uranium present in ocean water around the globe was reported as 3.0 ppb,<sup>287</sup> although our results of 2.0 ppb are lower. The discrepancy may be due to the designed flow rate of the sampler of 100 mL.min<sup>-1</sup> that was used, which may be too rapid for efficient extraction with the sorbents used and the present system. When artificial seawater was pumped from the bottom of the glass column some channelling was observed in our laboratory. This channelling could have occurred in the Teflon<sup>TM</sup> columns, as the samplers were designed to suck seawater from the bottom of the column, which may have caused channelling during the actual seawater evaluation. The possible channelling could have resulted in the smaller value of uranium reported in our study. Changes to the sampler design have to be made to ensure that this problem does not occur. Another possible reason is that the average of the uranium concentration published is for 35% salinity, and in our case the salinity

was reported by the Institute of Ocean Sciences as being 29.5%. Generally, it has been found that the uranium concentration increases with salinity.<sup>288</sup>

It was of interest to us to check the isotope ratios for uranium  $U^{238}/U^{235}$  in the eluate from Chelite N and Duolite ES 346. These two resins were chosen as they were the only ones that were capable of extracting uranium from actual seawater. Isotope ratio measurements were done by Dr. Gregoire (Geological Survey of Canada, Ottawa, Canada) using their ICP-MS instrument, and are an average of five separate isotope ratio determinations. The average isotope ratio for the above amidoxime-based resins (i.e. Chelite N and Duolite ES 346) was  $137.8 \pm 1.05$  and this correlates well with the reported value of  $138.0 \pm 0.3$ <sup>289</sup> for naturally-occurring uranium. These isotope ratio measurements were conducted to see if these resins had a selective capability to extract a particular isotope of uranium. The measurements show that this is not the case, and that the terrestrial uranium isotope ratio was the same as that found in seawater at Patricia Bay (B.C., Canada).

## 5.6 Conclusion

Chelex 100, Chelite P, Chelite N, Duolite ES 346 and Duolite ES 467 were all capable of extracting uranium from artificial seawater but when these sorbents were used with actual seawater only the amidoxime-based resins (i.e. Chelite N and Duolite ES 346) had the capability of extracting uranium. The inability of Chelex 100, Chelite P and Duolite ES 467 to extract uranium from actual seawater was attributed to the presence

of organics (i.e. ligand species, humic and fulvic acids, etc.) in actual seawater.

Based on the ICP-MS analysis of the eluates from Chelite N and Duolite ES 346 resins, the apparent concentration of uranium in seawater was found to be 2.0 ppb. This concentration would be the actual concentration of uranium in seawater provided one assumes that all of the uranium was sorbed onto the resin and that all of the uranium on the resin was recovered. This assumption is true in ideal conditions of extraction, but may not be the case in our study. The real concentration of uranium in seawater may be higher than 2.0 ppb, but by how much is not known.

More accurate results can be obtained by decreasing the flow rate through the column, thus enabling more contact time between the sorbent and seawater, increasing the column length, and pumping the seawater through the column from the top thereby decreasing the chance of channelling that may occur as noticed in the glass column experiment.

Chelite N and Duolite ES 346 can be reused, and have been shown to withstand at least ten sorption/desorption cycles without any loss in extraction capability. The two resins, i.e. Chelite N and Duolite ES 346, can be used for a number of other trace metal determinations, as shown in Table 5.5, and is a suitable column material for use with the Seastar™ In-situ Water Sampler.

## CHAPTER VI

### CONCLUSION

This chapter describes the work done for the thesis and its possible applications in analytical chemistry and industrial chemistry.

Chapter II describes a continuous flow spectrophotometric method (CFSM) for the analysis of uranium was developed using a flow cell and a diode array spectrophotometer with Arsenazo III as the photometric reagent. The CFSM is less time consuming than the classical spectrophotometric method used for the analysis of uranium because the tedious process of cleaning, rinsing and handling of a cuvette is avoided. The classical method would involve the addition of an acid and Arsenazo III solution to the sample solution, followed by dilution with water to a specific volume. The tedious process of transferring a sample, acid and Arsenazo III solution into a standard flask, followed by dilution, is avoided in CFSM. A major advantage of CFSM is that the time between reagent addition and absorbance measurement is always a constant and that more than 60 samples can be analyzed in an hour.

