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Review

Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination—an overview

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Abstract

The need for the preconcentration of trace and ultratrace amounts of uranium(VI) and thorium(IV) in conjunction with various detection techniques was clearly brought out in the introductory part. Subsequently, various off-line and on-line procedures developed for uranium(VI) and thorium(IV) prior to their analytical determination since 1990 were critically reviewed in terms of enrichment factor, retention/sorption capacity, validation using certified reference materials and application to complex real samples. The relative merits and demerits of various preconcentration and/or separation of uranium(VI) and thorium(IV) prior to quantitation by a plethora of analytical techniques are discussed in concluding part of the review article.

Keywords: Preconcentration; Uranium; Thorium

Contents

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1. Introduction

Uranium metal in its pure form is chemically active, anisotropic and has poor mechanical properties. On the other hand, uranium alloys are useful in diluting enriched uranium liquid fuel meant for nuclear reactors and pure uranium coated with silicon and canned in aluminium tubes are used in production reactors. However, uranium and its compounds, like lead are highly toxic which cause progressive or irreversible renal injury and in acute cases may lead to kidney failure and death. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 μg/kg of body weight per day [1–3]. The WHO, Health Canada and Australian drinking water guidelines fixed the maximum uranium concentration in drinking waters to be less than 9, 20 and 20 μg/l [1,2]. The inhalation of uranium compounds results in deposition of uranium in lungs and reaches kidneys through blood stream.

Unlike uranium, thorium and its compounds and alloys find widespread use. Thus, thorium can be used as an alternate nuclear fuel by converting into ^{233}U. Thorium oxide finds application as catalyst, high temperature ceramic and high quality lenses. Furthermore, the alloys of thorium with Mg is used in air craft engines and in air frame construction and with W is used in electric filaments. The handling of thorium results in two types of hazards: (1) a hazard from ingestion of an α-ray emitting member of thorium which can be fatal in case of a large scale permanent damage of bone, kidney and liver and (ii) hazard from proximity to γ-ray emitters during working hours. The extent of danger depends on the history of thorium, especially upon time elapsed from its last purification. Regarding the occupational hazard, the person engaged in the manufacture of mantles using thorium has been known to get affected by a form of diffuse dermatitis. This, with the additional swelling of the hand causes the formation of deep skin cracks. In view of the extensive usage of uranium and thorium for various industrial purposes and their toxicity, precise determination of these metals in environmental, metallurgical, geological materials is of utmost importance prior to pollution control measures or its use as alloys or in understanding the correlation between diseases of animals and aquatic organisms and soil chemistry and to prepare soil maps.

1.1. Analytical chemistry of uranium(VI) and thorium(IV)

Spectrophotometry and spectrofluorimetry have similar absorption and fluorimetric spectra when they are reacted with a chromogenic reagent. Hence, it is difficult to determine uranium(VI) or thorium(IV) when they are present together or in the presence of other actinides. Flame atomic absorption spectrometry (FAAS) provides individual determination of traces of uranium(VI) and thorium(IV) but is not that sensitive due to the formation of refractory oxides in the flame region and has been used only scarcely. Graphite furnace AAS (GFAAS) is useful for the trace determination of uranium(VI) and thorium(IV) and is sensitive unlike FAAS. On the other hand, the interference due to matrix (in case of real sample analysis) is more pronounced and is not that popular. Spectrography was extensively used in 1970s but requires elaborate and cumbersome sample preparation. Energy dispersive, wavelength dispersive and total reflectance X-ray fluorescence spectrometric techniques are multi-element techniques but requires elaborate sample preparation, in addition to being not sensitive for liquid samples. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is also multi-elemental technique but cannot be used for differentiating various radionuclides of uranium and thorium. Traditionally used neutron activation analysis (NAA) and more popular ICP-mass spectrometry (ICP-MS) are the techniques which are widely sought after for the determination of not only uranium, thorium and their radionuclides but also other actinides. However, the direct analysis of geological and environmental samples by NAA or ICP-MS is still difficult because of the very low concentrations of uranium and thorium and also the presence of complex matrix. Additional problem, specific to biological samples, is the availability of the sample. One way of solving this problem is by coupling chromatographic techniques to NAA/ICP-MS. An alternative approach is the use of offline (static batch or dynamic column) and on-line preconcentration procedures in conjunction with various single element or multi-element analytical techniques mentioned above.

2. Preconcentration

Preconcentration also called enrichment is a generic term for the various processes employed to increase the ratio of determinant and matrix. Preconcentration is a process in which the ratio of the amount of a desired trace element to that of the original matrix is converted into a new matrix suitable for analytical determination. Preconcentration improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results, offers a high degree of selectivity and facilitates calibration [4,5]. The enrichment process usually consists of (i) stripping the major components from the minor ones and (ii) selective separation of the analyte into a second phase of less volume than the original phase. The preconcentration techniques, hitherto developed, for uranium(VI) and thorium(IV) are based on the physical, physico-chemical and chemical principles. These include liquid–liquid extraction, ion exchange, extraction chromatography, flotation, electrodeposition and solid phase extraction. During preconcentration studies prior to analysis, one has to be vigilant about the possibility of bulk or surface precipitation of thorium in neutral solutions as addition of ammonia or alkali hydroxide to thorium solution results in formation of white gelatinous precipitate of hydrous hydrate. Precipitation begins at a pH of about 3 and complete at a pH of about 6. However, common thorium complexing agents like hydroxy acids and poly hydroxyl alcohols prevent the formation of thorium hydroxide to certain extent.

The preconcentration techniques are classified into off-line and on-line techniques based on the mode of operation.

2.1. Off-line preconcentration methods

Prasada Rao and Gladis [6] and Prasada Rao and Preetha [7] have reviewed various enrichment procedures in which quinoline-8-ol or its derivatives and naphthols were used as chelating agents for preconcentration of inorganics including actinides. The survey of various offline preconcentration techniques reveal that the enrichment is usually carried out by batch or column modes.

2.1.1. Liquid–liquid extraction

Liquid–liquid extraction is based on the distribution of analyte of interest between two essentially immiscible solvents. The formation of an uncharged chemical species in aqueous phase by either chelation or ion-association is essential for extraction into suitable organic solvent. The distribution ratio of a particular analyte is usually defined as the ratio of its total concentration in organic phase to that in aqueous phase at equilibrium. While extracting the desired analyte, larger the distribution ratio of the analyte and smaller that of the matrix elements, higher the recovery of the analyte resulting in higher enrichment factors. When the matrix is removed by the extraction, the reverse is required for successful enrichment. The proper choice of extractant, pH or acidity of the aqueous phase, immiscible solvent, masking agents, salting out agents and modifiers are important. In some cases, after extraction, the selective stripping of the matrix elements from the organic phase into a small volume of the aqueous phase can also improve the enrichment factor [8–10].

2.1.1.1. Uranium. A selective and very efficient concentration method for uranium(VI) into ethyl acetate was developed by the homogeneous liquid–liquid extraction method based on the ion-pair phase separation of perfluorooctonate ion with tetrabutyl ammonium ion [11]. This procedure offers quite good enrichment factor of ∼330. However, the proposed enrichment procedure was tested for the recovery of uranium(VI) from synthetic sea water solutions only.

2.1.1.2. Thorium. Chloroform solution of crown hydroxamic acid is used for selective extraction of thorium(IV) from dilute aqueous solutions and has been directly introduced into the plasma of inductively coupled plasma atomic emission spectrometry (ICP-AES) [12]. This method is unique in that it allows the determination of thorium(IV) present in complex real samples ranging from monazite sand to sea water.

2.1.1.3. Uranium and thorium. ^{214}U and ^{230}Th were co-extracted with trioctyl-phosphine oxide followed by back extraction after diluting with caprylic acid [13]. The back extract was then analysed for uranium and thorium by aspirating into the plasma of ICP-mass spectrometry (ICP-MS). The accuracy of the developed preconcentration and determination procedure was successfully tested by analyzing a BIL-1 Lake Baikal bottom silt standard reference material.

2.1.2. Liquid membranes

The transport of uranium(VI) and thorium(IV) was enhanced by electrodialysis through a cation exchange membrane impregnated with di-2-ethyl-hexyl phosphoric acid (D2EHPA) in kerosene [14]. The cationic flux of uranium(VI) through cation exchange membrane is improved from 5.2×10^{-8} to 8.7×10^{-8} g equiv. cm^{-1} on impregnation with D2EHPA in kerosene. The technique of electrodialysis results in preconcentration of uranium(VI) by 2.8-fold to its initial concentration which is not that impressive. Gureli and Apak [15] have recovered uranium from carbonate solutions using strong anion-exchange resin columns and strongly basic anionic exchange membranes. Membrane separations were found to be effective only in dilute solutions of uranium due to limited surface area of membranes. Thus, the authors were able to establish the complimentarity between resin columns and membranes for recovery of different uranyl carbonate anionic species.

2.1.3. Ion exchange

Ion exchange means the exchange of ions of a like sign between an aqueous solution and a solid of highly insoluble body in contact with it. Ion exchangers consist of a frame work carrying a positive or negative surplus charge which is compensated by mobile counter ions of opposite sign. To concentrate dilute solutions, it is passed through a column of an appropriate ion exchange resin; the exchangeable ions will be exchanged. Subsequently, the exchanged ions can be concentrated by eluting with a small volume. The capacity of ion exchangers is usually defined in terms of the number of exchangeable counter ions in the material [16].

2.1.3.1. Uranium. Analizarin Red S (ARS) modified anion-exchange resin was prepared by a simple reaction of ARS with the anion exchanger Doulite A101 and used for the effective sorption of uranium(VI) from aqueous media [17]. The modified resin sorbs over a wide range of pH 2.8–5.0 with an impressive sorption capacity of 162 mg/g. Uranium(VI) has been effectively separated from natural waters and certified uranium ores using above ARS resin.

