CHAPTER I
INTRODUCTION

Thorium was discovered by Berzelius in 1828 in the mineral thorite and derive its name from Thor, Scandinavian God of war. The importance of thorium may be related to that, thorium can replace uranium. ^{232}Th can be transmuted to the fissionable U^{233} **(Perianez and Martinez, 1997).**

1.1. Chemistry of thorium:

Thorium metal is a silvery white when fresh, but oxidation takes place in air to give a dark grey or black tarnish, soft metal can be hammered, rolled. Its melting point is about 1,800º C and boiling point is 4,500º C. It is soluble in hydrochloric, sulfuric acids and aqua regia but it is insoluble in water.

Thorium has atomic number 90, and atomic weight of 232. Thorium belongs to group IV of the periodic table and like uranium it belongs also to the actinide series, where it is one of two sources of fissionable materials.

The principal valency of thorium is 4 and its compounds resemble those of tetravalent cerium and to some extent, also those of other tetravalent elements such as titanium, zirconium and hafnium. The element is fairly basic and forms many complex ions in solution.

Its average in the earth ´s crust amounts to 12ppm and is therefore considered a relatively abundant element where it approaches in content that of Pb or Mo.

Thorium element is indeed found in a large number of minerals in association with uranium and rare earth elements. However, minerals having a high content of thorium like thorianite and thorite are actually

rare. The mineral monazite, which is the phosphate of cerium group of rare earth elements, is considered the principal source of thorium.

This mineral commonly occurs in beach sand deposits admixed with several other minerals e.g. magnetite, ilmenite, rutil and zircon. The thorium content in monazite can attain up to 30% and Egyptian monazite assays 5.8% ThO_2.

It is also found in small amounts in most rocks and soils, where it is about three times more abundant than uranium. Soil commonly contains an average of around 6 parts per million (ppm) of thorium.

1.2. Occurrence of thorium and its world deposits:

Thorium distributed in small amount in most rocks and soils. The average abundance in the earth's crust is 10 to 20 ppm. It occurs in several minerals, the most common ones are monazite sand, thorianite, thorite and thoganite found in Brazil, India, Russia, Scandinavia, South Africa, Turkey, Egypt and U.S.A. (**Semenov, 2001).**

The main deposits of monazite are located in India, Brazil, Australia, Malagasy, Ceylon, South Africa, Canada and U.S.A. From all these the most important is that of India, with huge deposits of ore with a concentration that averages about 9% of thorium oxide.

1.2.1. Distribution

Distribution of thorium resources is poor because of the relatively low-key exploration efforts arising out of insignificant demand. Under the prevailing estimate, Australia and India have particularly large reserves of thorium (Table 1), India is believed to have 25% of the world's thorium reserves. The prevailing estimate of the economically available thorium reserves comes from the US Geological Survey, Mineral Commodity Summaries (1997-2006) (Fig. 1).

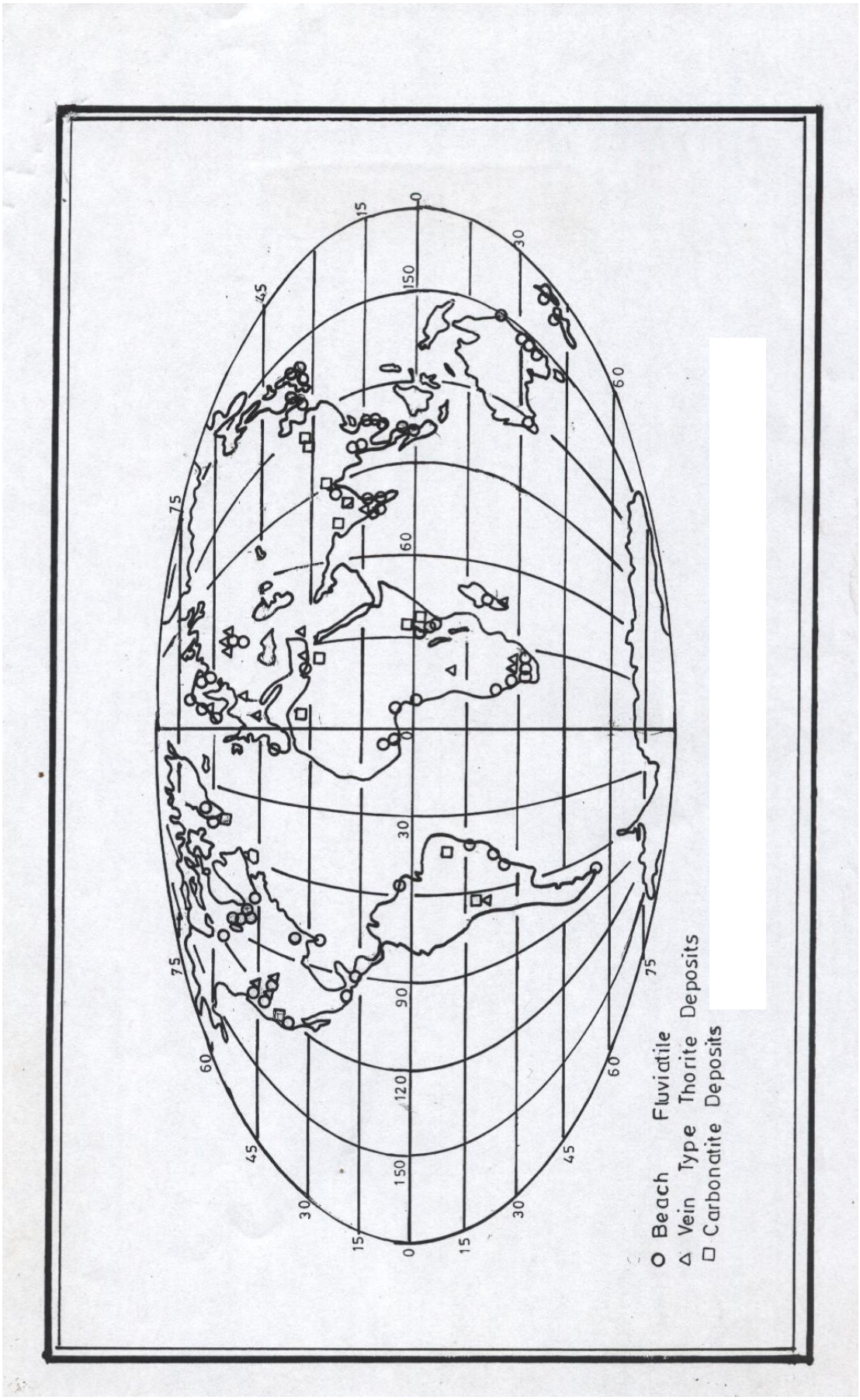


Fig. (1): Thorium deposits in the world

Table (1): Distribution of thorium and uranium quantities in the countries.

