II.1.1.1. Detectors for Ion Chromatography

There are many types of detectors applicable to ion chromatography. Optical detectors based on ultraviolet-visible absorption constitute over 70% of HPLC detection systems. It is not necessary that the wavelength selected for HPLC coincides with the wavelength where maximum absorption occurs. True sensitivity will suffer, but any wavelength within the absorption envelop will be usable. Efficient detectors should fulfill the following characteristics:

-*Response time:* Response time should be at least 10 times less than the peak width of a solute in time units to avoid distortion of the peak area.

-*Detection limit:* Typically the concentration of the solute peak in the detector ranges from 1/5 to 1/350 of the initial sample concentration at injection because of the dilution factor. For precise quantitation, a tenfold greater concentration than this estimate is needed, keeping in mind that narrow-bore columns dilute small samples less than large-bore columns.

-*Linearity and dynamic range*: For quantitative work, the signal output of the detector should be linear with concentration (concentration-sensitive detector or mass sensitive). A wide linear dynamic range, perhaps 5 orders of magnitude, is desirable in order to handle major and trace components in a single analysis.

II.1.1.2. Anion and Cation Chromatography

In anion and cation chromatography, or simply ion chromatography (IC), low-capacity ion-exchange resins are used to separate analyte ions. A dilute aqueous solution is used as eluent. A typical packing is 3-quaternary aminopropyl for anion exchange and 3-propyl sulfonic acid for cation exchange. Also available are a weakly basic anion-exchange packing composed of diethyl-aminoethyl (DEAE) groups and a weakly acid carboxymethyl (CM) cation exchanger.

Anions can be classified into four groups;

1- Weakly held anions such as fluoride or monofunctional organic acids.

2- Mono- and divalent inorganic anions, and divalent organic acids.

3- Mono- and divalent highly polarizable inorganic anions, such as iodide, thiocyanate, and thiosulfate, and trivalent organic acids.

4- Metal oxides, such as chromate and perrhenate.

Cations can similarly be classified into four groups; namely,

1- Alkali metals and ammonium ions.

2- Alkaline-earth meats.

3- Transition metals.

4- Rare earth metals and Actinides.

II.1.2. Ion Chromatography of Uranium, Thorium and Rare Earth Elements (REE)

A number of methods have been developed for determination of uranium, thorium and REE by liquid chromatography. Barkley et al. in 1986[(12)] and Cassidy et al. in 1990[(13)] reported a separation method for the study of uranium dioxide, uranium-thorium dioxide fuels and uranium ore in refining processes. Later, Harold et al.[(14)] and Shaw et al.[(15)] investigated the use of a cation-exchange system for this determination U and Th. This system incorporated the use of additional chelating column for either preconcentration and/or matrix effect elimination. Many of the mentioned systems displayed good separation and detection qualities for uranium, thorium or a mixture of both metal ions. However, in complex matrices such as monazite minerals, with large amounts of other metal ions present, some of the systems lose their capacity and become not applicable in real samples. An example of this is the determination of uranium and thorium in the presence of high concentrations of REE. Typical ratios of REE/Th and REE/U in phosphate fertilizer samples are around 350 and 2770, respectively (Al-Shawi and Dahl, 1995)[(16)]. Some systems require the use of complex matrix elimination steps and hence increasing the complexity of the separation.

The method of Al-Shawi and Dahl[(16)], which was studied for the determination of Th and U in nitrophosphate fertilizer solution by ion chromatography is based on cation-exchange coupled with spectrophotometric post-column detection with Arsenazo III at 660 nm. Elution is performed with a gradient concentration of hydrochloric acid or nitric acid and ammonium sulfate. This authors have indicated that U forms weaker cationic species than Th with hydrochloric and nitric acids, in the form of UO_2Cl^+ and $UO_2NO_3^+$. When the chloride concentration of the eluent is increased, the concentration of the cationic species retained on the stationary phase decreases because the solution equilibrium is displaced to higher complex species. In sulfate acid media, U can form retainable complexes on a strong cation-exchange resin in the form of $[UO_2(HSO_4)]^+$. This hydrogensulfato complex of uranyl ion cannot be formed from a neutral sulfate solution such as ammonium sulfate. Uranium, in fact, is eluted very close to the solvent front when the concentration of the sulfate ion is more than 0.1 M in the initial gradient program.