2.1.3.2. Uranium and thorium. The radionuclides of uranium and thorium were preconcentratively separated with specific ion exchangers like HYPHAN and POLYORGS and subsequently determined by ICP-MS and/or alpha spectrometry [18]. The above preconcentration and determination procedure was tested with spiked tap water samples only.

2.1.4. Extraction chromatography

Extraction chromatography is a variant of ion exchange chromatography, with a liquid ion exchanger [19]. In this technique, the mobile phase consists of a solution of an aqueous buffer and the stationary phase contains an organic extractant, chelate or ion pair formed is soluble in the stationary phase. Thus, retention is determined by the ability to form the ion pair as well as the solubility of the complex in the stationary phase. This method of separation is popular in radiochemical analysis. The main drawback of this technique is the bleeding of organic residues from the column during preconcentration.

2.1.4.1. Uranium. Extraction chromatographic preconcentration of uranium from Laki hot springs has been examined with aluminium oxide, followed by acid dissolution of the precipitate. Precolumn derivatization is carried out with bis(salicylaldehyde) propylenediamine. Elution and separation have been carried out from YMC pack ODS 5 mm column with a mixture of methanol:acetonitrile:water (60:10:30). This method allows an impressive enrichment factor of 390 [20].

A new extraction chromatographic resin developed for strong retention of uranium(VI) from a wide range of acid concentrations comprises a novel liquid stationary phase consisting of equimolar mixture of diamyl amylphosphonate and cyanex 923 (*R*) (a commercially available trialkylphosphine oxide) sorbed on silanized silica or Amberchrom CG-71 [21]. The accuracy of this procedure was neither tested by analyzing certified reference materials nor being applied to real sample analysis.

2.1.4.2. Thorium. As the alpha spectrometry offers very poor detection limits for ^{232}Th compared to other isotopes of thorium, recovery corrected preconcentration radiochemical NAA (PCRNAA) technique offers one order of magnitude below compared to earlier preconcentration–NAA methods [22].

2.1.4.3. Uranium and thorium. A reversed phase chromatographic method combined with on-line matrix elimination procedure is described for the determination of uranium and thorium in the nitric acid digest of phosphate rocks [23]. Uranium(VI) and thorium(IV) trapped on the C_{18} column whilst the transition and lanthanide elements were washed with phenylhydroxy acetic acid due to their weak retention. Subsequently, uranium(VI) and thorium(IV) were separated and quantified using α-hydroxyisobutyric acid eluent with visible detection at 658 nm after post-column reaction with Arsenazo III.

Pin and Zalduegi [24] have sequentially separated light rare earth elements, thorium and uranium by miniaturized extraction chromatography column packed with TRU Spec (transuranic element specific) and Ln spec (lanthanide specific). For most geological samples, TRU spec "resin" affords a straight forward separation of LREE, uranium and thorium with high yield, good purity and satisfactory blank levels. The developed method has been successfully applied for the analysis of LREE, uranium and thorium in a variety of silicate rocks.

Uranium, thorium, plutonium and americium were preconcentrated onto TRU(TM) resin (Elchrom) prior to elemental separation by extraction chromatography and α-spectrometric determination [25]. The developed method has been validated by analyzing human tissue samples, previously analysed for americium, plutonium, uranium and thorium in the United States Transuranium and Uranium Registries (USTUR). Furthermore, two National Institute of Standards and Technology (NIST), Standard Reference Materials, SRM 4351 – Human lung and SRM 4352 – Human liver were also analysed.

Yokoyama et al. [26] have developed a new chemical separation technique to isolate uranium and thorium from silicate rocks by using two kinds of commercial extraction chromatographic resins. Both uranium and thorium fractions obtained by these procedures were sufficiently pure for thermal ionization mass spectrometric (TIMS) analysis.

Uranium(VI) and thorium(IV) were preconcentrated onto iron(III) hydroxide and then separated using UTEVA resin [27]. The accuracy of the above procedure was tested by analyzing uraninite ore, coral and granite reference materials. The above extraction chromatographic procedure provides a more rapid separation using less reagents compared to anion-exchange procedure.

2.1.5. Flotation

Flotation is a process by which finely divided solids are suspended in a solution and floated to the surface of the liquid (Fig. 1). When hydrophilic substances are to be floated, they are generally rendered hydrophobic and precipitated at the interface by equilibrating with suitable immiscible organic solvents [28]. In some cases, desired trace elements present in an aqueous solution are quantitatively collected on a small amount of inorganic or organic collector precipitates and subsequently floated by bubbling with or without the aid of surfactant ions of opposite charge to the precipitate surfaces. Khalifa [17] has floated uranium—Alizarin Red S chelate from aqueous media at pH ∼ 4 by using oleic acid as a surfactant. Uranium(VI) has been effectively separated from natural water samples and certified uranium ores.

2.1.6. Adsorptive accumulation

Metal–chelate complexes were accumulated onto a variety of electrode materials and then determined by stripping either anodically or cathodically. The adsorption of metal–chelate complexes offer a selective enrichment of metal ions from dilute aqueous solutions containing other matrix species.

2.1.6.1. Uranium. The uranium(VI)–quinolinate complex was accumulated onto a mercury electrode by adsorption from chloroform solutions and then determined by cathodic stripping voltammetry [29]. The calibration graph was lin-

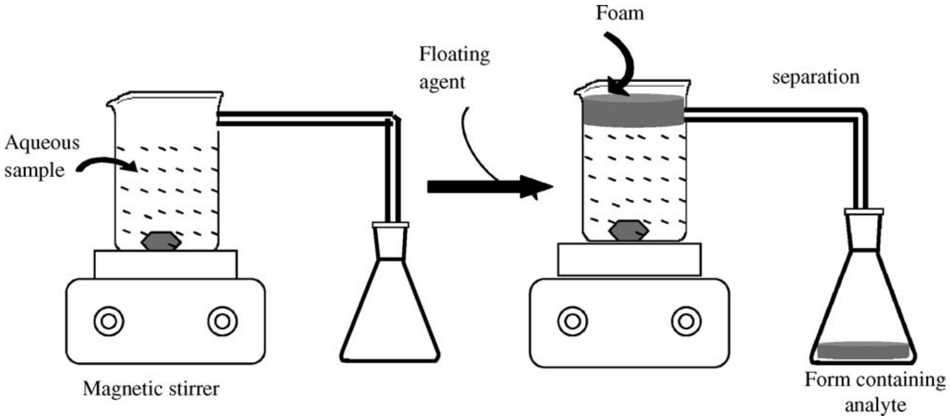


Fig. 1. Conventional froth flotation preconcentration technique.

ear over the range 0.5–80 μM with the detection limits of 0.4 μM, which are not that good. However, the R.S.D. of 5 μM of uranium solutions is 1.5%, which is quite good.

Wang and Setiadji [30] have accumulated uranium(VI)–cupferron via adsorption onto mercury electrode and determined by stripping voltammetry/potentiometry. This procedure improves the selectivity while retaining sensitivity of previously reported adsorptive stripping schemes. The adsorption properties of dioxouranium–phthalate complexes onto hanging mercury drop electrode are exploited in developing a highly sensitive and selective linear sweep cathodic (LSCSV) and differential pulse cathodic (DPCSV) stripping voltammetric procedures for the determination of uranium(VI) [31]. As low as 0.5 and 4.8 μg/l uranium(VI) was determined with accumulate time of 240 and 120 s using DPCSV and LSCSV respectively which are quite impressive. Pretty et al. [32] have accumulated uranium(VI)–propyl gallate complex at a mercury thin film electrode (MTFE). With a 10 min accumulation time, a meagre 24-fold signal enhancement was achieved. Quantitative performance was tested on NAAS-4 open ocean sea water (2.68 ± 0.12 μg/l of uranium) by using calibration plot and standard addition methods.

2.1.6.2. Thorium. Setiadji et al. [33] have determined thorium by stripping voltammetry, which utilizes a catalytic adsorptive peak of the thorium–cupferron complex. The developed procedure offers improved sensitivity over a previous stripping scheme for thorium. Quite impressive detection limit of 50 ng/l was reported by these authors. However, the R.S.D. during the determination of 5 μg/l is 4.4%, which is rather poor.

2.1.7. Solid phase extraction (SPE)

Solid phase extraction (SPE) is currently being used as an enrichment technique when low concentration analytes has to be recovered. The basic principle of SPE is the transfer of metals from the aqueous phase to the active sites of the adjacent solid phase; it can also be termed as solid–liquid extraction. The transfer is simulated by the selection of appropriate optimal conditions in the system of three major components—water (liquid phase), target metal and sorbent [34]. The metal after sorption on the solid phase is either desorbed with a suitable eluate and thus recovered (see Fig. 2). The mechanism involved in SPE depends on the nature of the sorbent and metal ion to be recovered. Thus, SPE is carried out by means of adsorption, coprecipitation, ion exchange, chelation, ion-pair formation, etc. SPE has been widely used for the removal of organics as seen from various review articles [34–36].

Hitherto, liquid–liquid extraction (LLE) was most often used among various enrichment/separation techniques in view of its simplicity, rapidity, ready adaptability of scale up studies and easier recovery of metal and extractant. SPE offers several advantages over LLE. These include [37,38]:

1. flexibility,
2. higher enrichment factors,
3. absence of emulsion,
4. low cost because of lower consumption of reagents,
5. more importantly environment friendly.

The sorbents employed in SPE can be broadly classified into inorganic based (inorganic oxides) and organic based (natural and synthetic polymer) sorbents (see Fig. 3). The most important inorganic based sorbents are silica gel, C_{18} bonded silica gel, modified silicas, alumina, fluorisil, diatomaceous earth and other inorganic oxides. However, these inorganic based sorbents are beset with an additional problem due to formation of suspensions. Hence, organic based sorbents are more popular and have been divided into polymeric and non-polymeric sorbents.