Country	Th reserves (tones)	Th reserve base (tones)
Australia	300,000	340,000
India	290,000	300,000
Norway	170,000	180,000
United States	160,000	300,000
Canada	100,000	100,000
South Africa	35,000	39,000
Brazil	16,000	18,000
Malaysia	4,500	4,500
Other Countries	95,000	100,000
World Total	1,200,000	1,400,000

The average abundance of uranium in the earth's crust is between 2 and 4 parts per million. However, the different rock types can contain much higher concentrations, to the point of forming an economic deposit. The thorium uranium ratio in the earth's crust is between three and four. Table (2), shows the average content of uranium and thorium in common rocks.

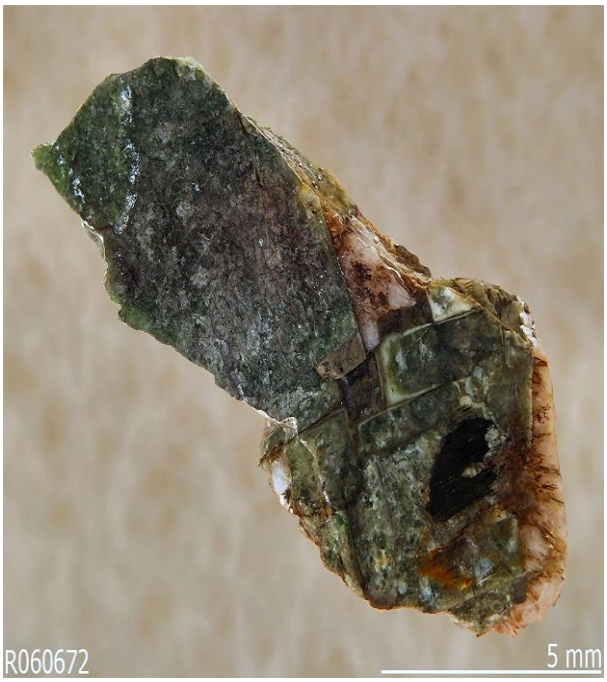
Table (2): Average uranium and thorium content in common rocks.

Rock type	Uranium (ppm)	Thorium (ppm)
Granite, rhyolite	3.0-4.7	12
Diorite, andesite	1.8-3.5	5
Gabbro, basalt	0.5-1.5	3
Syenite, alkali granites	up to 100	up to100
Limestone, dolomite	1.3-2.5	1
Sandstone, conglomerate	0.5-2.5	5
Shale, argillite	1.2-4.1	12
Phosphorites	up to 300	up to12
Quartzite	1.5	5
Schists	2	6.0-10.0
Amphibolites	0.3	2
Gneisses	0.6-3.8	10
Pegmatites	3.2-6.9	up to 200

The chemical methods for thorium determination are generally complex. The analytical chemistry of thorium is indeed complicated using its single valance state. The lack of selective and sensitive reagents, by the refractory nature of its ores and its association analytical problems **(Grimaldi et al., 1955).**

Thorium was widely distributed in small amounts over the earth's surface, the average thorium in the earth crust is ranging between 10 to 20 ppm. Many minerals contain thorium element in its constituent such as Kivuite, arapovite, ciprianiite and thorianite (Fig. 2)

Kivuite
$(Th,Ca,Pb)H_2(UO_2)_4(PO_4)_2(OH)8•7(H_2O)$



Arapovite
$((U,Th)(Ca,Na)_2(K1\text{-}x[\ ]x)Si_8O_20•H_2O,\ x=0.5)$

Ciprianiite
$Ca_4[(Th,U)(REE)]_2(Al,[])_2[Si_4B_4O_{22}](OH,F)_2$

Thorianite
(ThO_2)

Fig. (2): Some types of thorium minerals.

1.3. Importance of thorium:

Thorium and its compounds are very important which have relatively few uses, such as:

- Source of nuclear energy.
- Used to coat tungsten wire used in electronic equipment because it has a low work-function and high electron emission.
- Alloying element for magnesium.
- Oxide is used in electric lamps, high temperature laboratory crucibles, Glasses containing thorium oxide have a high refractive index and low dispersion, high quality camera lenses, scientific instruments and were used as a catalyst for the conversion of ammonia to nitric acid, petroleum cracking and sulphuric acid production.

1.4. Solvent extraction technique:

Solvent extraction is one of the most widely used techniques for preconcentration and separation of elements because of its simplicity, speed and wide scope. The technique has become more useful in recent years due to the development of several selective chelating agents, with proper choice of extracting agents. One can achieve group separation or selective separation of elements with high efficiency.

1.4.1. Role of solvent extraction in determination of thorium

The role of organic solvent extraction in thorium determination is related to:

1- Increased the accuracy and precision of determination by elimination the effect of interferences of the other elements.

2- Improved the concentration of the desired element.

3- Separation of thorium from the components, which may be analyzed by analytical methods, then determined using spectrophotometric techniques.

Solvent extraction plays a vital role in the production and processing of thorium for using as a fuel in the front-end of the nuclear fuel cycle. Solvent extraction separation process is based on the differences in the solubility of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is an aqueous solution and the second phase is an organic solvent immiscible with water **(Marczenko, 1986).**

Solvent extraction process involves the following two operations:

1- Extraction process: The metal value in the aqueous phase is extracted by the agitation with an immiscible organic solvent, by shaking the aqueous solution with the organic solvent (extractant) in a separating funnel, the element is extracted into the organic phase. After allowing the aqueous and organic phases to separate in the funnel, the organic extractant is removed from contact with the aqueous layer where the aqueous phase is discarded or recycled and the loaded organic phase is saved.

2- Stripping process: It is also called re-extraction, back extraction and scrubbing process. The recovery of the metal values from the loaded organic phase is done by agitation with a suitable volume of the solution. The stripped solvent is then recycled, in this way a concentrated solution containing the metal values in a relatively pure form is obtained. In the stripping process, two purposes are achieved:

1- Recovery of the metal values from the organic phase.