The combination of high charge and low hydrolysis makes Th ion particularly retainable on cation-exchange resins from HCl and HNO_3 at concentrations below about

1.0 M. Separations from other cations are thus facilitated, and trace amounts of Th may be concentrated. Complexing agents such as citric acid, oxalic acid, hydrofluoric acid, carbonate and sulfate are necessary for its elution from the column. This implies that Th forms weak cationic species with a sulfate ligand in the form of $ThSO_4^{2+}$. The retention times of Th decrease with increasing concentration of sulfate ion in the initial gradient program.

In case of $HCl-(NH_4)_2SO_4$ elution system, the mass distribution ratios for Th, U and other potential interfering metals at different HCl concentrations imply that an initial elution with HCl would separate U from Th and would resolve Y from calcium and iron(III). When the U ion has been totally eluted, the Th ion can be eluted by the introduction of a sulfate ligand as Th has a much lower mass distribution ratio with sulfate. For example thorium has a strong affinity for the sulfonate stationary phase when elution is carried out with 0.4 M HCl, while uranium has a much weaker affinity for the same stationary phase. Thorium, however, would loose this strong affinity when the sulfate ligand was introduced and therefore would be eluted after the uranium ion.

II.2. BREAKDOWN OF MONAZITE SAND CONCENTRATE

Several methods of monazite breakdown have been actually studied and reported in the literature. These include mainly the acid treatment methods, the alkali caustic soda opening methods beside chlorination. As a matter of fact, both sulfuric and caustic soda destroy the chemical structure of monazite sand, however, they selectively digest different components. The former results in the formation of a monazite sulfate solution of U, Th and REEs and leaves any silica, zircon or other admixed gangue in an insoluble form. On the other hand, the caustic soda digestion of monazite dissolves the impurities or the undesired components (phosphate and possible silica) leaving the valuable metals as solid components of a slurry which after filtration, washing and drying results in a dry cake of the hydrous oxides of these metals. The latter could then be dissolved in a suitable acid for their processing.

Some other methods have also been studied e.g. Joseph and Mony(17) have applied NH_4F upon powdered monazite and found that this more convenient reagent is as effective as the bifluoride. Also, Chendrayan(18) was indeed able to dissolve Th from monazite by bacterial action using Thiobacilllus-Thiooxidans.

II.2.1. Acid Opening Methods

Beside sulfuric acid, which is commercially used for monazite opening, other acids have been studied. These involve mainly nitric and perchloric acids. Also, Marchand(19) had reported a method for the decomposition of monazite sand using pyrophosphoric acid.

II.2.1.1. Sulfuric Acid Opening Method

The most common method of opening monazite sands is dissolving with heated sulfuric acid, forming a monazite sulfate solution of Th, REE and U and leaving a filterable residue that consists of any silica, zircon or other gangue material present in the monazite concentrate. This method uses cheap, easily obtained chemicals and is suitable for large-scale production. Fig. (6) is a schematic process flow diagram for the sulfuric acid digestion process (Shaw et al.)(20). This process was early developed for application in the atomic energy program at Ames Laboratory, Iowa State College, USA(20, 21). Although this method presents for uranium some difficulties, it has been used most extensively in the USA (Parker and Baroch)(22). Depending on the acid/ore ratio, temperature and concentration, either Th or REE can be selectively solubilized or both Th and REE are totally solubilized (Shaw et al.(20) and Wylie(23)). Rare earths and Th are subsequently recovered from solution.

The process of REE recovery, based on thire double sulfate precipitation, was largely developed by Pilkington and Wylie(24) and has actually found industrial application (Pilkington and Wylie(24), Smutz(25) and Hilal et al.(26)). Yttrium and HREE double sulfates are quite soluble and go with Th. Even in the stepwise neutralization procedure investigated at Ames (Smutz et al.(27) and Barghusen and Smutz(28)), yttrium and HREE are precipitated along with Th as basic compounds. The REE, however, are recoverable from the Th fraction during the solvent extraction for the purification of Th and U. Solvent extraction with TBP from an aqueous 8N nitric acid solution of Th and mixed REE permits the recovery of Th, U, Ce and Ce-free REE.

In fact, the sulfuric acid digestion process carries along with the valuable elements the phosphate ion, and introduces the sulfate ion, both of which have a detrimental effect upon subsequent Th purification step (Cuthbert, 1958)(1). Therefore, the sulfuric acid process does not yield pure products and is no longer in commercial use (Gupta and Krishnamurthy)(4).