EXTRACTION STUDIES OF SOME LANTHANIDES AND ACTINIDES USING CYANEX AND CROWN ETHERS

A SYNOPSIS OF THE Ph.D. THESIS SUBMITTED TO

SHIVAJI UNIVERSITY, KOLHAPUR

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

UNDER THE FACULTY OF SCIENCE

BY

MR. NAMDEV SATYAPPA MADANE

M.Sc.

UNDER THE GUIDANCE OF

PROF. B. S. MOHITE

M.Sc., Ph.D.

(I.I.T. POWAI MUMBAI)

DEPARTMENT OF CHEMISTRY

SHIVAJI UNIVERSITY,

KOLHAPUR – 416 004

(M.S.) INDIA

MARCH 2012
Title of research work: Extraction Studies of Some Lanthanides and Actinides Using cyanex and Crown Ethers.

Absorption spectrophotometry in the ultraviolet and visible region is considered to be one of the oldest physical methods for quantitative analysis and structural elucidation. We know that infrared and NMR techniques are mainly used for structural elucidation and qualitative analysis. On the other hand, ultraviolet and visible spectrophotometry is mainly used for quantitative analysis and serves as a useful auxiliary tool for structural elucidation.

Spectrophotometry is mainly concerned with the following regions of the spectrum. Ultraviolet, 4000-2000 Å; visible 8000-4000 Å and colorimetry. Colorimetry is concerned with the visible region of the spectrum. Spectrophotometry is currently used extensively in all routine analytical labs and undoubtedly will be for many years to come. Nevertheless, elemental analysis has been used by many industrial operators, particularly when very rapid answers are necessary. Initially colorimetry and spectrophotometry were used to ascertain the concentrations of simple colored solutions. Over the years, however, it became recognized that many metals react with organic reagents to form intensely colored compounds. The reagents used have been studied and modified for many years. Very sensitive and selective analytical procedures have been developed for the determination of trace metal trace metal components in solutions with concentration as low as 1 ppm and less.

Obtaining reproducible results by means of spectrophotometric analysis often requires skills, attention, and a considerable knowledge of chemistry. On the other hand the equipment is generally inexpensive, and most laboratories are able to handle this type of analytical work. Spectrophotometry provides the basis for many routine methods of analysis.

In the present work we developed analytical methods for extraction and separation of uranium(VI), thorium(IV) using cyanex 272. Also we have developed an analytical method for extraction and separation of cerium(III)
using cyanex 923. We have also developed an analytical method for extraction and separation of thorium(IV) using dibenzo-18-crown-6. The spectrophotometric determination of uranium(VI), thorium(IV) and cerium(III) is of greater interest because of the high extraction efficiency of these metals. The study includes determination of optimum parameters for quantitative extraction and separation of these elements and use of the developed method for the analysis of these metal ions from geological and real samples.

Thesis is divided into two parts i.e. part I and part II

**Part I**

Part I of thesis is divided into five chapters.

**Chapter 1:** Introduction to solvent extraction

**Chapter 2:** Introduction to cyanex

**Chapter 3:** Liquid-liquid extraction of uranium(VI) using cyanex 272 in toluene from sodium salicylate medium

**Chapter 4:** Liquid-liquid extraction of thorium(IV) using cyanex 272 in kerosene from sodium salicylate medium

**Chapter 5:** Liquid-liquid extraction of cerium(III) using cyanex 923 in kerosene from sodium acetate medium

**Part II**

Part second of thesis is divided into two chapters.

**Chapter 1:** Introduction to Crown Ethers

**Chapter 2:** Liquid-liquid extraction of thorium(IV) using dibenzo-18-crown-6 in xylene from L-histidine medium

**Chapter 1: Introduction to solvent extraction**

This chapter describes historical aspects of solvent extraction, theory of spectrophotometry and colorimetry, Lamberts law, Beers law, basic principals
of solvent extraction, experimental setup and instruments are very well explained in this chapter.

Chapter 2: Introduction to cyanex

This chapter includes introduction to cyanex compounds, properties of different cyanex compounds, their chemical structure, stability, toxicity and applications. The review of literature survey of cyanex compounds in solvent extraction for separation of metals are also given in this chapter.

Chapter 3: Liquid-liquid extraction of uranium(VI) using cyanex 272 in toluene from sodium salicylate medium

Liquid-liquid extraction of uranium(VI) from sodium salicylate media using cyanex 272 in toluene has been carried out. Uranium(VI) has been quantitatively extracted from $1 \times 10^{-3}$ M sodium salicylate with $5 \times 10^{-4}$ M cyanex 272 in toluene. It has been stripped quantitatively from the organic phase with 1 M hydrochloric acid and determined spectrophotometrically as its complex with arsenazo-III at 660 nm. The effect of concentration of sodium salicylate, extractant, diluents, metal ion and strippants have been studied. The quantitative extraction of uranium(VI) was obtained by stripping with 0.5-8 M hydrochloric acid, 1-8 M nitric acid, 0.1-8 M sulphuric acid, 0.5-7 M hydrobromic acid 0.5-8 M perchloric acid and 3-8 M acetic acid. It was found that 10 mL of $5 \times 10^{-4}$ M cyanex 272 solution in toluene was sufficient to extract 500 µg of uranium(VI) quantitatively. Separation of uranium (VI) from other elements was achieved from binary as well as multicomponent mixtures. The method permits the separation of uranium(VI) from other elements such as thorium(IV), beryllium(II), lead(II), nickel(II), copper(II), manganese(II), magnesium(II), molybdenum(VI), barium(II), strontium(II). The method was extended for the determination of uranium(VI) in geological samples. The method is simple, rapid and selective with good reproducibility (approximately±2%).
Chapter 4: Liquid-liquid extraction of thorium(IV) using cyanex 272 in kerosene from sodium salicylate medium

