

## ABSTRACT

**Topic: *STUDIES ON THE ANALYTICAL APPLICATIONS OF 2,3-DIHYDROXYNAPHTHALENE, AN O-O' TYPE OF CHELATING DONOR LIGAND.***

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Bidentate O-O' type of ligands have been reported to be potential complexing agents for many metal ions. Formation of their metal complexes were studied in solution and their stability constants were also determined. Some of the complexes of these ligands have also been isolated in solid states and structural assessments were made by physico-chemical tools, including spectroscopy.

Interestingly, some of these ligands as such and their derivatives have been found to display distinct colours with a number of transition metals. Their colour reactions have also been exploited by many for the colorimetric determination of the metals. Mention may be made of catechol disulfonic acid which is also trivially known as tiron. This reagent has in the past been extensively used for the determination of elements like, iron, titanium, niobium, rare-earths etc. The name tiron was christened because of its specificity of reaction for both titanium and iron. Similarly, the reagent chromotropic acid which is a disulfonic acid derivative of 1,8-dihydroxynaphthalene has also been extensively used for the colorimetric determination for a host of metal ions because of its potential to form colour complexes with these metal ions at different reaction conditions. This reagent has further been coupled with diazonium salts of suitable amines to form various colour azo dyes like, Arsenazo-I, II, III and thorin, which are well known azo-based compounds for colorimetric determination of elements like, uranium, thorium, Zr and REEs.

In addition to the above, O-O' type of dihydroxyaryazo compounds like picramine epsilon, eriochrome black-T, calmagite etc., are well known complex forming analytical reagents. Even the complex forming ability of triphenylmethane reagents like pyrocatechol violet, eriochrome cyanine-R, chromazurol-S, as well as xanthine reagents like gallein, bromopyrogallol-red and various phenylfluorones is attributed to the presence of O-O' type of functional groups on benzene or fused benzene rings.

Metal complexes of catechol and its various derivatives including catecholamines such as adrenaline, nor-adrenaline, dopamine, dopa and isoproterenol all having O-O' sites form

complexes with Cu, Ni, Co, U, Mo, W, Pt, Pd etc. These complexes have been widely studied because of their unusual electronic effect and as such some of the systems present models for the biological transport of iron for some enzymes and for the primary photoelectron donor-acceptor centre in bacterial photosynthesis. They may also serve as models for metal ion interaction with ascorbate in the Woodenfriend system and ascorbate oxidase.

Catechol and substituted catechols bind strongly with many metal ions such as osmium, molybdenum, tungsten via the potential O-O' sites. Catecholamines are biogenic amines which function as neurotransmitters in the brain and nervous system of mammals.

Besides the extensive studies carried out on the complexes of catechol and its derivatives in solid forms (synthesis & structural assessments) as well as in solutions (equilibrium studies and analytical applications), similar studies, although scanty, are, however, not unprecedented with the ligand, 2,3-dihydroxynaphthalene(2,3-H<sub>2</sub>ND).

Complexes of molybdenum, tungsten, osmium, uranium, palladium and platinum with this reagent have been synthesized, isolated in solid forms and characterized. One such complex, cis-(NH<sub>4</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>5</sub>(ND)<sub>2</sub>].2H<sub>2</sub>O has been characterized by X-ray crystal structure determination. Surprisingly, there are few complexes known of this readily available ligand. There are solution studies on its complexation with boron, molybdenum, tungsten, uranium, iron, titanium, niobium, beryllium, aluminium and vanadium.

The isolated complexes are cis-[Ru(NH<sub>3</sub>)<sub>4</sub>(ND)]Cl, Sn(ND)<sub>2</sub> and (Bu<sub>4</sub>N)<sub>2</sub>[Sn(ND)<sub>3</sub>] (Et<sub>3</sub>N)[Ph<sub>3</sub>Sb(ND)Cl] and (pyH)[PhSi(ND)<sub>2</sub>] and bis (tri-n-butylammonium) tris(2,3-dihydroxynaphthalato) silicate. X-ray crystallographic studies were described for the latter three complexes.

Some workers in the past have studied the reaction of boron with 2,3-dihydroxynaphthalene in the determination of boron spectrophotometrically as well as fluorimetrically.