2- Regeneration of the extractant for recycles.

3- Selectively, when the organic phase is loaded with more than one metal ion, different concentrations of acids can strip the concerned metal ion.

1.5. Literatures and previous work:

Several investigations have been reported in literature to study the extractability of thorium element as well as the ways of separation using different organic extractants and techniques.

Ryan, et al. (1947), developed a method for the quantitative determination of thorium in presence of uranium. They found that thorium can be quantitatively precipitated by ferron in the pH ranges from 2 to 3.5, and it can be separated from twice its amount of uranium by a single precipitation and sulfate ion interferes in the precipitation of the complexes.

Madison and Guyon (1954), established a sensitive spectrophotometer technique for the determination of thorium, this method was based upon the reduction product of a presumed thorium molybdo-phosphoric acid hetero-poly complex. The optimum conditions had taken in place at the formation of the blue hue, then thorium could be cleanly separate using a solvent extraction procedure. This system was applied for the determination of thorium in the monazite sand.

Tilton, et al. (1954), studied the determination of thorium using isotope dilution Mass Spectrometer. They found that the method of isotope dilution permits accurate determinations of micrograms and sub-microgram quantities of thorium.

Adler and Axelrod (1955), studied the fluorescent x-ray spectrographic method for determination of thoria in rock samples using thallium as an internal standard. They found that the lowest limit of detection of thoria

is 0.294, where the particle size effect is minimized by grinding the sample components with a mixture of silicon carbide, aluminum and briquette.

Carron, et al. (1955), studied the determination of thorium and rare earth elements in cerium earth minerals and ores by precipitation using ammonium sebacate solution and oxalic acid. They found that thorium is separated as the sebacate at pH 2.5, while rare earths are precipitated with ammonium sebacate at pH 9. Maximum errors for combined weights of thorium and rare earth oxides on synthetic mixtures are 0.6 mg and maximum error for separated thoria is 0.5mg.

Moeller and Tecotzky (1955), found that naphthazarin (3,8-dihydroxy-1,4-naphthoquinone) gives with thorium ion purple solutions containing a complex cation in which the ratio of thorium in the complex of Th and naphthazarin was 2:1. The color is detectable at concentrations as low as 0.001 mg. of thorium per milliliter. The complex was optically stable for at least several hours, and its solutions adhere closely to Beer's law. The colored complex formed between naphthazarin and thorium ion provided a sensitive method for the detection of the latter and determination of thorium at concentration of about 10^{-5} to 10^{-6} mole per liter. The absorption spectrum of the thorium-naphthazarin system has absorption peaks at 5700 and 6185 A$\mathring{}$ with an inflection at 5375 A$\mathring{}$.

Sarma and Rao (1955), developed a colorimetric procedure for the estimation of thorium in presence of rare earths based on Alizarin-S, which gives a red color with thorium. The absorption characteristics of Alizarin-S and its-thorium complex have been studied in their dependence on the pH values. The thorium- Alizarin-S complex was

studied by different optical methods to correspond Th- Alizarin-S method and the absorption spectrum was recorded at 520 mμ.

Banerjee (1957), develop a direct colorimetric method for thorium determination, in general thorium is colorless but its derivative is colored. This method depended on the stability of the thorium-SPADNS complex in the acid medium forming a blue violet color. The developed method can be used for micro concentration of thorium (0.04γ in 25ml) with pH adjustment, and addition of SPANDS then measurement at absorption spectrum 570 nm.

Datta (1958), studied a direct spectrophotometic method using azodye prepared from diazotized amino salicylic acid and di-sodium salt of chromo tropic acid which produces a reddish violet soluble thorium complex. The color reaction exhibits an absorbance maximum at a wavelength of 580 mμ and conforms to Beer's law. This method was developed for the determination of thorium in dilute solutions, but iron, zirconium, cerium(lV), gold, phosphates, and fluorides were interfered. The interference of iron(III) could be removed by adding ascorbic acid. Thorium had also been extracted and estimated in monazite and black sands with this dye.

Lott et al. (1960), studied a highly selective spectrophotometeric method for determination of thorium based on the colored complex formed with thorium and Eriochrome Black T. The reaction showed a sensitivity of 0.004 μg of thorium per square cm. per 0.001 absorption unit at 700 mμ. The procedure was free from the interference of most cations, particularly the rare earths. Masking agents prevent foreign ions from reacting with the dye. Thorium can be determined in presence of the alkali metals,

alkaline earths, most transition metals, rare earths, and heavy metals like bismuth. The Absorption spectrum was recorded at 620 mμ.

Zingaro and White (1960), used the tri-n-octylphosphine oxide (TOPO**)** in cylcohexane to extract thorium from its nitrate solution. They found the complex appears as $Th(NO_3)_4 \cdot 3TOPO$.

Boitei and Gerace (1961), studied the reaction between thorium ion and β-hydronaphthazarin disulphonate (dipotassium 1, 2, 3, 4-tetrahydro-5, 8-dihydroxyl, 4-diketonaphthalene-2, 6-disulphonic acid) spectrophoto--metrically and found that two water soluble complexes are formed (green and blue complexes). The green complex has a maximum absorption at wavelength 460 mμ while the blue complex has a maximum absorption at wavelength ranges between 570 and 610 mμ.

Korkisch and Janauer (1961), described a sensitive and accurate method for the spectrophotometric determination of microgram amounts of thorium using the Solo-chromate Fast Red. This dyestuff reacts with thorium in hydrochloric acid-methanol solutions to form an orange complex, which shows a maximum absorption at 490 mμ. Application of this method was used in the determination of thorium in minerals and rocks.

Vdovenko et al. (1961), showed that when trace concentrations of thorium are extracted from H_2SO_4 solutions by primary octyl amine, the extracted species is $2(RNH_3)_2SO_4.Th(SO_4)_2$. However, when macro amounts (0.0086-0.029M) were extracted by the same solvent, the extracted compound was $(RNH_3)_2SO_4.Th(SO_4)_2$.

Thus, when micro amount of thorium are extracted (trace conc.), the extracted species may be different from those when macro amounts are extracted.

Prasad and Dey (1962), studied the precipitation of thorium hydroxide by pH adjustment between different concentrations of thorium chloride and sodium hydroxide. It was observed that the complete precipitation in every case of pH change occurs near pH 7. The results also showed that the concentrations of thorium have a little effect on pH of complete precipitation.