A simple and selective spectrophotometric method was developed for the extraction and separation of thorium(IV) from sodium salicylate media using cyanex 272 in Kerosene. Thorium(IV) was quantitatively extracted by $5 \times 10^{-4}$ M cyanex 272 in kerosene from $1 \times 10^{-5}$ M sodium salicylate medium. The extracted thorium(IV) was stripped out quantitatively from the organic phase with 4 M hydrochloric acid and determined spectrophotometrically with arsenazo-III at 620 nm. The effect of concentrations of sodium salicylate, extractant, diluents, metal ion and strippants has been studied. The stripping of thorium(IV) was quantitative with 0.5-6.0 M hydrochloric acid, 2.0-8.0 M nitric acid, 0.1-8.0 M sulphuric acid, 1.0-8.0 M perchloric acid, 0.5-8.0 M hydrobromic acid and 5.0-8.0 M acetic acid. It was found that 10 mL of $5 \times 10^{-4}$ M cyanex 272 solution was adequate to extract thorium(IV) quantitatively up to 400 µg of sample solution. Separation of thorium(IV) from other elements was achieved from binary as well as multicomponent mixtures. Separation of thorium(IV) from other associated elements such as uranium(VI), strontium(II), rubidium(I), cesium(I), potassium(I), Sodium(I), Lithium(I), lead(II), barium(II), beryllium(II) was possible with this developed method. The method was extended for the separation and determination of thorium(IV) in geological and real samples. The method is simple, rapid and selective with good reproducibility (approximately±2%).

Chapter 5: Liquid-liquid extraction of cerium(III) using cyanex 923 in kerosene from sodium acetate medium

A simple method has been developed for the extraction, separation and determination of cerium(III) using cyanex 923 in kerosene from sodium acetate medium. Cerium(III) was quantitatively extracted by $5 \times 10^{-3}$ M cyanex 923 in kerosene from 1 M sodium acetate medium. The extracted cerium(III) was stripped out quantitatively from the organic phase with 5 M hydrochloric acid and determined spectrophotometrically with arsenazo-III at 650 nm. The effect
of concentrations of sodium acetate, extractant, diluents, tolerance limits and strippants has been studied. Back stripping of cerium(III) was quantitative with 3-8 M hydrochloric acid, 4 M nitric acid, 1-8 M perchloric acid, 3-8 M hydrobromic acid while, sulphuric acid and acetic acid was found to be inefficient strippants. Separation of cerium(III) from other elements was achieved from multicomponent mixtures, such as uranium(VI), iron(III), lithium(I), potassium(I), Cesium(I) and molybdenum(VI ). The method was extended for the separation and determination of cerium(III) in geological and real samples. The method is simple, rapid and selective with good reproducibility (approximately±2%).

Part II

Part second of thesis is divided into two chapters.

Chapter 1: Introduction to Crown Ethers

This chapter describes histology of crown ethers and various types of crown ethers. The nomenclature of crown ethers and characteristics of various crown ethers are explained. The extraction equilibria with crown ethers in separation of metals and factors influencing extraction by crown ethers are very well explained in this chapter. This chapter also includes review of the use of different crown ethers in separation of metals by solvent extraction.

Chapter: 2 Liquid-liquid extraction of thorium(IV) using dibenzo-18-crown-6 in xylene from L-histidine medium

A very simple method has been developed for extraction and separation of thorium(IV) using dibenzo-18-crown-6 in xylene from L-histidine medium. Thorium(IV) was quantitatively extracted by 5x10⁻⁴ M dibenzo-18-crown-6 in xylene from 5x10⁻⁴ M L-histidine medium. The extracted thorium(IV) was stripped out quantitatively from the organic phase with 6 M nitric acid and determined spectrophotometrically with arsenazo-III at 620 nm. The effect of
concentrations of L-histidine, effect of concentration of extractant, effect of diluents, and strippants has been studied. Back stripping of thorium(IV) was quantitative with 0.5-8.0 M nitric acid, 1.0-6.0 M sulphuric acid, 0.1-8.0 M perchloric acid, 4.0-7.0 M hydrobromic acid. While hydrochloric acid and acetic acid were found to be insufficient strippants for quantitative extraction of thorium(IV). Separation of thorium(IV) from other elements was achieved quantitatively from binary mixtures such as barium(II), strontium(II), beryllium(II), Lithium(I), sodium(I), potassium(I), Cesium(I), rubidium(I), cobalt(II), nickel(II), cadmium(II) and zinc(II)). The method was extended for the separation and determination of thorium(IV) in geological and real samples. The method is simple, rapid and selective with good reproducibility (approximately±2%). The results obtained by this developed method were in good agreement with the reported one.

**Highlights of the research work done are summarized below:**

1. Low reagent concentration is required for quantitative extraction and separation of actinides and lanthanides.
2. The extraction procedure is a single stage therefore it avoids the loss solvents.
3. Cyanex compounds are organophosphorus compounds and are effective extractants.
4. The solvent used are toluene and kerosene and are best solvents. These solvents can be recovered and reused for further extraction processes and beneficial one.
5. Extraction procedure is free from interference of a large number of foreign ions which are associated with uranium(VI), thorium(IV) and cerium(III) in its natural occurrence.
6. The developed method is used for the separation of group metals like thorium and uranium.
7. Reliability of the procedures was tested by carrying analysis of geological and real samples.

8. The developed methods are simple, rapid, reliable and reproducible used for extraction and separation of uranium(VI), thorium(IV) and cerium(III).

Prof. B. S. Mohite    Namdev S. Madane
Research Guide     Research Student

Place: Kolhapur
Date:

Forwarded through:

Prof. and Head
Department of Chemistry,
Shivaji University, Kolhapur