DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF FACTORIAL DESIGN IN OPTIMIZATION OF PRECONCENTRATION PROCEDURE FOR SOME LANTHANIDES DETERMINATION IN AQUEOUS SOLUTION

by
Cem GÖK

August, 2005
İZMİR

APPLICATION OF FACTORIAL DESIGN IN OPTIMIZATION OF PRECONCENTRATION PROCEDURE FOR SOME LANTHANIDES DETERMINATION IN AQUEOUS SOLUTION

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M. Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"APPLICATION OF FACTORIAL DESIGN IN OPTIMIZATION OF PRECONCENTRATION PROCEDURE FOR SOME LANTHANIDES DETERMINATION IN AQUEOUS SOLUTION"** completed by **CEM GÖK** under supervision of **ASSOC. PROF. DR. MELEK MERDİVAN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Purposes of this study are preconcentration and determination of La(III) and Ce(III) using factorial design with the aim of reducing the number of experiment, which is based on solid phase extraction.

The impregnation of octacarboxymethyl-C-methylcalix[4]resorcinarene into a polymeric matrix, Amberlite XAD-16, was supplied and characterized by infrared spectroscopy. The ligand sorption capacity of impregnated resin was determined spectrophotometrically and also gravimetrically.

The optimization process was caried out using 2^3 factorial design and three variables (pH, concentration of metal ion, sorption flow rate) were regarded as factors. The optimized values are; pH 5, concentration as 4 μg ml^{-1}, flow rate 1.5 ml min^{-1} for La(III) and pH 6, concentration as 0.25 μg ml^{-1}, flow rate 1.5 ml min^{-1} for Ce(III).

The resin was used successfully for the separation and enrichment of La (III) and Ce(III) ions, additionally which has good chemical stability, reusability and faster rate of equilibrium. The influence of alkali metals, common anions and some heavy metal ions as interferents was discussed. Furthermore, the method has been applied to sequential separation of La(III) and Ce(III) on synthetic solutions with a good reliability. The procedure proposed allowed the determination with detection limit 830 ng l^{-1} for La(III) and 250 ng l^{-1} for Ce(III), and relative standad deviation (%RSD) 2.27 for lanthanum and 1.97 for cerium. The preconcentration factors of La (III) and Ce(III) were 125 and 83, respectively. The enrichment procedure showed a linear calibraiton curve within concentration range from 1.0-7.5 μg ml^{-1} lanthanum and 0.50-10.0 μg ml^{-1} for cerium. Moreover, this procedure was applied to seawater

and well water samples prove the reliability of the proposed preconcentration method for its application to various kinds of analytical matrix samples.

Keywords: Factorial design, solid phase extraction, lanthanides, preconcentration, resorcinarene, impregnation, Amberlite XAD-16.

SULU ÇÖZELTİDE BAZI LANTANİTLERİN TAYİNİ İÇİN ÖNDERİŞTİRME YÖNTEMİNİN UYGUNLUĞUNA FAKTÖRİYEL TASARIM UYGULANMASI

ÖZ

Bu çalışmanın amacı, katı faz ekstraksiyon ile faktöriyel dizayn kullanılarak La(III) ve Ce(III) iyonlarının önderiştirilmesi ve tayinidir.

Polimerik matriks, Amberlit XAD-16, üzerine emdirilen oktakarboksimetil-C-metilkaliks[4]resorsinaren infrared spektroskopisi ile karakterize edildi.. Emdirilmiş reçinenin ligand tutunma kapasitesi spektrofotometrik olarak ve ayrıca gravimetrik olarak belirlendi.

Optimizasyon 2^3 faktorial dizayn ile gerçekleştirildi ve üç faktör (pH, metal iyonu derişimi ve tutunma akış hızı) dikkate alındı. Optimize edilen değerler lantan için pH 5, derişim 4 μg ml^{-1}, akış hızı 1,5 ml dak^{-1}; seryum için pH 6, derişim 0,25 μg ml^{-1} ve akış hızı 1,5 ml dak^{-1}'dir.