Shirvington and Florence (1962), studied the separation of uranium and thorium from diverse elements by extraction with tributyl phosphate (T.B.P.) in kerosene-type diluents. This method was widespread for use in nuclear fuel processing and in analytical chemistry.

Cerrai and Ghersini (1966), studied a simple and direct colorimetric determination of thorium extracted from chloride solution with di-(2-ethyl hexyl) orthophosphoric acid. The color is developed in the organic phase by adding arsenazo III and then isopropanol forming deep green complex, which shows a maximum absorbance at 660 nm and Beer's law was obeyed within limited ranges. They found that the serious interferences occur from U (VI), Se (IV), Ti(IV), Y, the rare earth elements and common anions. Only large amounts of sulphate were slightly interfered.

Saleh (1969), studied the effect of diluents on the extraction of thorium nitrate with tributyl phosphate diluted with various diluents. The result proved that the best extraction condition was performed by TBP diluted

with a commercial kerosene than other diluents such as toluene, rising sun kerosene, benzene, n-hexane, *o*-xylene, carbon tetrachloride, diethyl ether and di-isopropyl ether.

Ritcey and Lucas (1971), separated uranium and thorium from an aqueous acid solution using a water-immiscible organic solution of high molecular weight primary or secondary amine. Uranium and thorium were then easily separated from the loaded amine solution either by selective stripping or by co-stripping with selective extraction.

Onishi and Sekine (1972), described a method for the spectrophotometric determination of microgram amounts of zirconium, uranium, thorium and rare earths with Arsenazo III. Thorium was next extracted into *o*-xylene solution of thenoylfluoroacetone (TTA) at pH 1.5 and the absorption spectrum was recorded at the wavelength 665nm.

James (1977), studied the determination of uranium and thorium at level ranges between 10 and 100ppm in different geological sedimentary and igneous rock types samples using x-ray emission spectrometry and wavelength-dispersive x-ray emission spectrometry. He observed that the difference value between fluorimetric method and x-ray method for different samples containing uranium and thorium from 1.0 to 20ppm was 0.8ppm.

Alin et al. **(1987),** studied the solvent extraction of thorium from mixed organic aqueous nitric acid media by the tri-n-octylphosphine oxide (TOPO). The extraction equilibria of Th in TOPO was (TOPO)–HNO_3–H_2O systems had been investigated in both the absence and presence of water-miscible alcohols and acetone.

Hirose (1988), determined thorium isotopes in seawater by means of adsorption of the Xylenol Orange /XO: H6A/ complex onto XAD-2 resin at pH = 3, sub- sequent purification using an anion-exchange resin, and finally with alpha-spectrometry. The dissolved ^{232}Th concentration in the Western North Pacific surface water was found to range from 0.8 to 1.2 ppm.

Pathak and Argekar (1992), studied the extraction chromatographic separation of thorium (IV) with tri-n-octylphosphine oxide (TOPO) and found that thorium was extracted from a mixture of nitric acid and $NaNO_3$ of 0.01M each at pH 2.2 on a column of silica gel coated with TOPO. Thorium was separated from alkalis, alkaline earths, chromium, iron, cobalt, nickel, zinc, cadmium, mercury, lead, trivalent rare earths, platinum group metals, chloride, phosphate and acetate in binary mixtures by selective extraction of thorium. Thorium was separated from cerium (IV), zirconium, uranium and molybdenum by a selective elution of thorium with 0.01M H_2SO_4.

Du et al. (1993), reported that thorium and lanthanides were extracted by a-sym-dibenxo-16-crown-5-oxy acetic acid. At pH 4.5, Th was quantitatively extracted by the crown ether carboxylic acids. The extraction did not require specific counter anions and is reversible with respect to pH. The complexation depended on the oxidation state and hydrolysis species of the actinide present in the aqueous phase. The extraction efficiency thus was a strong function of pH, which may be used as a basis for their separation. These types of ionizable crown ethers have potential selective chelating agents for solvent extraction of actinides and lanthanides.

Chen et al. (1994), developed a simple method to determine micromolar concentrations of Nd(III), Th(IV) and U(VI) in brine. The method involves the extractive separation of these cations from brine matrix species using chlorophosphonazo III as an extractant with 1-butanol as a solvent and the spectrophotometer determination of the concentration of the extracted species in the butanol phase. So chlorophosphonazo III and its formed complexes with Th(IV) can be extracted from the aqueous solution into the butanol phase at pH 2 with dilute HNO_3. In neutral aqueous solution, thorium did not extracted, while in high acidity the butanol dissolved in the aqueous phase. The Absorption spectrum was recorded at 670 nm.

Osthols (1994), studied the sorption of Th on amorphous colloidal particles of SiO_2 (Aerosil OX 200). The study was occurred in perchlorate media, which could be explained by the following surface complexation reactions:

$$SiOH \rightarrow SiO^- + H^+$$

$$2SiOH + Th^{4+} \longrightarrow (SiO)_2Th^{2+} + 2H^+$$

The sorption of Th on silica was only important in the pH range 3 - 6.

Gupta and Bertrand (1995), studied the technique for the direct determination of some trace and ultratrace elements in the geological materials. They indicated that the microwave digestion involving heating the sample with HF, aquaregia, H_3BO_3 and EDTA in a Teflon pressure vessel is effective for the rapid dissolution of various silicate rock and sediment reference samples.

Trace and ultratrace amounts of yttrium, thorium, uranium and lanthanides could be determined using inductively coupled plasma-mass spectrometry (ICP-MS) without any separation or pre-concentration of

these elements. The result was compared to United States Geological Survey (USGS) reference rock BCR-1 (basalt) and Canadian Certified Reference Materials Project (CCRMP) reference rocks SY-2 (syenite) and MRG-1 (gabbro) for accuracy and precision.

Khan et al. **(1995),** studied the extraction of thorium (IV) from nitric acid solutions by di-n-butyl sulfoxide (DBSO) in *o*-xylene. The extracted species was supposed to be $Th(NO_3)_4 \cdot 2DBSO$. The extraction was found to be almost independent of thorium concentration in the range between 4.3×10^{-4}–4.3×10^{-2}M and inversely dependent on the temperature factor.