The reaction of boron with 2,3-dihydroxynaphthalene followed by its extraction with crystal violet into organic solvent was the basis for sensitive determination of boron. Besides, the boron-2,3 H<sub>2</sub>ND complex in aqueous solution was detected by measuring the fluorescence intensities (I<sub>ex</sub> =300 nm, I<sub>em</sub>=340nm). The relative standard deviation at 20 ppb level was 2.6% (n=6). The limit of detection was 0.04ppb.

Recently, 2,3-dihydroxynaphthalene (2,3-H<sub>2</sub>ND) has been used in the fluorimetric determination of manganese(II) by the catalytic oxidation of 2,3-H<sub>2</sub>ND in the presence of ethylenediamine and hydrogen peroxide. Of late [Fe(2,3-H<sub>2</sub>ND)<sub>n</sub>] complex has been used to estimate traces of iron in sea water by voltametry.

Recently, a ternary complex of boron, with 2,3-dihydroxynaphthalene and insulin has been used in the flow-injection analysis of boron.

As mentioned in the preceding section, many workers in the past have synthesized, isolated and characterized the solid complexes of many such elements with 2,3-dihydroxynaphthalene(2,3-H<sub>2</sub>ND). In addition to these, some of the complexes have been studied in solution and even many of the colour complexes of ortho-dihydroxybenzene and naphthalene have been used for high frequency titration.

Recently, ternary complexes of titanium with 2,3 dihydroxynaphthalene and bovine serum albumin were formed, and thorough biochemical studies were carried out. Serum albumin, the most abundant protein in human plasma (700 μM), binds diverse ligands at multiple sites. While studies have shown that serum albumin binds hard metals in chelate form, few have explored the trafficking of these metals by this protein. Recent work demonstrated that serum albumin may play a pivotal role in the transport and bioactivity of titanium(IV) complexes, including the anticancer drug candidate titanocene dichloride. The compound, 2,3-dihydroxynaphthalene and its sulphonic acid derivative although was reported to form colour complexes with host of elements such as V, Ti, Mo, Fe, Cu etc., its analytical utility has not been thoroughly explored until recently. It is pertinent to state that tiron is generally used for the sensitive estimation of titanium and iron but we have found that the reagent 2,3-dihydroxynaphthalene is far better than tiron for titanium determination in terms of sensitivity and selectivity ( molar absorptivity of titanium-2,3-dihydroxynaphthalene complex is two fold more than that of its tiron complex). The enhanced sensitivity of metal complexes with this reagent prompted us to explore its analytical potential. Through extant literature survey it was found that except for one or two primary reports (one on the estimation of few transition elements like, V, Ti, Mo, Fe, Cu etc., and another on the liquid-liquid extraction of total REEs), the potentiality of the reagent has not been explored further. However, as stated earlier, a few workers in the

past have used this reagent in the spectrophotometric determination of boron and the fluorimetric determination of a few REEs.

The presence of O-O' type of non-innocent functional groups on ortho position of naphthalene ring attracted our attention to further probe into the analytical potential of this reagent. In doing so, we have investigated the complexation of elements like, Ti, Fe, Mo, V with this reagent in line with the findings of V.Patrovsky. As has already been discussed in the preceding section about the complex forming ability of the reagent, 2,3-dihydroxynaphthalene, we, in our laboratory, have thoroughly investigated the analytical potential of this readily available reagent.

Unlike the report of Patrovsky on the extraction of iron ( $\text{Fe}^{3+}$ ) with 2,3-dihydroxynaphthalene(2,3- $\text{H}_2\text{ND}$ ) at pH 4.5-4.7 under the influence of the counter-cation, tri-n-butylamine ( $\text{Bu}_3\text{N}$ ) followed by its determination by measuring the absorbance of the ion-associate at 510 nm, in the system developed in our laboratory, the neutral complex formed of 2,3- $\text{H}_2\text{ND}$  and  $\text{Fe}^{3+}$  at pH 4-5 was made use of by measuring its absorbance either in aqueous solution or by extracting the same in ethyl acetate without any counter cation. Also, the reddish-orange anionic complex of 2,3- $\text{H}_2\text{ND}$  with  $\text{Fe}^{3+}$  formed over the pH range, 8 to 10 was used for the spectrophotometric determination of iron in aqueous solution. However, the method was made more selective and robust by extracting the reddish-orange anionic complex into ethyl acetate under the influence of cetyltrimethylammonium(CTA) cation, and then measuring the absorbance of the complex in ethyl acetate. The molar absorptivity and Sandell's sensitivity of the complex are,  $1.2 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$  and  $0.001 \mu\text{g cm}^{-2}$ , respectively. The method has been found very useful in the determination of iron in silicate rocks, ores, sediments, soils and allied products.