2.1.7.1. Uranium. Polyurethane foam. Uranium present in natural waters was preconcentrated by percolating a suitable aliquot of sample whose pH was adjusted to 6.0–6.5 through a tri-*n*-butylphosphate plasticized dibenzoylmethane loaded polyurethane bed [39]. Uranium on the foam was eluted with 0.6 mol/l of HCl solution and then determined spectrophotometrically using Arsenazo III as a chromogenic reagent. A β-diketone and phenyl phosphonic acid functional groups were incorporated into polyurethane foam in a simple and

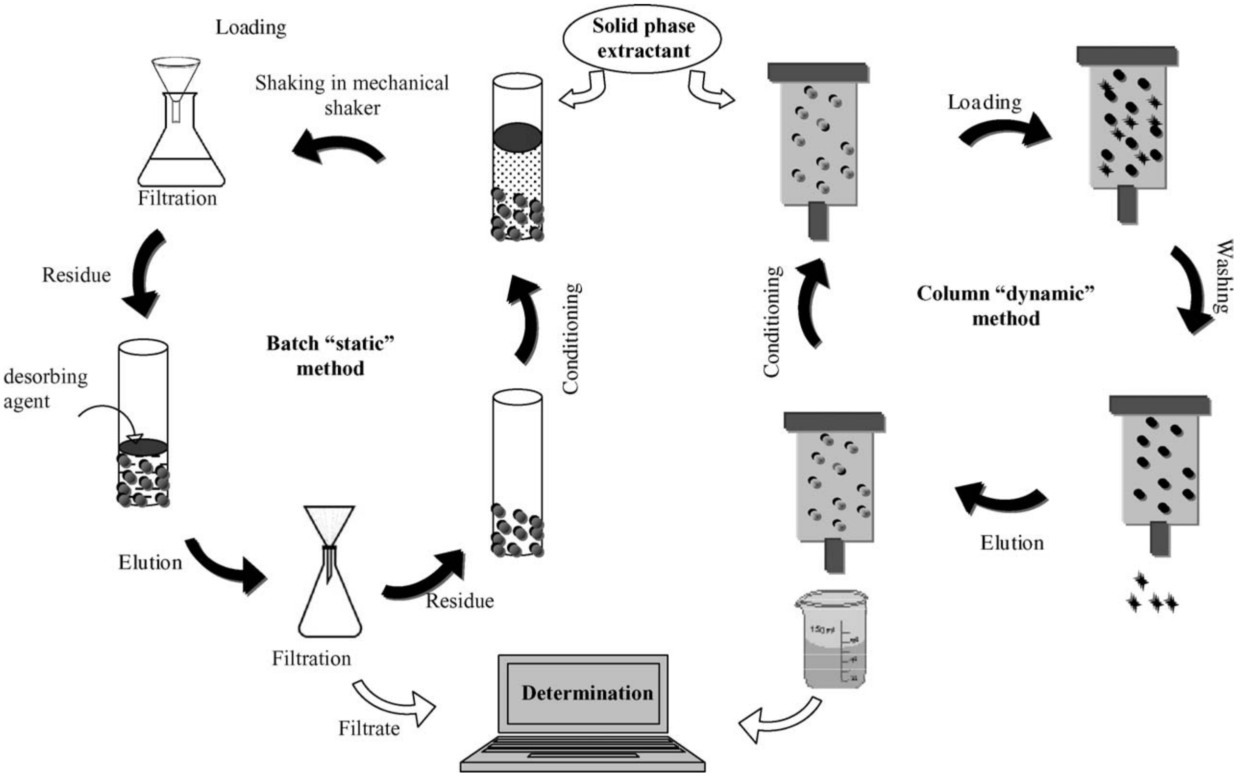


Fig. 2. Principle of solid phase extraction.

inexpensive manner [40,41]. These materials showed greater extractability of uranium at all temperatures and pH values when compared to blank polyurethane foam without functional groups. Carvalho et al. [42] preconcentrated ng/ml levels of uranium as its salicylate complex on powdered polyurethane foam at pH 4.0. The resulting foam was filtered through a filter paper and used for X-ray fluorescence measurements. The reported detection limit is 5.5 μg/l of uranium, which is quite good. Furthermore, the developed procedure finds successful application to reference materials, waste water, mine drainage and sea water.

Amberlite XAD resins. Uranium(VI) was preconcentrated onto 1-(2-thioazolylazo)-2-naphthol/1-(2-pyridylazo)-2-naphthol/sodium diethyl dithiocarbamate [43]; quinoline-8-ol [44] and succinic acid [45] functionalized Amberlite XAD-4 resins from weakly acidic solutions, i.e. pH 4.0–8.0. Schemes 1 and 2 show the process of chemical immobilization of quinoline-8-ol and succinic acid onto Amberlite

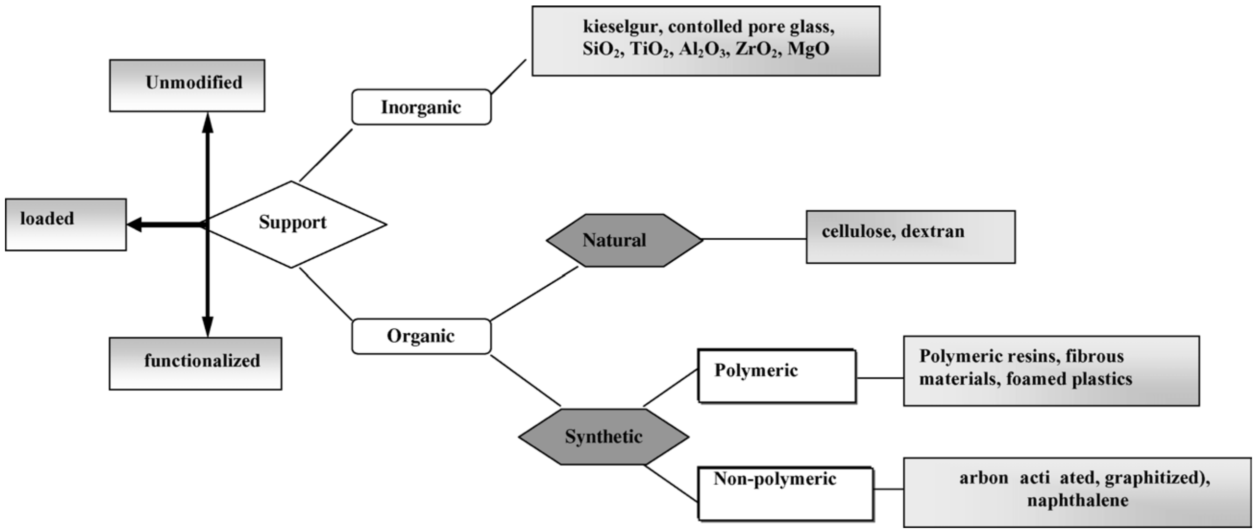
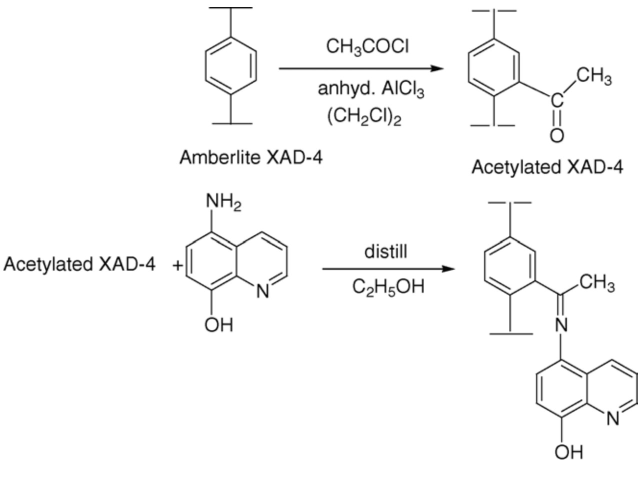
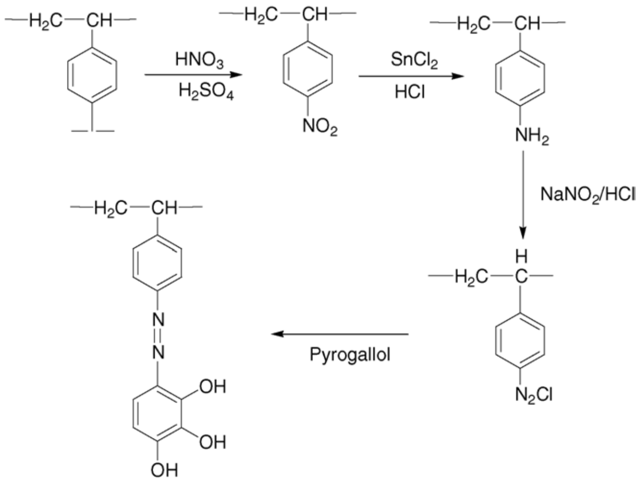


Fig. 3. Sorbents used in solid phase extraction.



Scheme 1. Synthesis of quinoline-8-ol functionalized Amberlite XAD-4 resin.

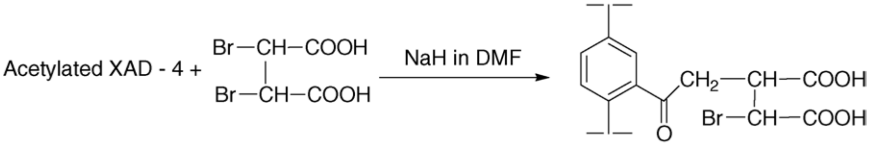


Scheme 3. Synthesis of pyrogallol functionalized Amberlite XAD-2 resin.