Reçine, iyi bir kimyasal kararlılık, tekrar kullanabilirlik ve hızlı dengeye ulaşmasıyla La(III) ve Ce(III) iyonlarının ayrılmasında ve önderiştirilmesinde başarıyla kullanıldı. Alkali metallerin, sıkça bulunan anyonların ve bazı ağır metallerin etkileri incelendi. Bunun yanında metot La(III) ve Ce(III) iyonlarının sentetik çözeltilerde yüksek güvenirlilikle sıralı ekstraksiyonda da uygulandı. Önerilen yöntem ile lantan için 830 ng l^{-1}, seryum için 250 ng l^{-1} belirtme alt sınırı ve lantan için % 2,27, seryum için %1,97 bağıl standart sapma sağlandı. Önderiştirme faktörleri La(III) ve Ce(III) için sırasıyla 125 ve 83'tür. Önderiştirme süreçlerinde lineer kalibrasyon aralığı lantan için 1,0-7,5 μg ml^{-1} ve seryum için 0,50-10,0 μg ml^{-1} 'dir. Ayrıca, yöntemin doğruluğunu belirlemek için deniz ve kuyu sularına uygulandı.

Anahtar sözcükler : Faktöriyel dizayn, katı faz ekstraksiyonu, lantanitler, önderiştirme, kaliks[4]resorsinaren, emdirme, Amberlite XAD-16.

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CHAPTER ONE
INTRODUCTION

1. The Lanthanides

The lanthanides are a group of 15 elements (with atomic number 57-71) which exhibit very similar chemical properties. The lanthanide series is named after lanthanum, and this element is often included in the series by convention. All Lanthanides are f-block elements except lutetium. A strict correlation between periodic table blocks and chemical series would include lanthanum in the series and place lutetium in the transition metals (Marczenko, 1986).

Lanthanides are chemically similar to each other, to scandium and yttrium, and to the actinides. The lanthanides are typically placed below the main body of the periodic table in the manner of a footnote. The full-width version of the periodic table shows the position of the lanthanides more clearly (Winter, 2005).

1.1 Chemical Properties

All the rare-earth elements occur in the +3 oxidation state in compounds, and can be separated and determined in this form. Rare-earth element hydroxides, $M(OH)_3$, precipitate from nitrate solution at pH values above 6.3-7.8 and reveal no amphoteric properties. The rare-earth elements yield acid-insoluble fluorides and oxalates, and soluble EDTA, tartrate, and citrate complexes. The lanthanides are all very reactive and electropositive. Despite the high charge, the large size of the Ln (III) ions results in low charge densities and their compounds are predominately ionic in character (Massart, & Hoste, 1963).

The ionic radii decrease smoothly across the series. This decrease in size is the famous 'lanthanide contraction'. The lanthanide contraction is caused by the increase in effective nuclear charge across the series due to the poor shielding ability of 4f electrons. This is seen in every period as a shell is filled (Winter, 2005). The Ln(III)

ions are class-a or hard in character so they tend to bond to O, N and F-donors with F preferred to Cl > Br > I (Winter, 2005).

The smooth decrease in the ionic radii results in a regular variation in chemical properties. As the Ln(III) radius decreases across the series, the salts become (somewhat) less ionic (Winter, 2005).

1.2 Lanthanum

Lanthanum is a chemical element in the periodic table that has the symbol La and atomic number 57. Lanthanum is silvery white, malleable, ductile, and soft enough to be cut with a knife. It is one of the most reactive of the rare-earth metals. It oxidizes rapidly when exposed to air. Cold water attacks lanthanum slowly, and hot water attacks it much more rapidly. The metal reacts directly with elemental carbon, nitrogen, boron, selenium, silicon, phosphorus, sulphur, and with halogens. It is a component of, misch metal (used for making lighter flints). Monazite (Ce, La, Th, Nd, Y)PO_4, and bastnasite (Ce, La, Y)CO_3F, are principal ores in which lanthanum occurs in percentages up to 25 percent and 38 percent respectively (Winter, 2005).

Naturally occurring lanthanum is composed of one stable (^{139}La) and one radioactive (^{138}La) isotope, with the stable isotope, ^{139}La, being the most abundant (99.91% natural abundance) (Winter, 2005).