CFSM can be used for a wide variety of spectrophotometric analyses, which are currently being done by classical methods, especially when dealing with hazardous materials, or when a large number of samples have to be analyzed. Spectrophotometric analyses by CFSM can be relatively inexpensive as it requires very small amounts of



reagent solution.

CFSM does not require any complex switching valves or sample injection loops or carrier liquids that are normally used in flow injection analysis or segmented flow analysis. Although the method of flow injection analysis and segmented flow analysis is well known in analytical chemistry, the advantages of CFSM are that it is simple, inexpensive and can be readily adapted to other systems which are currently being performed by the classical spectrophotometric method. Complex spectrophotometric analyses that require the addition of a number of reagents in a particular sequence can be performed by CFSM using a peristaltic pump with multi-tubing capability, and more than one flow mixer at different stages may be necessary.

The survey of commonly available sorbents that was described in Chapter III for the selective uptake of uranium could prove useful to an analyst when working with relatively simple matrices. The results of the survey showed that 76 percent of commonly available sorbents that were evaluated were capable of extracting uranium when the matrix was a simple aqueous solution (i.e. uranyl acetate solution) but when the matrix became more complex (i.e. in the presence of other competing ions) only 53 percent of the sorbents were capable of extracting uranium. The survey also revealed that poly- $\beta$ -diketone has superior ability, among the sorbents evaluated, to selectively extract uranium from an aqueous solution containing several competing ions. Poly- $\beta$ -diketone was not commercially available and this led us to synthesize a

sorbent with a  $\beta$ -diketone group for use in column chromatography.

Chapter IV describes three new sorbents that were developed in our laboratory, namely  $\beta$ -diketone foam, phosphonic acid foam, and a polyacrylonitrile (Orlon™) fabric with amidoxime functional groups. The three new sorbents were capable of extracting uranium over a wide range of temperature (i.e. between 4°C and 70°C) and over a wide range of pH (i.e. between 3 and 11). These sorbents were unable to extract the uranium species that formed at the extreme ends of the pH scale, suggesting the use of strong acids or bases as possible eluting agents. Possible applications of these newly synthesized sorbents could be in the effluent treatment of uranium mine tailings, home water treatment plants, and large scale clean-up of rivers, streams, etc. and as column materials in analytical chemistry.

In the nuclear industry, these sorbents would be useful in the manufacture and reprocessing of high grade fuel rods and more importantly these sorbents may play a role in the clean-up procedures for spills involving uranium in the nuclear industry and other radiochemical facilities. These new sorbents could also be used for extraction of other heavy metals, as shown by some resins with similar functional groups in Chapter V (i.e. phosphonic acid and amidoxime functional groups). Industrial and commercial applications of the three new sorbents may be promising due to the low cost of production, relatively simple production technique, and the ability to produce these sorbents with high porosity. The porosity in the foam can be controlled by the

size of bubbles that are produced during the foaming process. The porosity in the modified Orlon fabric can be controlled by changing the structure of the weaving or knitting pattern during fabric production.

The process of incorporating functional groups into the foam during the foaming process opens up the synthesis of a wide range of new polyurethane foams that would be capable of extracting various organic and inorganic species. Polyurethane foams with functional groups incorporated into them during the foaming process exhibit extraction properties similar to those of a solvent with given functional groups, as shown in Chapter IV with  $\beta$ -diketone foam. Various reagents have been developed in the last several decades for use in the selective extraction of organic and inorganic species by solvent extraction. The successful incorporation of these reagents into polyurethane foams would result in sorbents that can be packed into a column for laboratory or industrial separations.

Column extractions generally are considered to be more complete as new sorbent is always being available when compared to batch extraction. Column extractions are usually preferred over solvent extraction as they are convenient and less time consuming. The use of large amounts of solvents that are required in solvent extraction can be avoided with the use of a column extraction.

European-made resins (i.e. Chelite N, Chelite P, Duolite ES 467 and Duolite ES 346)

that are relatively new to the market and have rarely been used in analytical chemistry, were evaluated for the sorption of uranium from seawater, along with Chelex 100 which has been commonly used for the sorption of trace metals. The results obtained in Chapter V showed that only amidoxime-based sorbents (i.e. Chelate N and Duolite ES 346) had the ability to sorb uranium from actual seawater. Changes need to be made to the Seastar™ In-situ Water Sampler to obtain better extraction results, i.e. slowing the flow rate, increasing the column length, and pumping the seawater from the top to bottom of the column to avoid channelling of the sorbent material.