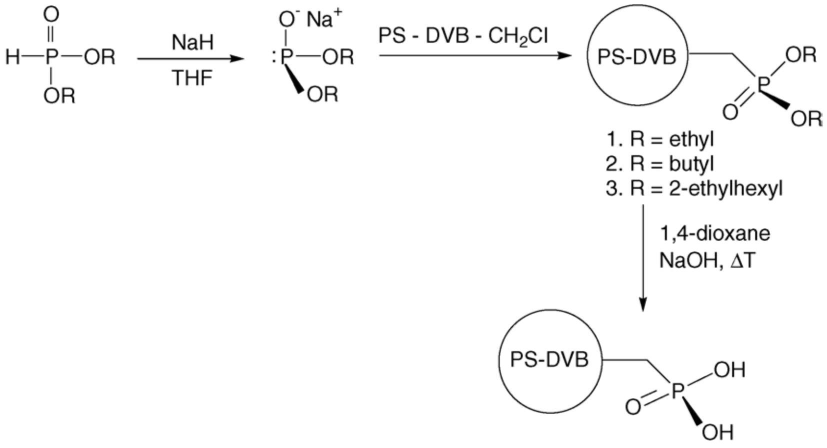
XAD-4 resin respectively. The accuracy of the latter two procedures was tested by analyzing the certified reference materials and successfully employed for the determination of uranium(VI) in soil and sediment samples using a simple technique like spectrophotometry. Again, the detection limits of the latter two procedures are quite good, i.e. 5 ng/ml. However, the procedure developed by Vacha and Sommer [43] is applied to water samples only.

N,*N*-Dibutyl-*N*′-benzoyl thiourea (DBBT) impregnated Amberlite XAD-16 resin was prepared by direct adsorption of chelating ligand onto macroporous support [46]. The results demonstrated that uranium(VI) can be preconcentrated onto 0.1 g of chelate modified resin from pH 4.5 to 7.0 solutions. The sorption capacity of the impregnated resin is quite good (214.2 mg of uranium per g of resin). Kumar et al. [47] have synthesized chemically immobilized pyrogallol onto Amberlite XAD-2 resin through an azo (–N=N–) spacer group (see Scheme 3) and has been used for preconcentration of uranium(VI), in addition to transition and heavy metals. A very good detection limit of 1.0 ng/ml was reported for uranium(VI). However, the developed procedure was tested for the determination of uranium(VI) in well water samples only. Amberlite IR-118H, a strongly acidic cation exchanger was tested for the adsorption of uranium(VI) in presence of various metal cations [48]. The metal cations suppress uranium(VI) adsorption differently depending on their ionic radii. Though the adsorption data were processed using Frumkin–Fowler–Guggenheim equation, the developed procedure has not been tested for the analysis of certified reference materials or any real samples.

Other chelating resins. Phosphonate derivatized polystyrene–divinyl benzene (PS–DVB) resins [49] have been prepared from chloromethylpolystyrene–divinyl benzene (Cl-CH_2-PS–DVB) by Arbuzov reaction using lithium or sodium alkyl chlorophosphites. Base promoted hydrolysis of the diethylphosphite-derivatized resin in refluxing 1,4-dioxane resulted in phosphonic acid derivatized PS–DVB resins (see Scheme 4). Both the free phosphonic acid as well as the diethyl, dibutyl and bis-(2-ethylhexyl)phosphonate derivatized sorbents possess a high selectivity for uranium(VI) with an optimum pH of 4. The developed procedure has not been applied to any of the real samples. Lee et al. [50,51] have recovered uranium(VI) from four geological standards and one domestic granite rock from pH 5.4 to 5.5 solutions using a minicolumn filled with 0.2 g of 4-(2-thiazolylazo) resorcinol functionalized resin after addition of 1,2-diamino cyclohexane *N*,*N*,*N*′,*N*′-tetraacetic acid (CDTA) and ammonium fluoride as complexing agents. The results of four replicate analyses were in good agreement with certified values. Uranium was quantitatively collected with an Empore (TM) chelating resin disc at a flow rate of 100–150 ml/min from pH 5 solutions in presence of ammonium acetate and CDTA [52]. The analytical results of uranium in mineral waters is in good agreement with literature values and standard methods such as ICP-MS/α-ray spectrometry. A very high enrichment factor of 200 was achieved by these authors. Anion exchanger (Dowex 1 × 8 resin) was treated with aqueous $KMnO_4$ solution to prepare amorphous MnO_2 deposited resin [53]. Uranium is trapped only to an extent of 85% while passing natural waters containing traces of uranium.



Scheme 2. Synthesis of succinic acid functionalized Amberlite XAD-4 resin.



Scheme 4. Synthesis of phosphonate derivatized chlorometylated polystyrene–divinylbenzene resin.

Naphthalene/benzophenone. Puri et al. [54,55] have preconcentrated uranium(VI) by adsorption of their chelate or ion-association complexes of quinoline-8-ol and trifluoroethyl xanthate-cetyltrimethyl ammonium bromide respectively onto microcrystalline naphthalene from weakly acidic solutions (pH ~ 4.5–8.0). The metal has been desorbed with HCl and determined with differential pulse polarograph. The methods were then applied to a whole range of complex real samples like alloys, coal fly ash, biological, synthetic and waste water samples. Uranium(VI) as its 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex was preconcentrated from large volume of aqueous samples onto ammonium tetraphenyl borate modified naphthalene filled in the column in the pH range 7.0–9.5 and at a flow rate of 2 ml/min [56]. The method finds application to coal fly ash, Zr-based alloys and some synthetic samples corresponding to alloys. Solid phase extraction of uranium(VI) was demonstrated by Gladis and Rao [57] and Preetha and Rao [58] wherein 5,7-dichloroquinoline-8-ol or dicyclohexano-18-crown-6 modified naphthalene were used as adsorbents. Both the complexes were preconcentrated from weakly acidic solutions (pH 4.5–7.0). 1-(2-Pyridylazo)-2-naphthol modified benzophenone/naphthalene was used as solid phase extractant to enrich uranium(VI) from complex aqueous solutions containing other metal ions [59]. Again, impressive detection limits of ~2 ng/ml were reported by these authors. Furthermore, in addition to testing the accuracy of the developed preconcentration procedures by analyzing MESS-3, a marine sediment reference material supplied by National Research Council, Canada, the developed procedure has been applied to soils and sediments.

Textile based solid sorbent. McComb and Gesser [60] have employed poly(acrylamidoxime) cloth for use as a passive monitor for trace metals including uranium onto cloth using a continuous flow chamber. The monitors consist of amidoxime chelating groups bound to the surface of a textile enclosed in a common 35 mm slide holder. Placement of this device in the water to be sampled resulted in the uptake of metals by the chelating groups.

Octylsilane (C_8). Uranium(VI) as its quinolinate complex was preconcentrated onto octyl silane (C_8) SPE cartridge. A preconcentration factor of ~100 was achieved [61]. The proposed method was successfully used for the determination of uranium in Caspian sea and Persian Gulf water samples.

Octadecyl silica membrane discs. A simple and reliable method for the selective extraction and determination of uranium(VI) was developed using bis(2-ethylhexyl) hydrogen phosphate [62] and tri-*n*-octyl-phosphine oxide [63] modified octadecyl silica membrane discs. The detection limit of the former procedure is 40 ng/l, which is better than latter procedure, i.e. 100 ng/l. Both the methods were applied to the extraction and determination of uranium in natural waters.

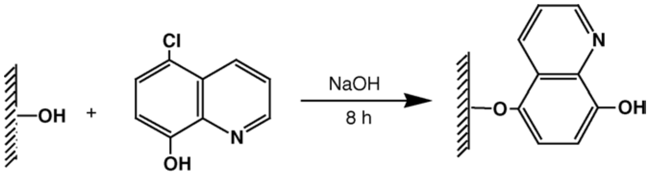
Silica gel. *N*-Tripropionate or (*N*-triacetate) substituted tetraazo macrocycles [64] or catechol [65] bound silica gel has been used for preconcentration of uranium(VI) from dilute aqueous solutions. The former procedure finds application for decontamination of real effluents containing traces of uranium, plutonium and americium. The latter procedure has been applied to the analysis of soil and sediment samples.

Activated carbon. Diarylazobisphenol (DAB) and DAB modified activated carbon [66] were synthesized, characterized and latter has been used for preconcentration of traces of uranium(VI) present in soil and sediment samples. A very good detection limit of 5 μg/l was reported by these authors. The accuracy of the developed preconcentration method in conjunction with Arsenazo III procedure was tested by analyzing marine sediment certified reference material (MESS-3).

2.1.7.2. Thorium.

Benzophenone. 5,7-Dichloroquinoline-8-ol modified benzophenone was prepared and has been used for preconcentration of traces of thorium present in dilute aqueous solutions and pure rare earth chloride solutions [67]. A very good detection limit of 0.5 ng/ml was reported by these authors using a simple technique like spectrophotometry.

Cellulose. Cellulose was functionalized by coupling with 5-chloroquinoline-8-ol in the presence of alkali as per Scheme 5 [68]. The resulting polymer has been character-



Scheme 5. Synthesis of quinoline-8-ol functionalized cellulose.

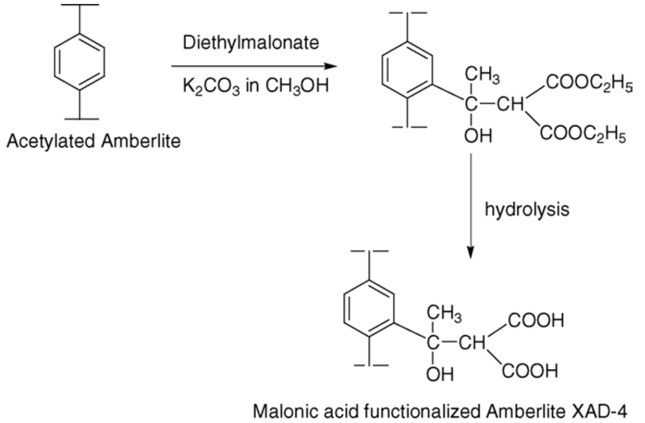
ized by IR spectra and has been used for preconcentrating thorium(IV) from dilute aqueous and rare earth chloride solutions. The optimum pH value is 5.0–7.0. Very good detection limit and enrichment factors of 2 μg/l and 200 respectively were reported by these authors.