Similarly, in our laboratory a highly sensitive and selective aqueous and extraction spectrophotometric method has been developed for the determination of titanium in silicate rocks using the reagent, 2,3 dihydroxynaphthalene (2,3- $\text{H}_2\text{ND}$ ).

2,3- $\text{H}_2\text{ND}$  forms a yellowish-orange chelate with Ti(IV), which is readily extracted into ethyl acetate over the pH range, 4-9. The method is highly sensitive ( $\epsilon = 3.2 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ ) and free from interference of most elements present in silicate rock matrices.

The method is two fold more sensitive than tiron, chromotropic acid and

diantipyrilmethane methods. Interestingly, unlike the above methods, by selective extraction of the Ti-2,3 H<sub>2</sub>ND complex into ethyl acetate, interferences from Fe, Nb, Mo, Mn etc have been eliminated.

The application of the method has been further extended to columbite-tantalite minerals for the selective determination of titanium. Niobium, present in the minerals, interferes seriously in the determination of titanium by most methods, including the well known one with Hydrogen Peroxide. However, titanium in these samples could be accurately determined using 2,3-H<sub>2</sub>ND method by selectively separating it from the niobium rich matrix of columbite-tantalite minerals by solvent extraction of Ti(IV)- 2,3-H<sub>2</sub>ND complex at controlled pH.

Recently in our laboratory, an interesting and useful extraction spectrophotometric method has been developed for the accurate determination of manganese in diverse samples, including rock, minerals, ores, soils, sediments, waters and plant ash.

The method developed is unique in the sense that 2,3-H<sub>2</sub>ND forms an anionic chelate with manganese, irrespective of its valance states. This is readily extractable into ethyl acetate under the influence of the counter cation, CTA<sup>+</sup>, displaying a distinct colour(bluish-violet), characteristic of manganese. The reaction is very specific to manganese. Manganese can be determined with high degree of accuracy (results attested from those obtained by AAS and ICP-AES) from ppm to percentage (%) level after a prior removal of iron by resorting to solvent extraction of Fe<sup>3+</sup> at pH 4-5 using the same reagent (2,3-H<sub>2</sub>ND). The application of the method was further extended to the ultra trace determination of manganese in water samples by co-precipitating it along with hydrated iron oxide, dissolving the precipitate in dilute HCl and then determining the pre-concentrated manganese using GF-AAS. The GF-AAS determination of manganese ion was preceded by the solvent extraction of iron at pH 4-5 using the same reagent, 2,3-H<sub>2</sub>ND. Manganese was extracted as Mn-2,3-H<sub>2</sub>ND-CTA ternary complex into ethyl acetate, stripped it off and then determined spectrophotometrically in aqueous solution.

The method is highly selective with molar absorptivity ( $\epsilon$ ) being  $1.2 \times 10^4$  L.mol<sup>-1</sup>cm<sup>-1</sup>. It yields highly reproducible results for manganese determinations.

Very recently, a novel method has been developed for the extraction spectrophotometric determination of niobium in silicate rocks and columbite-tantalite minerals. The method

is based upon the formation of a ternary complex of niobium(V) with 2,3-H<sub>2</sub>ND and acetate ion in the pH range, 8-10. The ternary complex displays a yellowish orange colour on extraction into ethyl acetate. The complex absorbs maximum at 390 nm. The molar absorptivity and Sandell's Sensitivity of the method are  $4.6 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1}$  and  $2 \text{ ng cm}^{-2}$ , respectively. The detection and determination limits of the method are  $20 \text{ ng mL}^{-1}$  and  $60 \text{ ng mL}^{-1}$ , respectively. As Ti(IV) also absorbs at this wave length, a prior extraction at pH 4-5 using the same reagent (2,3-H<sub>2</sub>ND) completely removes Ti(IV) along with Fe<sup>3+</sup>, V(V), etc., thereby rendering the method more selective.