In conclusion, we developed and evaluated new sorbents for the sorption of uranium from aqueous systems which involved the preparation of three new sorbents, i.e.  $\beta$ -diketone foam, phosphonic acid foam, and amidoximated polyacrylonitrile fabric that are capable of extracting uranium over a wide range of temperatures (i.e. between 4°C to 70°C) and over a wide range of pH (i.e. between pH = 3 and pH = 11). New European resins, i.e. Chelate N, Chelate P, Duolite ES 346 and Duolite ES 467 were evaluated for the extraction of uranium from actual seawater and their extraction abilities were compared to the existing Chelex 100 which is commonly used for the uptake of trace metals. Our study showed the resins with amidoxime groups (i.e. Chelate N and Duolites ES 346) performed much better than the Chelex 100 resin in extracting uranium from seawater. The Chelate N and Duolite ES 467 resin also showed better extraction capability for Fe, Cu and Zn, Chelate P for Si and Mg, Duolite ES 467 for Mn, Cr, Sr, and Al, Chelex 100 for Ca, K and P, Chelex 100 or

Duolite ES 467 for V and S, Chelex 100 or Duolite ES 467 or Chelite P for Ti, Co and Ni. From the above it can be seen that not one particular resin was capable of extracting all the trace metals. For the extraction of uranium, sorbents with amidoxime groups show greater selectivity towards the uptake of uranium from seawater.

Our study has shown that Chelite N and Duolite ES 346 resins are capable of separating and preconcentrating uranium from seawater. The seawater matrix is the most complex of the natural water systems and these resins are capable of separating uranium from the major constituents of seawater, thus enabling the monitoring of uranium in seawater possible. The seawater matrix usually interferes with most instrumental methods of analysis, resulting in inaccurate values. For the preconcentration of uranium from aqueous solutions with a simpler matrix three new sorbents were synthesized which were capable of sorbing uranium from solutions with a wide range of pH and temperature values. The use of the above sorbents for separation and preconcentration of uranium would result in more accurate monitoring of uranium in the environment and more accurate analysis of uranium in general.

G. Wilkinson<sup>290</sup> in an article (1984, Chemistry in Britain) on the profitable extraction of uranium from seawater says "A major factor in a project such as this is to ensure that the energy ultimately derived from the uranium is not outweighed by that required for extraction. Using tidal flows and ocean currents is a sensible alternative to

pumping seawater through the resin. The team is therefore working on a resin-loaded polyurethane foam that can be submerged and left to pick up uranium as seawater ebbs and flows past it. Producing a poly(hydroxamic acid) fibre and then weaving an endless belt is another idea being considered. Theoretically, a belt 200 m long, 20 m wide and 1 cm thick could pick up 6 tonnes of uranium in a year: a challenge well worth tackling." The two polyurethane foams, i.e.  $\beta$ -diketone foam and phosphonic acid foam, along with the amidoximated polyacrylonitrile fabric that were developed in our laboratory appear to answer the above challenging problem and need to be evaluated for the economical extraction of uranium from seawater.

Suggestions for further work related to this study would be:

- a) to design a better 10 cm quartz flow cell to prevent air bubbles from lodging at the windows or the use of a switching valve to prevent air intake;
- b) to study the use of CFMS for other spectrophotometric analyses currently being performed by more classical methods;
- c) to study the effectiveness of other oxidizing agents such as  $H_2O_2$ , superoxide, etc., for the oxidation of PVA to P $\beta$ DK;
- d) to study the effect of incorporating compounds with two functional groups (i.e. nitrile plus hydroxy groups) into the foam and then producing amidoxime foams;

- e) to study the sorption capability of  $\beta$ -diketone foam, phosphonic acid foam and modified Orlon for the uptake of uranium from seawater and to determine their capacity, reusability and elution data;
- f) to study the use of the sorbents developed for the sorption of other metals from aqueous solutions and from seawater.

In conclusion, we have developed a simple, fast and inexpensive way to analyze for uranium in simple aqueous solutions. We prepared three new sorbents that are relatively inexpensive and easy to make, namely  $\beta$ -diketone foam, phosphonic acid foam, and amidoximated polyacrylonitrile fabric for the uptake of uranium from aqueous solution with a wide range of pH and temperature values. We have evaluated some commercially available resins that have rarely been used in analytical chemistry for the uptake of uranium from seawater.

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