Amberlite XAD-4. A new chelating polymer has been developed wherein Amberlite XAD-4 has been functionalized by coupling it with diethylmalonate after acetylation (see Scheme 6) [69]. The resulting resin has been characterized by IR spectral and microanalysis studies and has been used for preconcentrative separation of thorium(IV) from weakly acidic solutions in the presence of alkali, alkaline earth, transition elements and lanthanides. A high sorption capacity of 19.28 mg/g of polymer with an enrichment factor of ∼500 was reported by Metilda et al. [69]. The detection limit of the developed procedure is 0.2 μg/l, which is quite impressive. Further, thorium(IV) content of rare earth chloride solution established by the present procedure compare favourably with standard ICP-AES value.

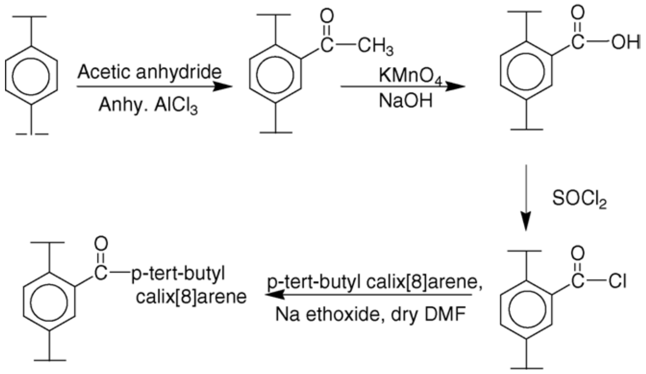
Polyurethane foam. Polyurethane foam loaded with 2-ethylhexyl phosphonic acid was used for preconcentration of thorium(IV) present in natural water samples [70]. The results were in good agreement with reference values of water samples at 95% confidence level.

2.1.7.3. Uranium and thorium. Amberlite XAD resins. Demirel et al. [71] impregnated carboxymethyl-1-methyl calix[4]resorcinarene into a Amberlite XAD-4 polymeric matrix and has been used for sorption of thorium(IV) and uranium(VI) from aqueous solutions. Chromatographic separation of thorium(IV) and uranium(VI) was accomplished by adjustment of pH to 3.0 and 6.0, respectively. The sorption capacities for thorium(IV) and uranium(VI) are 62.64 and 64.26 mg/g of polymer respectively which are quite good. P-*tert*-butyl-calix[8]arene was chemically bound to Amberlite XAD-4 polymeric support (see Scheme 7) and has been used for sorption of uranium(VI) and thorium(IV) [72]. The authors claim selectivity of uranium(VI) and thorium(IV) over other metal ions only.

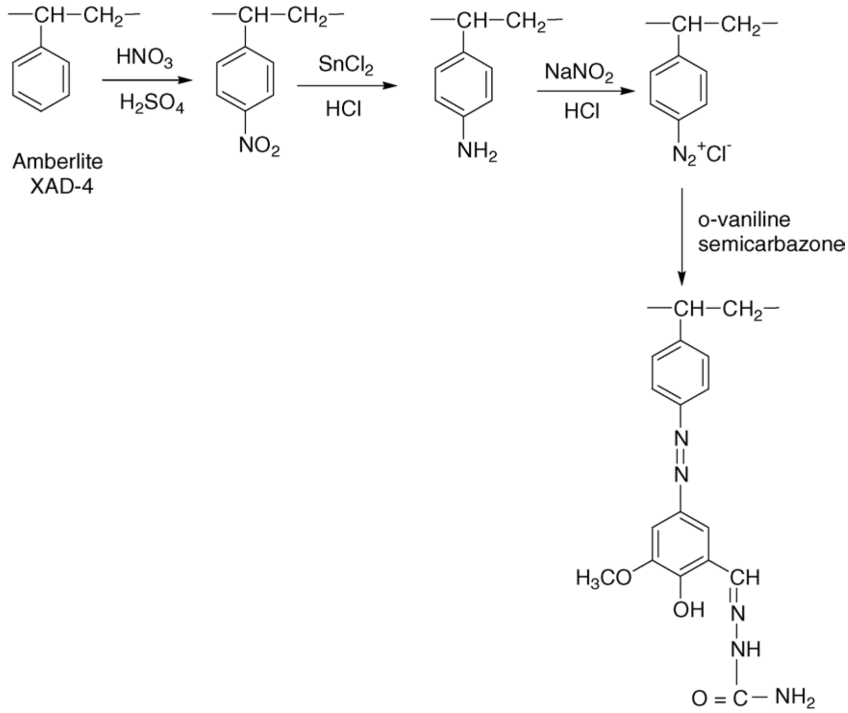
Jain et al. [73] functionalized Amberlite XAD-4 with *o*-vanillin semicarbazone (see Scheme 8) and its analytical properties for uranium(VI) and thorium(IV) have been studied. The chelate modified resin exhibits good chemical stability, reusability and faster rate of equilibrium for their determination by spectrophotometry. Both the uptake and stripping of these metal ions were fairly rapid, indicating a better accessibility of the chelating sites. The proposed procedure though allows determination of uranium(VI) in simulated river water samples, the retention/sorption capacities are very low, for example, 2.89 and 3.23 mg of uranium(VI) and thorium(IV) per g of chelate functionalized resin. Trace amounts of selected lanthanides, uranium(VI) and thorium(IV) were quantitatively retained on the bicine functionalized Amberlite XAD-4 (see Scheme 9) resin and recovered by eluting with 1 M HCl [74]. The retention capacities reported by these authors are higher than that of any other chelate functionalized Amberlite XAD resins viz. 90.44 and 58.0 mg of uranium(VI) and thorium(IV) per g of resin. However, the developed procedure has not been (i) tested for its validation using certified reference materials or (ii) applied to real samples. A new grafted polymer has been developed by the chemical modification of Amberlite XAD-16 polymeric matrix with [(2-dihydroxyarsinoylphenylamino)-methyl]phosphonic acid as per Scheme 10 and has been characterized by ^{13}C CPMAS, ^{31}P solid state NMR, FT-NIR–FIR–Raman spectroscopy, CHNPS elemental analysis and thermogravimetric analysis [75]. The metal sorption capacities are quite good 59.9 mg of uranium(VI) and 109.04 mg of thorium(IV) under optimal pH conditions respectively. Quite impressive enrichment factors, viz. 365



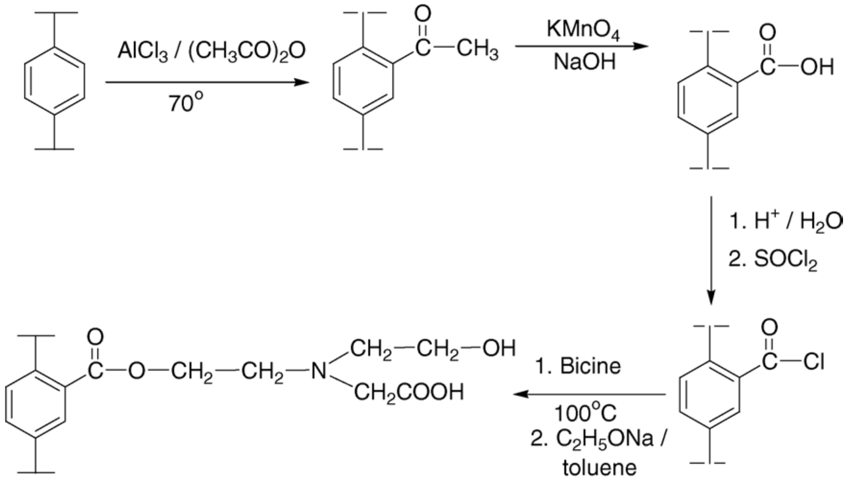
Scheme 6. Synthesis of malonic acid functionalized Amberlite XAD-4 resins.



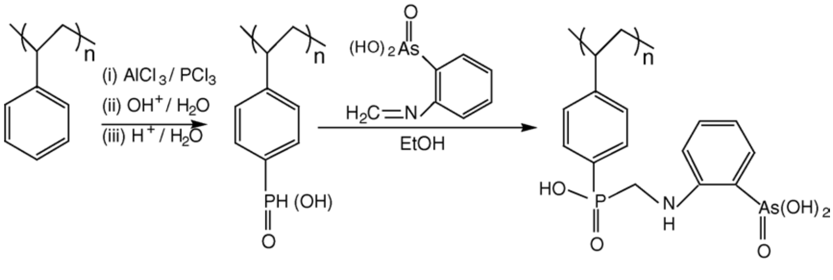
Scheme 7. Synthesis of *p*-*tert*-butyl calix[8]arene functionalised Amberlite XAD-4 resin.



Scheme 8. Synthesis of *o*-vanillin semicarbazone functionalized Amberlite XAD-4 resin.



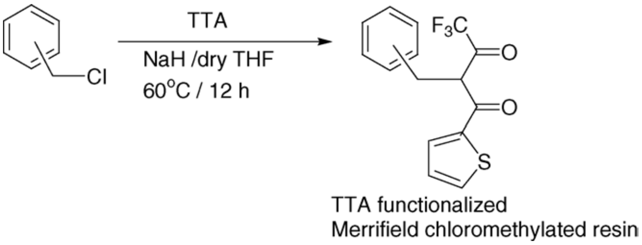
Scheme 9. Synthesis of bicine functionalized Amberlite XAD-4 resin.



Scheme 10. Synthesis of phosphonic acid functionalized Amberlite XAD-16 resin.

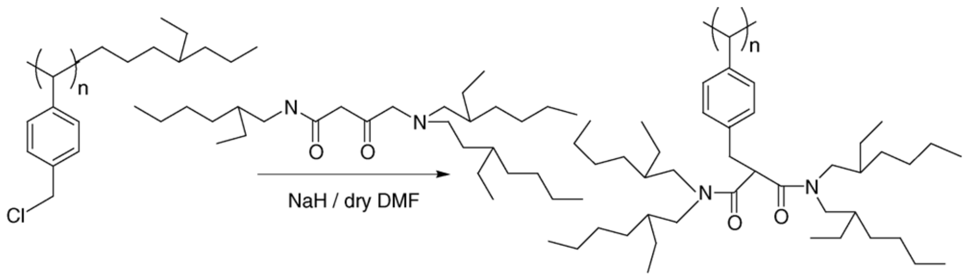
and 300 for uranium(VI) and thorium(IV) were reported. However, the applicability of the developed procedure was not tested with real samples although the practical ability to analyse synthetic nuclear spent fuel, sea water mixtures, natural waters and geological samples was reported.