The method was applied to a host of silicate rocks as well as a set of columbite-tantalite minerals. The results obtained were found to be in excellent agreement with those obtained from the standard thiocyanate method and ICP-AES method.

It is worth mentioning here that the binary complex of Nb(V) with 2,3-H<sub>2</sub>ND is not suitable for spectrophotometric measurements because its sensitivity is very low ( $\epsilon = <10,000 \text{ L.mol}^{-1} \text{ cm}^{-1}$ ) and precision of results obtained is also not good. Therefore, the novel ternary system has substantial advantages over the corresponding binary system. In addition to the colour complexes formed of 2,3-H<sub>2</sub>ND with various metal ions, a number of colourless complexes, having analytical relevance are also formed of this reagent with certain metals ions, like, UO<sub>2</sub><sup>2+</sup>, Th, Zr and rare earth elements(REEs) etc.

In our laboratory, a useful fluorimetric method for the determination of uranium has been developed using the reagent 2,3-dihydroxynaphthalene.

The reagent, 2,3-H<sub>2</sub>ND forms a 1:3 anionic complex with UO<sub>2</sub><sup>2+</sup> at pH 10-12. This anionic complex is extracted into ethyl acetate using the counter cation, CTA<sup>+</sup>(cetyltrimethyl ammonium ion) leaving many interfering ions in aqueous solution. However, prior extraction at pH 4-5 using the same reagent has completely removed iron which when present at 10% level in the sample interferes in the fluorimetric determination of uranium by quenching the fluorescence intensity of uranium. Along with iron, many other elements which quench, although to a lesser extent, the uranium fluorescence are also removed through this extraction. These elements are Th, Al, V, Cu, Ni etc.

The elements like Mn, Co and Cr which are serious quenchers are also extracted as anionic complexes with 2,3-H<sub>2</sub>ND under the reaction conditions optimized for the

extraction of uranium, thereby seriously interfering in its fluorimetric determination. However, EDTA completely masks these elements, and as such, does not allow these three interfering elements to be extracted along with uranium, thereby rendering the method quite selective for the estimation of uranium.

Thorium too, forms 1:2 neutral complex with 2,3-H<sub>2</sub>ND in the pH range, 4 to 10. This complex is readily extracted into ethyl acetate without any counter cation.

However, in the pH range, 4-6 the extraction is never complete i.e., the extraction is ~80%. Nearly 20% thorium remains in aqueous solution even after using salting out agent like saturated sodium acetate. At an elevated pH i.e., 8 to 10 >99% thorium is extracted into ethyl acetate.

The extraction behavior of rare earth elements has been observed to be similar to that of thorium.

Rare earth elements (REEs) are not extracted into ethyl acetate at pH 4-6. And no amount of sodium acetate or for that matter, no salting out agent or electrolyte could enhance the percentage extraction in this pH range. However, as observed in the case of thorium >99% REEs are extracted into ethyl acetate in the pH range, 8-10, in the presence of saturated sodium acetate.

Interestingly, a procedure has been evolved for the extractive separation of thorium from rare earth elements before their respective spectrophotometric determinations using Arsenazo-III. Both REEs and thorium at pH 8-10 are readily extracted into ethyl acetate in the presence of saturated sodium acetate. They are separated by selective stripping off of REEs at pH  $6.2 \pm 0.1$  into water leaving thorium in the organic phase.

After stripping off of thorium into water at still lower pH ( $<6.2 \pm 0.1$ ) it could be accurately determined by Arsenazo-III. By making use of the different solvent extraction and stripping behavior of REEs, thorium and uranium, their separation and selective determinations in monazite and related samples are possible.

In our laboratory, based upon the above philosophy selective hydrometallurgical extraction of uranium, thorium and rare earths (total) from monazite and bastnaesite samples have been made possible.

This thesis has been divided into 8 different chapters.