Matthew et al. (1995), examined thorium sorbed per mole hematite sites, which indicating that the overall free energy of Th adsorption is independent of adsorption density. Modeling of Th sorption was conducted with the Triple Layer Model of Davis and Leckie; reactions considered included solution- phase hydroxy and carbonato complexes of thorium, and carbonate/hematite surface complexes. The entire Th sorption isotherm could be modeled with a single surface complex formation reaction

$$\text{--- Fe - OH} + \text{Th}^{4+} \leftrightarrow \text{---Fe-OTh}^{3+} + \text{H}^{+}$$

Sorption to changes in ionic strength suggested the formation of inner-sphere surface complexes. Thorium sorption onto hematite suspended in a simple electrolyte solution was rapid with equilibrium attained within a few minutes; sorption was irreversible on the time scale of the experiments (4 days).

Preston and Preez. **(1995),** studied the extraction of uranium (VI) and thorium (IV) from sodium nitrate media using N-alkyl amides in toluene

where N,N-dialkyl amides act as monomers, and also studied the effect of the steric effect on the extraction efficiency of thorium (IV) and uranium (VI). The increasing of the steric bulk of the alkyl groups R and R' was found to cause a marked decrease in the extraction of thorium (IV), with a much smaller effect on the extraction of uranium, thus considerably enhancing the separation between these metals.

The distribution ratios for both uranium (VI) and thorium (IV) depended on extractant concentration (N-alkyl and N,N-dialkyl amides) showing 2^{nd} and 3^{rd} order dependence.

Tarek et al. (1995), studied the determination of thorium using phenylfluorone (PF) and quercetin (Quer) in presence of cetylpyridinium bromide (CPB) and polyvinylpyrrolidone (PVP) as surfactant, respectively. They found that the 1:3:4 (Th-PF-CPB) ternary complex and the 1:3 (Th-Quer) binary complex in presence of PVP, are formed in the pH range 8.0-8.6 and 9.8-10.6, at 568 and 445 nm, respectively.

Alba et al. (1997), studied the method of multivariate calibration and Partial Least Squares Type 1 (PLS-1) which allows the simultaneous spectmphotometric determination of uranium (VI) and thorium (IV) ions with Arsenazo III as a chromogenic agent which extremely sensitive colorimetric reagent in strongly acidic medium. A separation step must be held first in case of presence of uranium (VI) and thorium (IV) in the mixture due to the formation of spectral overlap of the complexes formed.

The evaluated calibration model is satisfactorily applied to the determination of these ions in samples that resemble sulfuric acid leach solution obtained from a uranium ore. Absorption spectrum was recorded between 600 and 750 nm against a blank.

Fukuda and Sayama (1997), determined traces of uranium and thorium in barium (II), strontium (II) titanate ((Ba, Sr)TiO_3) ferroelectric materials by inductively coupled plasma mass spectrometry (ICP-MS). Two steps of separation technique involving leaching and anion-exchange were applied. The content of uranium and thorium was subsequently measured by ICP-MS. The method was successfully applied to the determination of uranium and thorium in three synthetic (Ba, Sr)TiO_3 samples spiked with the analytes at levels of 1, 5 and 10 ng g^{-1} and three (Ba, Sr)TiO_3 ferroelectric samples containing sub-ng g^{-1} levels of the analytes.

Hassan et al. (1997), investigated a sample of pure monazite prepared from beach sands from Abu-Khashaba area near Rosetta. Using gamma ray peaks at 311.8 and 277.6 keV of active measurements were used for the estimation of thorium and uranium concentration values. The values obtained were between 46 ± 2 and 59 ± 2 ppm for uranium, 687±34, and 729 ± 36 ppm for thorium.

Patti et al. (1997), described that the distribution of Th(IV) between aqueous sulfuric acid and organic phases of N-n-octylaniline in *o*-xylene where they found the extracted species to be $(RR'\text{-}NH_2^+)2Th(SO_4)_3$ where R= C_6H_5 and R'= C_8H_{17}.

Wang et al. (1997), stated that extaction ratios of U (VI) and Th (IV) using N,N,N',N'-tetrabutyl-succinylamide (TBSA) in n-dodecane from nitric media were 1:2:1 and 1:4:1,respectively, which were identified using IR spectra of saturated extract.

Wang et al. (1997), studied the color developments of the complexes concerning molybdothoric acid (Mo) with three basic dyes (BD),

rhodamine, butylrhodamine and nile blue in aqueous acidic solution in presence of poly(vinyl alcohol). The ratio of thorium in the complexe of Th:Mo:BD was 1:12:3. and the absorption maxima was in between 570 and 590 nm. Beer's law was obeyed in between 0.7 and 0.8 µg thorium per 25 ml. The proposed methods were applied to the determination of trace amounts of thorium in some geological samples.

Aslani et al. (1998), investigated the basic features of thorium adsorption from aqueous systems by silk fibroin. The study showed that this bio-polymer has a high efficiency for U(VI) adsorption. It is well-known that thorium, which is a tetravalent metal is a more reactive element than uranium. Thorium (IV) adsorption proved to be very rapid and dependent on pH, temperature, retention time, concentration of ion, amount of fibroin, volume of solution and volume-to-mass ratio.

Khalifa and Hafez, (1998), studied the ternary purple colored complex formed between Th^{4+}, bromocresol orange (BCO) and cetylpyridinium bromide (CPB) in acidic medium spectrophotometrically They found that the formation of 1:1:1, Th:BCO:CPB complex in aqueous solution is obtained at pH≈0.5 and room temperature. The color of the ternary complex was used for the determination of thorium (IV) in the range 0.02–2.6 µg ml^{-1} Th^{4+}, at 560 nm. Due to the high sensitivity of BCO, thorium was highly selected in presence of great number of transition metal ions, rare earths and different anions. With high accuracy using titration method by disodium ethylenediaminetetraacetate (Na_2EDTA) using BCO as an indicator at pH≈0.5. The end point was detected either visually or spectrophotometrically (λ=560 nm).

Out (1998), studied the effect of temperature on the extraction of thorium (IV) from nitric acid solutions into solutions of 2-ethylhexyl phenyl-phosphonic acid, micellar dinonyl naphthalene sulfonic acid extractants and mixture of the two extractants. He found that the temperature has a little influence on the extraction efficiency of thorium in temperature ranges from 15 to 75. While stoichiometry studies showed that temperature did not affect the extraction.