Merrifield chloromethylated resin. Thenoyl trifluoroacetone [76] di-bis(2-ethylhexyl) malonamide (DB2EHM) [77], 11,23-disemicarbazono-26,28-*n*-dipropoxy-25,27-dihydroxy calix[4]arene semicarbazone [92] and quinoline-8-ol [79] were crosslinked onto Merrifield chloromethylated resin (see Schemes 11–13). TTA anchored resin offers quantitative extraction in the pH range 4–5 and 2–4 and good sorption capacities of 33.32 and 27.84 mg/g of resin were reported for uranium(VI) and thorium(IV), respectively. Again, this procedure has not been tested for its applicability to real samples [76]. DB2EHM anchored resin [77] offers reasonably good sorption capacities of 62.5 and 38.2 mg/g of resin for uranium(VI) and thorium(IV) at 5 M HNO_3. This sorbent has been tested for extraction of above actinides from a synthetic nuclear spent fuel solutions.

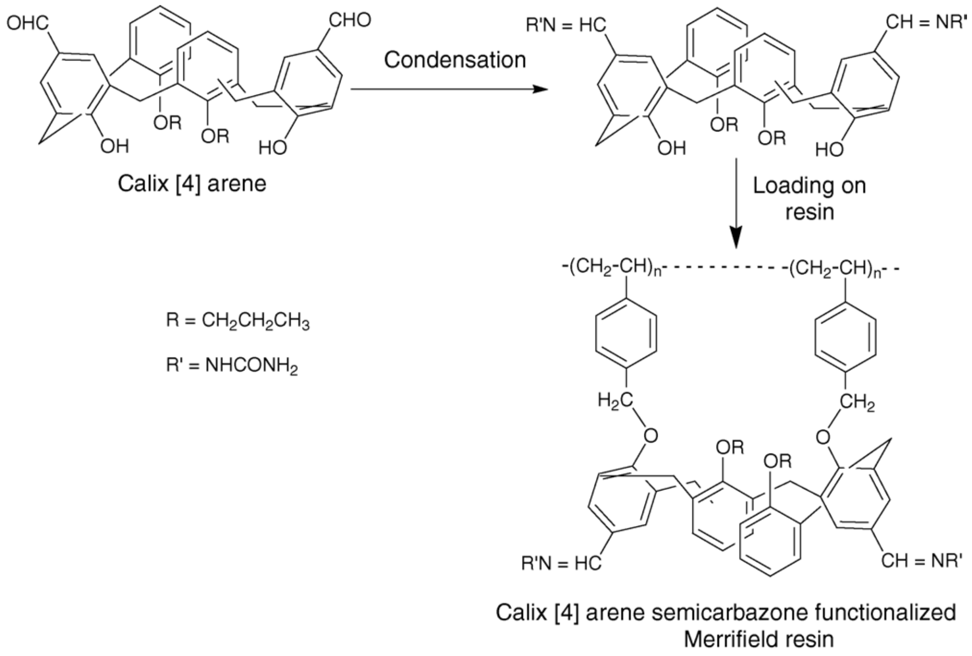


Scheme 11. Synthesis of TTA functionalized Merrifield chloromethylated resin.

Calix[4]arene semicarbazone derivative of resin [78] showed good separating ability with maximum sorption between pH 2.5 and 4.5 for thorium(IV) and between pH 5.5 and 7.0 for uranium(VI) respectively. Reasonably good enrichment factors of 103 and 102 were reported for uranium(VI) and thorium(IV) and has been applied to monazite sand and some standard geological materials. Anchoring of a simple molecule like quinoline-8-ol to Merrifield chloromethylated offer 100-fold enrichment of uranium(VI) in addition to



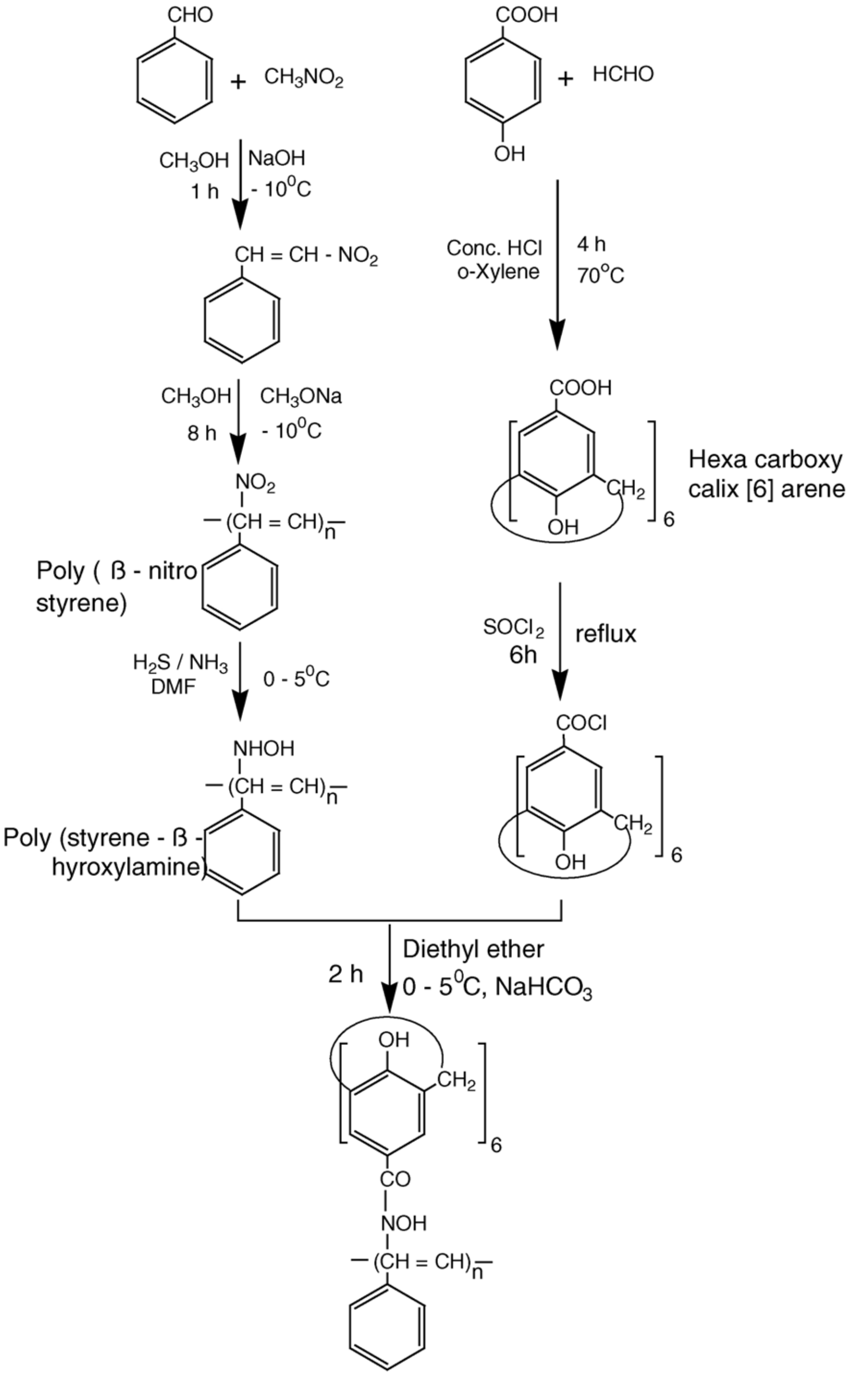
Scheme 12. Synthesis of di(bis-2-ethylhexyl) malonamide functionalized Merrifield chloromethylated resin.



Scheme 13. Synthesis of calix[4]arene semicarbazone functionalized Merrifield chloromethylated resin.

having maximum sorption capacity of 120.30 mg/g of resin [79]. The developed preconcentration procedure in conjunction with Arsenazo III Spectrophotometry allows the determination of as low as 5 μg/l of uranium(VI) in certified reference and real samples of soils and sediments.

Poly(styrene β-hydroxylamine). A new polymer supported calix[6]arene hydroxamic acid has been synthesized by reacting the acid chloride of 37,38,39,40,41,42-hexahydroxy-1,8,13,19,25,31-hexacarboxy calix[6]arene with poly(styrene β-hydroxylamine) (see Scheme 14) [80]. The above resin was used for chromatographic separation of uranium(VI), thorium(IV) and cerium(IV) by the judicious adjustment of pH to 4.0, 6.0 and 7.5, respectively. The above rare elements were preconcentrated and determined in the presence of each other, monazite sand and environmental sample. In addition, the retention capacities were calculated to be 97.82, 108.34 and 55.3 mg of uranium(VI), thorium(IV) and cerium(IV) respectively which are the highest reported so far.



Scheme 14. Synthesis of polymer supported 37,38,39,40,41,42-hexahydroxy-1,8,13,19,25,31-hexacarboxy calix[6]arene hydroxamic acid.

TRU-spec resin. Selective separation of uranium(VI) and thorium(IV) was carried out with high recoveries using TRU-spec resin SPE material [81]. The developed procedure enables the determination of uranium(VI) and thorium(IV) at low-ppb range in silicate rocks.

Octadecyl silica membrane discs. Tri-*n*-octylphosphine oxide (TOPO) modified octadecyl silica membrane discs was employed for simple, rapid and selective separation of uranium(VI) from thorium(IV) from 0.5 M HNO_3 solutions [82]. Maximum capacity of the membrane discs modified by 50 mg of TOPO was found to be 938 μg/g of sorbent, which is quite low. The method was applied to the recovery of uranyl ion from two different soil samples.