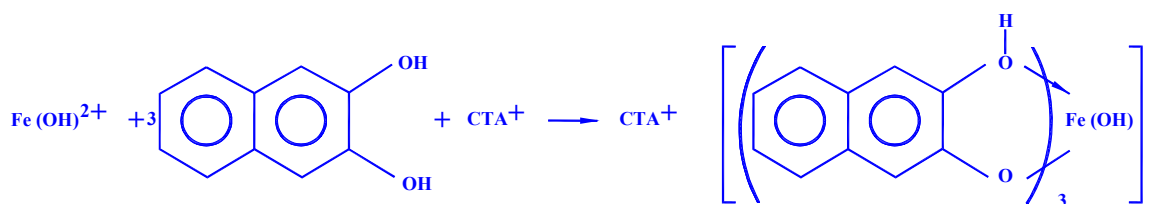


The **chapter-I** is the prelude of the thesis which gives an overview of the work carried out by different workers in the past using the cited reagent (2,3-dihydroxynaphthalene).

The **chapter-II** of this thesis describes the details of analytical methods and instrumentations involved in the analysis of metals chosen for present study.

The **chapter-III** describes the studies involving complex formation of Fe(III) with 2,3-dihydroxynaphthalene at various pH and their liquid-liquid extraction in suitable organic solvent for pre-concentration and separation from matrix elements. It also describes the details of systematic studies carried out in the development of a novel method for the selective and sensitive determination of iron in real samples like rocks, minerals, soils, steam sediments and water samples after suitable optimization of variables.

2,3-dihydroxynaphthalene forms a 1:3 ( $\text{Fe}^{3+}$  to 2,3-  $\text{H}_2\text{ND}$ ) reddish orange anionic complex at pH 8-10 as per the tentative reaction scheme:



In the presence of cetyltrimethylammonium ion ( $\text{CTA}^+$ ) the complex is easily extracted into ethylacetate as an ion-associate. The reaction parameters and extraction conditionalities have been studied in detail. The method has been applied to a number of samples of diverse matrices, including waters, and silicate rock samples, and the results obtained compare favourably with those obtained from standard methods. The method has been found to be highly selective for iron determination.

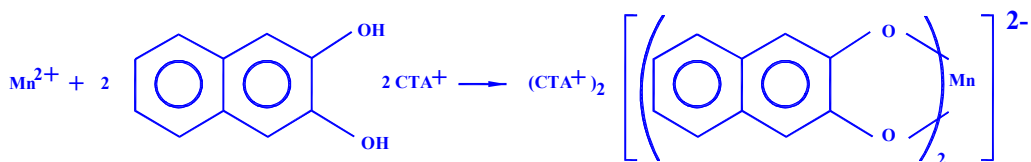
The **chapter-IV** encompasses the details of studies on variables involved in the complex formation of Ti(IV) with 2,3-dihydroxynaphthalene as shown in the reaction scheme and



its selective extraction in to organic solvents followed by its sensitive extraction spectrophotometric determination in silicate rocks and columbite-tantalite minerals.

The reagent 2,3-dihydroxynaphthalene forms a strong chelate with titanium over the pH range 4 to 9. At pH 4–5, titanium is extracted into ethyl acetate along with iron, leaving behind V, Nb, Mo, and a host of elements present in complex matrices of rock samples. In the extract, titanium is easily separated from iron after raising the pH of the medium and re-extracting. The method is free from any interference. The sensitivity of the method is  $3.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The method has been applied to a number of diverse samples including rocks and minerals. The precision of the method is excellent. This method has been compared with tiron, chromotropic acid, diantipyrilmethane (DAM) and other existing spectrophotometric methods used in the analysis of rocks, ores and minerals. The proposed method has definite advantages over most spectrophotometric methods in terms of sensitivity, selectivity, reproducibility and simplicity.

The **Chapter V** of this thesis deals with the studies (i) involving the variables affecting the optimization of a novel reaction of Mn with 2,3-dihydroxynaphthalene irrespective its valence state as shown in the reaction scheme,



(ii) Selective ion associate extraction of the anionic complex of Mn-2,3-H<sub>2</sub>ND in the presence of cetyltrimethylammonium cation and (iii) its selective and sensitive

extraction spectrophotometric determination in diverse samples like, rocks, soils, stream sediments and plant ash.