Yokoyama et al. (1998), investigated the separation of thorium and uranium from silicate rock samples using two commercial extraction chromatographic resins. The chemical separation technique to isolate Th and U from silicate rocks was established using two kinds of commercial extraction chromatographic resins. In the first column procedure with U/TEVA·spec resin, all elements except Th and U were eluted by 4 M HNO_3. Thorium was then separated using 5 M HCl, and U was finally isolated by successive addition of 0.1 M HNO_3. This technique could be used not only for the analysis of igneous rock samples, but also for the analysis of soils, marine sediments, carbonates, phosphates, seawater, groundwater and surface water.

Altar et al. **(1999),** used the Dowex as anion-exchange separation of thorium and uranium in Eskisehir-Beylikahir ore in Turkey ore which contains rare earth elements and thorium as bastnaesite mixed with barite, calcite and fluorite as well as small amounts of uranium. Successive anion-exchange and solvent extraction procedures were carried out to separate U and Th from each other and from the accompanying interfering elements.

Kato et al. (1999), established a sensitive analytical method for the determination of Th and U in activated concrete samples. The method combines an anion-exchange separation step with an ICP-MS determination technique. A few μg $mL^{-1}$of Al and Ca, Mn, La, Ce, Nd and Pb as well as μg mL^{-1} amounts of Li, Zr, Nb and Ba coexisting in the anion-exchange fraction of Th and U. No adverse interference effects were observed in real sample analyses.

The analytical precisions and the accuracies obtained by the analysis of GSJ rock standard samples were –18.1 to 0.4% for Th determination and –14.0 to –5.7% for U determination. This method uses the conventional absolute calibration curve.

Malkhede et al. (1999), showed that thorium (IV) was quantitatively extracted at pH 7.5 with 0.0001M of hexa acetato calix(6) arene in toluene and after stripping with 0.05M nitric acid, it was determined spectrophotometrically at 545 nm with thoron. Thorium (IV) was separated from commonly associated elements in fission products like uranium (VI), cesium (I), lead (II), strontium (II) and cerium (IV) in varying proportions. This method is simple, rapid, selective and applicable for the microgram concentrations of thorium (IV).

Tan et al. **(1999),** showed that N,N,N',N'-tetrahexylsuccinylamide (THSA) was used in the extraction of U(VI) and Th(IV) ions from nitric acid media into n-dodecane. As a function of nitric acid concentration the distribution ratio of extraction change at low acidity, it was found that THSA as a new extractant is superior in some aspects to TBP for extraction of U(VI) and Th(IV). They also found that the favored ratio for the extraction of uranium(VI) and thorium(IV) from nitric acid media

using THSA was 1:2:1 and 1:4:2, respectively which were identified using IR spectra.

Fujino et al. (2000), studied the determination of the actinide elements (uranium and thorium) in apatite minerals by inductively coupled plasma atomic emission spectrometry (ICP-AES) with solvent extraction separation. Diisobutyl ketone was selected as the extraction organic solvent. Uranium and thorium were quantitatively extracted over pH 2 and could be separated from the apatite composites. The organic phase was injected directly into the ICP-AES spectrometer. Uranium and thorium contents of Florida, USA, were found to be 103±2.2 and 8.84±0.19 ppm respectively. These results were quite comparable to those measured with ICP-mass spectrometry (ICP-MS).

Holmes and Pilvio (2000), showed that the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is suitable determining trace thorium element rather than radiometric techniques in both environmental and bulk samples. This method was applied for different materials, aiming to provide a suitable procedure for thorium measurement in different matrices.

Sahoo et al. (**2000),** studied the determination of the rare earth elements, thorium and uranium in forest, pasture, field and kitchen garden soils from a Russian territory and in certified reference materials (JLK-1, JSD-2 and BCR-1) using inductively coupled plasma mass spectrometer (ICP-MS). The obtained measurements contributed to the understanding of the background levels of these elements in an area contaminated due to Chernobyl accident.

Volk et al. (2000), extracted thorium and uranium in presence of hydrofluoric and nitric acids. Extraction of thorium was much reduced with the increase in the concentration of hydrofluoric acid, which could be regarded to the strong complex between thorium and fluoride ion in the aqueous phase.

Amin and Mohammed, (2001), found that Azodye plays an important role in thorium determination spectrophotometrically, this method depend on the reaction of thorium and rare earth elements with 5-(2',4'-dimethyl phenylazo)6-hydroxypyrimidine-2,4-dione (I) and 5-(4'-nitro-2',6'-dichlorophenylazo)6-hydroxypyrimidine-2,4-dione (II) in absence of cetylpyridinium chloride (CPC) to form red complexes.
Thorium has a sensitive reaction with reagent (I) and (II) which is indicated with the red color intensity.

Banerjee et al. (2001), studied the extraction of thorium by β-hydroxy naphthaldoxime in presence of neutral donors and the effects of neutral organophosphorous compounds on the extraction of thorium by β-hydroxy naphthaldoxime in *o*-xylene, and also studied various conditions in order to fix the optimum extraction parameters. They found that the variation of solvents follow the order in the following sequence *o*-Xylene > CCl_4 > $CHCl_3$> toluene > ether > MIBK in the extraction while the variation in the pH factor was in range from 1 to 7. They found that the maximum extraction takes place within pH range, 3 and 3.5.

Fukuma et al. (2001), established a method for the determination of thorium in uranium concentrate by a spectrophotometer with arsenazo (III). Preliminary solvent extraction procedures were used to eliminate the interfering species. Samples were dissolved in nitric, perchloric and

sulfuric acid and uranium was extracted from the solution using tri-octylamine. The aqueous layer was evaporated to dryness and the residue re-dissolved with hydrochloric acid. Thorium was extracted by tri-n-octyl phosphine oxide and stripped with oxalic acid. Hence, for an accurate determination of thorium, the U(VI):Th ratio was found to be kept below 6:1. Thus, an efficient separation of uranium from thorium was necessary for the analysis. The absorption spectrum had recorded at 665 nm.

Khan and Khan (2001), studied a rapid and sensitive spectrophotometric method for the determination of thorium using 0.04% arsenazo-III in a 2M perchloric acid solution. Absorbance had measured in 1 cm cell and the complex had a sensitive absorption peak at 654 nm. The bluish-green colour complex of thorium arsenazo-III was formed instantly in perchloric acid and remained stable for 45 minutes.

Martinez et al. (2001), studied a bivariate calibration method to simultaneous determination of U(VI) and Th(IV) ions as complexes with carminic acid by a visible absorption spectrophotometer. The results suggested that bivariate calibration method is a good alternative to the derivative spectrophotometer with the clear advantage that no mathematical treatment of spectral data is required.