Fly ash. Separation of uranium(VI) and thorium(IV) at ppm level present in monazite sand was effected by passing through a chelate modified fly ash bed thus avoiding oxalate precipitation [83]. This sorbent has been successfully used to remove uranium from contaminated waters.

2.1.8. Ion imprinting polymers

Ion imprinting is a versatile technique for preparing polymeric materials that are capable of high ionic recognition. Ion imprinting is a way of making artificial “locks” for “ionic keys”. The concept of ion imprinting technology is described in Fig. 4.

The selected key ion (targeted metal) is first mixed with a variety of lock building monomers (functional monomers). The building blocks and the key are allowed to attach each other strongly or loosely. The so formed complexes consisting of building blocks and key are glued together in order to fix the building block position around the key by polymerization. Finally by removing the ionic key, it leaves construction, which is selective for original key and not any other key.

Saunders et al. [84] described the synthesis of uranyl ion-imprinted copolymer with chloroacrylic acid and ethylene glycol dimethacrylate (EGDMA) which after removal of the template, selectively extracts uranium from dilute aqueous solutions over a range of +2, +3 and +4 competitor ions. Uranyl IIP particles were synthesized by Bae et al. [85] comprising 5% uranium–vinyl benzoate binary complex and 4 wt.% divinyl benzene (DVB) in styrene, using chemical initiation by 1 wt.% 2,2′-azobisisobutyronitrile (AIBN). These particles were used for enrichment of uranyl ion from aqueous and sea water solutions. Say et al. [86] have synthesized uranyl IIP microbeads by polymerizing uranyl-methacryloylamido glutamic acid (MAGA) in presence of EGDMA. These authors report very high adsorption capacity of 181 mg/g of P(MAGA-UO_2^{2+}, EGDMA). Polymer-imprinted ionically permeable membranes were prepared by Akimoro et al. [87] for uranyl ion using uranylvinyl benzoate $[UO_2(VBA)_2]$ as the ion-imprinting complex.

The invention by John et al. [88] relates to the detection and extraction of uranyl ions by polymer imprinting, wherein complexable functionality has the formula CTCOOH, where T is a hydrogen or any halogen (preferably chlorine) methyl and halogen substituted forms thereof or CCOOH or PhCOOH. Dai et al. [89] prepared mesoporous sorbent materials by ion imprinting technique for separation of uranyl ions using bifunctional ligands such as amines, sulphonic acids and phosphonic acids. The inventions by John et al. [88] and Dai et al. [89] describes recovery of uranyl ion from aqueous solutions only and not in presence of other metal ions.

Tailored IIP materials are currently being increasingly explored for solid phase extraction compared to catalytic, membrane separations and in developing sensors. Recently, we have reviewed the preparation of tailored materials for the preconcentration of metal ions by IIP-SPE [90]. Gladis and Rao [91] patented a process consisting of synthesis of SPE materials by polymer imprinting suitable for recovery of uranyl ions from dilute aqueous and synthetic sea water solutions and also in presence of a host of +2, +3 and +4 metal ions. Same authors [92] also described a novel synthesis of IIP particles by employing UO_2^{2+}–DCQ–VP ternary complex in the presence of styrene, DVB and AIBN. These polymer par-

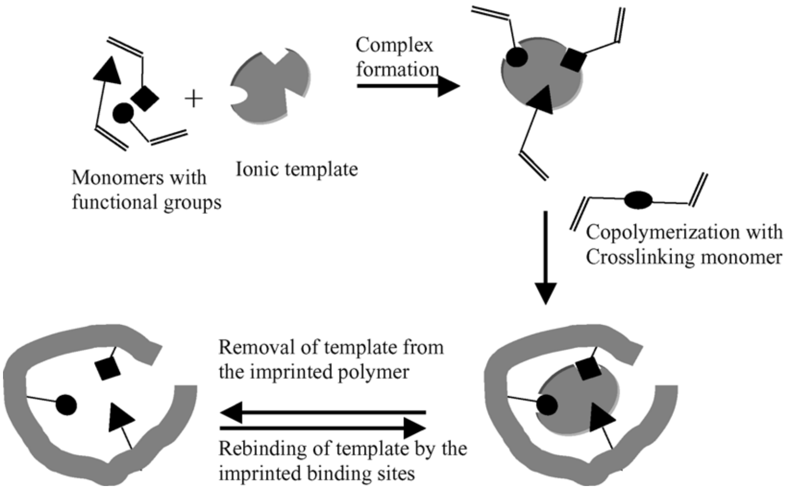


Fig. 4. Schematic representation of ion imprinted polymer-solid phase extraction process.

ticles were found to enrich uranyl ion from dilute aqueous and sea water solutions containing other metal ions. Furthermore, in addition to testing the accuracy of developed enrichment procedure by analyzing standard marine sediment reference material, MESS-3 supplied by National Research Council, Canada, the procedure has been used to analyze soil and sediment samples in combination with spectrophotometry. The results obtained by IIP-SPE spectrophotometry method agree well with ICP-MS values. Furthermore, the strength of interactions are greatly influenced by the properties of porogen employed in polymer synthesis, in particular, on polarity. Hence, a detailed study was conducted by changing porogens of low to medium and high polarity during enrichment of uranium and its separation from thorium [93]. Furthermore, the influence of binary/ternary complex of uranyl imprint ion on the enrichment of uranium was investigated and found that the quantitative recovery of uranium was possible only with ternary complex [94].

A comparison of retention/sorption capacities for uranium(VI) and thorium(IV) with various chelate functionalized sorbents employed since 1990 are summarized in Tables 1 and 2, respectively. As seen from these tables, in general, Amberlite XAD-16 and Merrifield chloromethylated resins gave higher retention capacities for uranium(VI) and thorium(IV). Again, among the chelates, calix[4]arenes offer higher retention capacities and probably will be dealt much more vigorously in coming years. Furthermore, ion imprinted polymers in general offer higher retention capacities for uranium(VI). The high retention capacity value reported by Say et al. [86] for uranium with glutamic acid chelate is obtained on equilibrating SPE sorbent with 2500 mg/l of initial uranium(VI) concentration. Hence, there is little ambiguity in the literature regarding the procedure adopted for calculating retention/sorption capacity as it is very much dependent on initial metal ion concentration used in a particular study. Hence, while reporting retention/sorption capacity, one has to mention the initial metal ion concentration used so as to reasonably adjudge where newly developed chelate functionalized SPE stand.

2.2. *On-line preconcentration methods*

2.2.1. *Uranium*

A flow in valve ion exchange [95] or solid phase extraction [96] coupled to spectrophotometry was developed using Duolite C-225 (H^+) and Teva Spec (M) resins. These procedures find application for the analysis of geological samples for uranium. A flow injection system incorporating a microcolumn of activated alumina was combined with ICP-MS for on-line trace enrichment and determination of uranium in surface waters and sea water [97]. A preconcentration factor of only 40 was reported by these authors. A new iminodiacetate chelating reagent, immobilized onto a controlled pore glass support was evaluated as a substrate for on-line matrix separation for ICP-MS [98]. The developed procedure was validated by accurate analysis of CRM’s SLEW-I (Estuarine

Table 1
Comparison of retention/sorption capacities of various SPEs prepared during offline enrichment of uranium(VI)

S. no.	Sorbent	Chelating agent	Impregnated (I)/derivatised (D)	Retention/sorption capacity (mg/g of SPE)	Reference
1	Amberlite XAD-4	Quinoline-8-ol	D	2.74	[44]
2	Amberlite XAD-4	Succinic acid	D	12.30	[45]
3	Amberlite XAD-4	Octacarboxymethyl-1-methylcalix[4] resorcinarene		64.26	[71]
4	Amberlite XAD-4	Bicine	D	90.44	[74]
5	Amberlite XAD-4	*o*-Vanillin semicarbazone	D	2.89	[73]
6	Amberlite XAD-16	*N*,*N*-Dibutyl-*N*′-benzoyl thiourea	I	214.2	[46]
7	Amberlite XAD-16	[1,2-Dihydroxy arsinoyl phenylamino)methyl] phosphonic acid	D	59.5	[75]
8	Amberlite XAD-2	Pyrogallol	D	6.71	[47]
9	Merrifield chloromethylated resin	Thenoyl trifluoroacetone	D	33.32	[76]
10	Merrifield chloromethylated resin	Di-bis(2-ethylhexyl) malonamide	D	62.5	[77]
11	Merrifield peptide resin	11,23-Disemicarbazono-26,28-*n*-dipropoxy-25,27-dihydroxy calix[4]arene		3.09	[78]
12	Poly(styrene β-hydroxylamine)	37,38,39,40,41,42-Hexahydroxy-1,8,13,19,25,31-hexacarboxy calix[6]arene	D	97.82	[80]
13	Naphthalene	5,7-Dichloroquinoline-8-ol	I	1.88	[57]
14	Benzophenone	Dicyclohexano-18-crown-6	I	2.42	[58]
15	Naphthalene/benzophenone	1-(2-Pyridylazo)-2-naphthol	I	2.34	[59]
16	Octadecyl silica membrane discs	Tri-*n*-octyl-phosphine oxide	I	4.03	[63]
17	Silica gel	Catechol	D	15.94	[65]
18	Activated carbon	Diarylazobisphenol	D	18.35	[66]
19	IIP-SPE	Glutamic acid	I	181.10	[86]
20	IIP-SPE	5,7-Dichloroquinoline-8-ol	I	30.10	[92]

Table 2
Comparison of retention/sorption capacities of various SPEs prepared during offline enrichment of thorium(IV)