This chapter is devoted to the studies involving the development of a new, simple, precise, selective and sensitive method for the extraction and spectrophotometric determination of manganese. Manganese(II) forms a bluish-violet anionic chelate,  $[\text{MnL}_2]^{2-}$  with 2,3-dihydroxynaphthalene( $\text{H}_2\text{L}$ ) in alkaline medium (pH 11-12). The colour of the anionic chelate gets intensified when the compound is extracted into ethyl acetate as an ion-associate,  $\text{Q}_2[\text{MnL}_2]$  with cetyltrimethylammonium( $\text{Q}^+$ ) counter cation. The molar absorptivity of the complex at 547 nm ( $\lambda_{\text{max}}$ ) is  $1.2 \times 10^4 \text{ L}\cdot\text{mol}^{-1} \text{ cm}^{-1}$  with the detection limit of  $0.04 \mu\text{g mL}^{-1}$  for Mn. The Beer's law is obeyed in the concentration range from 0 to  $5 \mu\text{g mL}^{-1}$ . Zn, Cd, Cu, Co, Ni, Al, Be, La, Ti, Zr, Y, Ta, W, U, Mo, As, Se and Bi do not interfere, while Fe does, so should be removed by prior extraction at pH 4-5 using the same reagent. The method has also been applied to the recovery of Mn present in silicate rocks, ores, minerals, soils, plant ash and hydrogeochemical samples. The results compared favourably with those obtained by oxidation of Mn to  $\text{KMnO}_4$  with  $\text{KIO}_4$  as an oxidizing agent, and further spectrophotometric and AAS investigations.

The **chapter-VI** describes the formation of a novel ternary complex of niobium, 2,3-dihydroxynaphthalene and acetate ion as shown in the reaction scheme,



and its extraction into a suitable organic solvent followed by spectrophotometric determination of niobium by measuring the absorbance of the yellowish orange ternary complex in organic medium.

A new and simple method for the separation of niobium by solvent extraction of its coloured mixed ligand complex with 2,3-dihydroxynaphthalene and acetate ion followed by its selective and sensitive spectrophotometric determination is described in this paper. The molar absorptivity of the method is  $4.6 \pm 0.05 \times 10^4 \text{ L}\cdot\text{mol}^{-1} \text{ cm}^{-1}$  at 397nm ( $\lambda_{\text{max}}$ ) with detection limit of  $20 \text{ ng niobium mL}^{-1}$ . A comparative study of extraction of niobium (V) in different organic solvents shows that the extractability, sensitivity and selectivity of the method are affected by the nature of solvents and hetero-ligands used. Niobium was successfully separated from Ti, V, Mo, Zr, Ta, W, Fe, Al, Cr, U, Th, Ni,

Co, Zn, Cd, Cu, and Mn, thereby eliminating the interference of these ions in its spectrophotometric determination. The method was applied to the recovery of niobium from silicate rocks, ores, and columbite-tantalite minerals.

The **chapter-VII** of this thesis is dedicated to the formation of anionic complex of uranium with 2,3-dihydroxynaphthalene followed by its extraction into a suitable organic solvent as ion associate with cetyltrimethylammonium ion (CTA<sup>+</sup>) as shown in the following scheme :

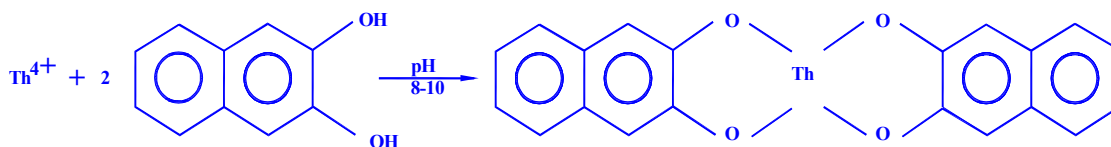


This chapter also describes the selective fluorimetric determination of uranium in traces in water samples after pre-concentration of the analyte by co-precipitating it with hydrated iron oxide, re-dissolving the precipitate in dilute HNO<sub>3</sub> followed by its removal by solvent extraction using the cited reagent (2,3-H<sub>2</sub>ND).

The **chapter-VIII** is the last chapter of this thesis and is dedicated to the formation of complexes of thorium and rare earths with 2,3-dihydroxynaphthalene as shown below, their extraction into suitable organic solvents and selective stripping off of the metal complexes at different pH followed by their determination spectrophotometrically or by ICP-AES.

**Tentative reaction Scheme:**

i) Thorium:



ii) REEs