Shrivastav et al. **(2001),** described a method for the pre-concentration and trace determination of thorium with crown hydroxamic acid (NHDTAHA).Thorium was extracted from the chloroform solution of NHDTAHA at pH 4 which gives a colorless extract. The extract is directly inserted in the plasma for ICP-AES measurements of thorium. The proposed method had been applied for the determination of thorium

in presence of several diverse ions in monazite sand, rare earth sand and in sea water.

Unsworth et al. (2001), improved a new method to determine U and Th with low levels in sea water sample, this method depends upon using an actinide-specific extraction resin (TRU-spec), followed by inductively coupled plasma mass spectrometry determination of thorium.

Carvalho et al. (2002), studied the pre-concentration of thorium from natural water and its determination directly by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). The first step consisted of thorium pre-concentration from slightly acid solutions on polyurethane foam (PUF) which showed a high reagent loading capacity. It was found that PUF impregnated with 2-etilhexylphosphonic acid (EHPA) with ratio of (1:1) can held up 50 % of thorium and the pre-concentration was a maximum at an acidity of 0.25 mol. l^{-1} hydrochloric solutions.

Torgov et al. (2002), developed a procedure for determining trace amounts of uranium and thorium isotopes in the bottom sediments of Lake Baikal. These studies involved a development of an quantitative extraction-back extraction procedure of uranium and thorium over a wide concentration range for the direct ICP MS analysis of the back extract and the method was used for the pre-concentration of uranium and thorium followed by the ICP MS determination of the mass concentrations of the analytes in bottom sediments. Trioctylphosphine oxide was used for the co extraction of uranium and thorium. The procedure was verified by analyzing a BIL-1 Lake Baikal bottom silt standard reference material using the developed procedure and independent methods.

Agrawal and Vora (2003), developed a method for the liquid–liquid extraction, separation, preconcentration and trace determination of thorium with N-phenylbenzo-18-crown-6-hydroxamic acid (PBCHA) Thorium was extracted from dichloromethane solution of PBCHA at pH 4.5 which gave a colorless extract.

Casartelli and Miekeley, (2003), studied the determination of thorium and light rare earth elements (LREEs) using inductively coupled plasma mass spectrometry (ICP-MS) coupled to size-exclusion chromatography (SEC) on-line with UV-detection, in soil and soil water samples from mineral deposit. It was found that SEC chromatograms of these waters showed the association of elements with different nominal high-molecular-mass ranges.

Santos et al. (2003), showed a detailed radiochemical procedure for alpha spectrometry measurements of thorium concentrations and the $^{230}Th/^{232}Th$. Th behavior during each step of the chemical processes was investigated using a ^{234}Th tracer, which is a gamma-ray emitter. The described chemical processing provides relatively high thorium yields which varied between 56% and 88%, in the analysis of GB-1 (granite) and BB-1 (basalt) Brazilian geological standards. Also, application of the established radiochemical method allowed the determination of both Th concentrations and activity ratios with high reproducibility.

Wei-fan et al. (2003), stated that the 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) is used as a solvent extraction of thorium traces from the hydrochloric acid media.

Guo et al. (2004), studied the liquid-liquid extraction of thorium (IV) and uranium (VI) using three ether-amide type. First compound is N,N,N',N',N'',N''-hexaethyl-2,2',2''- (nitrilo-trisethyleneoxy) tris (acet amide) (L1). Second compound is N,N,N',N',N'',N''-hexaisopropyl-2,2',2''-(nitrilotris ethylene oxy) tris (acetamide) (L2) and the third one isN,N,N',N',N'',N''-Hexaethyl-2,2′,2''-(nitrilotrisethyleneoxy-2-benzyloxy) tris (acetamide) (L3). They found that the extracting power of L1 and L2 for Th^{4+} is almost identical. The chain length of pervious compound has no effect on thorium extraction.

Li et al. (2004), studied the separation of thorium (IV) and extracting rare earths from sulfuric and phosphoric acid solutions by solvent extraction method. Bastnasite of Baotou (China) was roasted in a concentrated sulfuric acid at 250–300ºC and the calcined products were leached by water. Almost all rare earths were moved into the solution in a trivalent state along with some radioactive impurities. The purity of ThO_2 product recovered from the organic phase was above 99%.

Benkhedda et al. **(2005),** studied a sensitive and efficient flow-injection (FI) pre-concentration and matrix-separation technique coupled with the sector field ICP–mass spectrometry (SF-ICP–MS) for simultaneous determination of ultra-low levels of uranium (U) and thorium (Th) in human urine. The method was based on selective retention of U and Th from a urine matrix after microwave digestion on an extraction chromatographic TRU resin as an alternative to U/TEVA resin and their subsequent elution with ammonium oxalate. The accuracy of this method was checked by Spike-recovery measurements.

Bhattacharyya et al. (2005), investigated the sorption behavior of thorium and uranium on cation-exchange resins from nitric cation-exchange studies involved the sorption of UO_2^{2+} and Th^{4+} and their cationic complexes onto Dowex 50Wx8 and Dowex 50Wx4 resins (50–100mesh). The batch data yielded a separation factor *(*K d,Th /K d,U) value of >100 for the cation-exchanger, Dowex 50Wx4 at 1–2M HNO_3.

Separation of uranium from thorium was also carried out by a column method in nitric acid medium using the cation-exchangers, Dowex 50Wx4 as well as Dowex 50Wx8. While uranium elution was possible at 1M HNO_3 Th could be eluted only at higher concentration of nitric acid (>6M). The stripped solution emanating from a mixer settler employing di-2-ethyl hexyl isobutyramide as an extractant and feed solution similar to THOREX process comprising 350 mg/l U and 380 mg/l Th in 0.75M HNO_3 was loaded on the column and the decontamination factor value for U in the product was >1000.

Evans et al. (2005), developed a methodology for (U–Th)/He thermochronology on a variety of mineral species. With many laboratories initiating research in the area of (U-Th)/He thermochronology, they recognized that there may be interest in a review of analytical procedures for uranium and thorium determination in single crystals of apatite, zircon, rutile, and fluorite. Uranium and thorium were both determined by inductively coupled plasma mass-spectrometry using an isotope dilution method.