S. no.	Sorbent	Chelating agent	Impregnated (I)/derivatised (D)	Retention/sorption capacity (mg/g of SPE)	Reference
1	Amberlite XAD-4	Malonic acid	D	19.28	[69]
2	Amberlite XAD-4	Octacarboxymethyl-*c*-methyl calix[4]resorcinarene	D	62.64	[71]
3	Amberlite XAD-4	*o*-Vaniline semicarbazone	D	3.23	[73]
4	Amberlite XAD-4	Bicine	D	58.00	[74]
5	Amberlite XAD-16	[1,2-Dihydroxyarsinoyl phenyl amino methyl] phosphonic acid	I	109.04	[75]
6	Merrifield chloromethylated resin	Thenoyl trifluoroacetone	D	27.84	[76]
7	Merrifield chloromethylated resin	Di-bis(1,2-ethylhexyl) malonomide	D	38.2	[77]
8	Merrifield peptide resin	11,23-Disemicarbazeno-26,28-*n*-dipropoxy-25,27-dihydroxy calix[4]arene	D	2.78	[78]
9	Merrifield chloromethylated resin	Quinoline-8-ol	D	120.30	[79]
10	Poly(styrene-β-hydroxylamine)	37,38,39,40,41,42-Hexahydroxy,1,8,13,19,25,31-hexacarboxy calix[6]arene	D	108.34	[59]
11	Benzophenone	5,7-Dichloroquinoline-8-ol	I	1.10	[67]
12	Cellulose	Quinoline-8-ol	D	20.00	[68]

water) and CASS-2 (coastal sea water) supplied by National Research Council of Canada. FI manifold packed with commercially available TRU (TM) resin was used for on-line preconcentration and subsequent determination by ICP-MS [99]. This procedure offers a very good detection limit of 0.30 ng/l for ^{238}U. A flow injection method has been developed for the determination of uranium in natural waters and high purity aluminium by use of on-line preconcentration on a U/TEVA (TM) column and ICP-MS detection [100]. The sample solution prepared as a nitric acid solution in 3 mol/l was passed through the above column and was eluted with 0.1 mol/l nitric acid. The effluent was directly introduced into the nebulizer of the ICP-MS and the amount of ^{238}U was measured. An electrochemical preconcentration based on accumulation of uranium at an anodized glassy carbon electrode at −0.15 V and stripped at +1.15 V for on-line matrix elimination with ICP-MS detection [101]. A very good detection of 0.12 ng/l was possible with a 10 min accumulation time. Hirata et al. [102] developed an on-line column preconcentration method of trace metals using metal alkoxide glass immobilized quinoline-8-ol and the determination by ICP-MS. Metal alkoxide glass immobilized quinoline-8-ol (MAF-8HQ) was synthesized and packed in a home made column which was used to preconcentrate and separate several trace metals including uranium from sea water (Fig. 5). By using 120 s of sample loading times, 40–66-fold enrichment factors were obtained which are rather low. The method was validated by the analysis of trace metals in the two certified reference materials (CRMs) of sea water CASS-4 and NASS-5.

2.2.2. Uranium and thorium

Hao et al. [103] developed an on-line matrix elimination reversed phase chromatography for the determination of thorium(IV) and uranium(VI) present in phosphate rocks. Again, among the ligands investigated, mandelic acid gave the highest recoveries and maximum retention (high breakthrough volume) of the analytes was achieved [104]. The

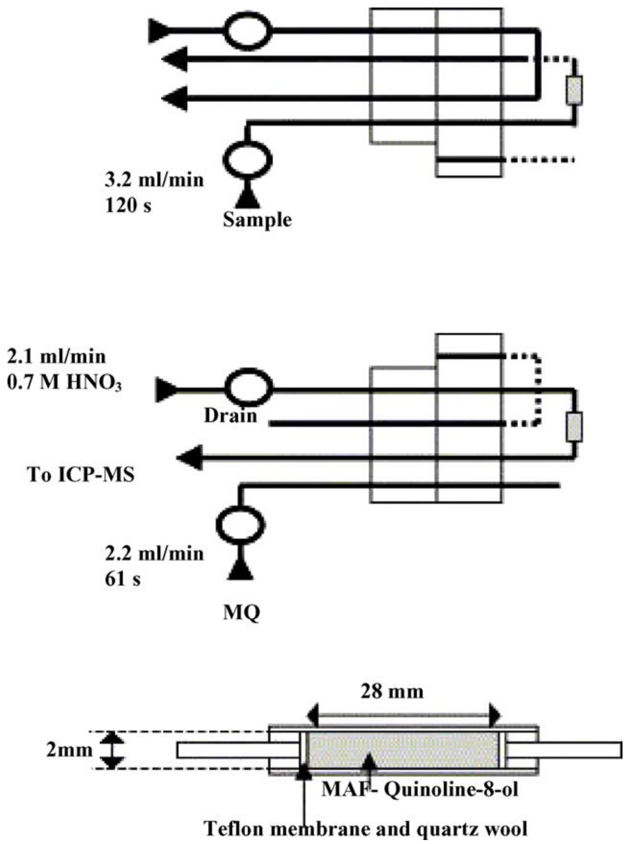


Fig. 5. Schematic diagrams of on-line column preconcentrating and eluting procedures.

higher formation constants of the solutes with α-hydroxy isobutyric acid (HIBA) resulted in a quantitative ligand-exchange reaction so that the solutes were separated as their HIBA complexes. The procedure has been applied only for the study of recoveries of μg/l levels of thorium(IV) and uranium(VI) spiked in sea water. A flow injection extraction chromatography coupled to on-line ICP-MS has been developed and validated for simultaneous determination of uranium and thorium in human body fluids [105]. The detection limits achieved are quite impressive, i.e. 0.06, 0.0014 and 0.05 ng/l for ^{232}Th, ^{235}U and ^{238}U, respectively. The technique was employed for simultaneous thorium and uranium analyses in human urine and blood samples after microwave digestion. Pavon et al. [106] preconcentrated thorium and uranium in a flow injection mode via on-line ion-exchange onto Dowex 50-X8 and determined by spectrophotometry. Again, the method is tested with different spiked water samples only at 0.5–100 μg/l concentration levels. An on-line solid phase extraction linked to ICP-MS has been developed to over come the problems of a high sample matrix concentration interfering with the determination of low levels of uranium and thorium using a TRU. Spec actinide specific extraction resin from aqueous and synthetic sea water samples [107]. There is an improvement over conventional ion exchange and chelating resins which give low recoveries in the presence of dissolved organic carbon. Truscott et al. [108] developed an on-line SPE method for the determination of ^{238}U and ^{232}Th biological and environmental certified reference materials using ICP-MS. A very good absolute detection limits were reported using ETV-ICPMS for ^{238}U and ^{232}Th, respectively. Same authors [109] have determined femtogram per g levels of actinide elements in environmental samples by solid phase extraction using a column containing TRU-spec (TM) resin coupled with sector field ICP-MS.

3. Conclusions

Although several preconcentration techniques are available for enrichment of uranium(VI) and thorium(IV), the two most common traditional methods are liquid–liquid extraction (LLE) and ion exchange. LLE offers the advantages of fast kinetics, high capacities and higher selectivity [110]. The finite aqueous solubility of the extractants, solvents and modifiers is, however, a significant disadvantage [10]. This not only adds to the cost of the procedure through loss of reagents, but contaminates the water with potentially toxic organics. There is also loss of organics through evaporation and entrainment [10]. In addition, solvent exchange is not recommended for dilute metal ion solutions due to the large volumes of extractants needed [111].

Ion-exchange resins operate on the same principles as solvent extraction. The resins contain functional groups capable of complexing or ion exchanging with metal ions. Because the functional group interacting with the metal ion is covalently bound to an insoluble polymer, there is no loss of extractant into the aqueous phase. The resins can be regenerated and reused for continuous purposes [112]. A disadvantage of ion-exchange resins can be slower kinetics compared to solvent extraction [113]. The increase of porosity of the resin or decreasing the bead size or crosslinking can help improve the kinetics by increasing the accessibility of the polymer supported ligands to the metal ions. However, the main drawback of ion exchange resins is the saturation of ion-exchange resins with innocuous ions, which are often present in greater concentrations, before the target metal ions can be removed to a significant extent.

Selectivity of ion exchange resins can be improved by preparing chelate functionalized neutral polymeric resins, which can selectively enrich target metal ion, i.e. by using various chelate functionalized resins as sorbents in solid phase extraction (SPE) [114]. The lack of hydrophilicity can be over come by utilizing more polar ligands or by incorporating both ion exchange and coordinating/chelating ligands into the polymer [115]. A variety of ligands, viz. amine, amidoxime, dithizone, carboxylic acid and hydroxamic acid, crown ether calixarene and phenol or phosphorus-based ligands have been employed to functionalize various polymeric supports. Thus, SPE is the most preferred futuristic preconcentration technique, not only for enriching uranium and thorium but also for other inorganics in general, in view of the several advantages, viz. higher enrichment factors, absence of emulsion, minimal costs due to low consumption of reagents, flexibility and more importantly environmental friendliness.

Ion imprinted polymers for solid phase extraction (IIP-SPE) is a recent innovation in SPE, which offers much higher selectivity and retention capacity (∼30–180 mg/g of polymer) while retaining the above mentioned virtues of SPE. Several tailored IIP-SPE materials were synthesized based on binary or ternary complex of the imprint ion, i.e. dioxouranium.

In view of the ultratrace amounts of uranium(VI) and thorium(IV) in geological, environmental and biological samples, SPE preconcentration is most often suited not only for the recovery of metal ions, but also for their subsequent quantification by suitable analytical techniques. Another constraint for biological samples in particular is the availability of the sample itself. In the latter case, on-line SPE techniques are most sought after for enrichment of uranium(VI) and thorium(IV). Furthermore, the on-line preconcentration techniques are always preferred in view of the number of samples that can be analysed per hour (∼30 with 1 min loading time). Again, the accuracy and good precision of the analytical procedures are far superior to offline techniques, as it is computer controlled.

Future trend in the field of preconcentration of uranium(VI) and thorium(IV) in particular and inorganics in general lies with increasing use of different chemically immobilized solid phase extractants prepared via new synthetic strategies and their utilization in on-line mode prior to determination by various analytical techniques.

Acknowledgements

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