Maiorov et al. (2005), stated that tributyl phosphate is considered one of the most efficient solvent in the extraction of thorium from concentrated aqueous $CaCl_2$ solution.

Aydin and Soylak (2006), investigated a simple and effective method for the separation and pre-concentration of thorium (IV) and uranium (VI) by solid phase extraction on Duolite XAD761 adsorption resin. Thorium (IV) and uranium (VI) 9-phenyl-3-fluorone chelates are formed and adsorbed onto the Duolite XAD761.Thorium (IV) and uranium (VI) were quantitatively eluted with 2mol l^{-1} HCl and determined by inductively coupled plasma-mass spectrometry (ICP-MS). The interference of a large number of anions and cations has been studied and the optimized conditions developed was utilized for the trace determination of uranium and thorium. The developed solid phase extraction method was successively utilized for the determination of traces thorium (IV) and uranium (VI) in environmental samples by ICP-MS.

El-Dessouky and Borai (2006), investigated the extraction of thorium ion by solid phase impregnated resins containing bi-functional organic extractants. Macroporous methyl methacrylate polymeric resin (XAD-7) was incorporated both acidic organophosphorous extractant (cyanex-301) and one neutral extractant from the followings: dibenzo 18 crown 6 (DB18C6), 18 crown 6 (18C6) and 15 crown 5 (15C5). A relatively high capacity of the chelating resin towards tetravalent thorium was found for 15C5. The capacity of the co-impregnated resins was 3.85mmol/g. The impregnated resin containing cyanex-301 and 15C5 could be utilized for selective separation and pre-concentration of thorium ion from nitrate medium in presence of several interfering metal ions.

Maiorov et al. (2006), studied the extraction of thorium using tributyl phosphate from chloride solutions. Thorium distribution in relation to concentration of thorium, HCl, metal chloride in aqueous solutions, nature of the diluent, and the tributyl phosphate concentration was

evaluated. It was found that thorium extraction from salt solutions increases in the order NaCl < $CaCl_2$ < $AlCl_3$.

Pyartman et al. (2006), studied the extraction of Th(IV), La(III), and Y(III) from aqueous solutions containing 0-4 M sodium nitrate with a composite solid extractant based on a polymeric support impregnated with trialkylmethylammonium nitrate (Aliquat-336). The extraction isotherms were analyzed assuming that lanthanides and thorium are extracted with the solid extractant in the form of complexes $(R_4N)_2[Ln(NO_3)_5]$ and $(R_4N)_2[Th(NO_3)_6]$, respectively.

Talip et al. (2008), studied the efficiency of the expanded perlite for the adsorption of using a batch adsorption technique under different experimental conditions. It was found that the adsorption capacity increases by the increase in the pH of the suspensions. The rate of thorium adsorption on expanded perlite was observed to be fast in the first hour of the reaction time. Adsorption isotherms were expressed by Langmuir and Freundlich adsorption models and the adsorption experiments conducted at 30±1°C showed that the adsorption isotherms correlated well with the Langmuir model.

Yousofi et al. (2009), studied the solid phase extraction and preconcentration of uranium and thorium in aqueous samples using a new synthesized modified mesoporous MCM-41 from 5-nitro-2-furaldehyde (fural) for measurement by inductively coupled plasma optical emission spectrometry (ICP OES). They found that the analyte ions were sorbed by the sorbent at pH 5.5. This sorbent exhibited fast adsorption/desorption kinetics and high adsorption capacity. The method had given very low detection limits and good RSD.

Amaral and Morais (2010), studied the extraction of thorium and uranium from sulfuric liquor generated in chemical monazite treatment through a solvent extraction technique. The results indicated the possibility of extracting simultaneously thorium and uranium from solvent containing a mixture of primene JM-T and Alamine 336 which reached over 99.9% for thorium extraction and 99.4% for uranium extraction. The stripping was carried out using a hydrochloric acid solution from a loaded stripping solution containing 29.3g/l of ThO_2 and 1.27g/l of U_3O_8.

Bayyari et al. (2010), studied the extraction of thorium ions from perchlorate media at high ionic strength using didodecylphosphoric acid (HDDPA). They found that the extracted species from perchlorate media into toluene diluent was $[Th(X)_4(HR_2)_Y]_{org}$, where X= ClO_4^- and Y=1 or 2 at different ionic strengths and the extraction of Th(IV) ion increases with the increase in ionic strength.

Biswas et al. (2010), studied the extraction of U(VI) and Th(IV) from nitric acid medium using tri(butoxyethyl) phosphate (TBEP) in n-paraffin. They found that the extraction of U(VI) and Th(VI) by TBEP from nitric acid medium proceeds via a solvation mechanism and the complexes formed are of the types $UO_2(NO_3)_2$-2TBEP and $Th(NO_3)_4$-3TBEP with U(VI) and Th(IV), respectively.

Bursali et al. (2010), studied the preconcentration and determination of uranium(VI) and thorium(IV) from aqueous solutions using olive cake as a low-cost abundantly available sorbent. They found that the sorption capacity of olive cake is in the range of 2,260–15,000 μg g^{-1} at pH 4–7 for Th(IV) and in the range of 1,090–17,000 μg g^{-1} for U(VI) at pH 3–7, the

elution of U(VI) and Th(IV) was performed with 0.3–1 M HCl/1–2 M HNO_3 and 0.3–0.8 M HCl/1 M HNO_3, respectively. The precision of the method was 1.8 RSD% for U(VI) and 2.5 RSD% for Th(IV) in a concentration of 1.0 μg ml^{-1} for 10 replicate analysis.

Ghasemi and Zolfonoun (2010), established a new method for the preconcentration and simultaneous spectrophotometric determination of uranium, thorium and zirconium using solid phase extraction and orthogonal signal correction partial least squares method. The results demonstrated that α-benzoin oxime loaded amberlite XAD-2000 is an effective sorbent for trace amounts of U(VI), Th(IV) and Zr(IV) ions that can be used for their preconcentration or removal from their dilute sample solution.

Hosseini and Bandegharaei (2010), studied the development of a new chelating polymeric sorbent as an extractant impregnated resin (EIR) from eosin B and amberlite IRA-410 resin for extraction of Th(IV). The newly impregnated resin exhibited a good affinity and selectivity to extract Th(IV) ions as an ion exchange ligand. The EIR showed a high considerable preconcentration of Th(IV) ions and could be successfully regenerated for 25 cycles of operation in the column**.**