1.2.1 Uses of Lanthanum

Carbon lighting applications, especially by the motion picture industry for studio lighting and projection. Small amounts of lanthanum added to steel improve its malleability, resistance to impact and ductility. Small amounts of lanthanum added to iron helps to produce nodular cast iron. A Small amounts of lanthanum added to molybdenum decreases the hardness of this metal and its sensitivity to temperature variations. Mischmetal, a pyrophoric alloy used e.g. in lighter flints, contains 25% to 45% lanthanum. The oxide and the boride are used in electronic vacuum tubes.

Hydrogen sponge alloys can contain lanthanum. These alloys are capable of storing up to 400 times their own volume of hydrogen gas in a reversible adsorption process. The other uses are petroleum cracking catalysts, gas lantern mantles, glass and lapidary polishing compound, La-Ba age dating of rocks and ores. Lanthanum Nitrate is mainly applied in specialty glass, water treatment and catalyst (Winter, 2005).

1.2.2 Environmental Effect of Lanthanum

Lanthanum has a low to moderate level of toxicity, and should be handled with care. In animals, the injection of lanthanum solutions produces glycohemia, low blood pressure and degeneration of the spleen and hepatic alterations (Winter, 2005).

Lanthanum has no known biological role. The element is not absorbed orally, and when injected its elimination is very slow. Lanthanum carbonate is being studied as a compound to absorb excess phosphate in cases of end-stage renal failure. Some rare-earth chlorides, such as lanthanum chloride ($LaCl_3$), are known to have anticoagulant properties (Winter, 2005).

1.3 Cerium

Cerium is a chemical element in the periodic table that has the symbol Ce and atomic number 58. Cerium is a silvery metallic element, belonging to the lanthanide group. It is used in some rare-earth alloys. It resembles iron in color and luster, but is soft, and both malleable and ductile. It tarnishes readily in the air (Winter, 2005). It occurs in its compounds in the III and IV oxidation states. Cerium (III) has the same chemical properties as all the other tervalent lanthanide ions. Cerium (IV) resembles thorum, zirconium, and uranium (IV) in many of its chemical properties but is also a powerful oxidant. White $Ce(OH)_3$ precipitates at pH 7.5, whereas yellow $Ce(OH)_4$ precipitates at pH ~ 1. Neither hydroxide is amphoteric. The stability of ceric compounds increases in alkaline medium. Cerium (III) can be oxidized in acidic

medium with bismuthate, silver (II) oxide, persulphate (in the presence of Ag^{+}), or bromate (in 9M HNO_3) (Marczenko, 1986).

Only europium is more reactive than cerium among rare earth elements. Alkali solutions and dilute and concentrated acids attack the metal rapidly. The pure metal is likely to ignite if scratched with a knife. Cerium oxidizes slowly in cold water and rapidly in hot water (Winter, 2005).

Because of the relative closeness of the 4f and outer shell orbitals in cerium, it exhibits an interestingly variable chemistry. For example, compression or cooling of the metal can change its oxidation state from about 3 to 4 (Winter, 2005).

Cerium is the most abundant of the rare earth elements, making up about 0.0046% of the Earth's crust by weight. It is found in a number of minerals including allanite (also known as orthite)—(Ca, Ce, La, Y)$_2$(Al, Fe)$_3$(SiO_4)$_3$(OH), monazite (Ce, La, Th, Nd, Y)PO_4, bastnasite (Ce, La, Y)CO_3F, hydroxylbastnasite (Ce, La, Nd)CO_3(OH, F), rhabdophane (Ce, La, Nd)PO_4-H_2O, and synchysite Ca(Ce, La, Nd, Y)(CO_3)$_2$F. Monazite and bastnasite are presently the two most important sources of cerium (Winter, 2005).

Large deposits of monazite, allanite, and bastnasite will supply cerium, thorium, and other rare-earth metals for many years to come (Winter, 2005).

Naturally occurring cerium is composed of 3 stable isotopes and 1 radioactive isotope; 136-Ce, 138-Ce, 140-Ce, and 142-Ce with 140-Ce being the most abundant (88.48% natural abundance). The isotopes of cerium range in atomic weight from 123 u (123-Ce) to 152 u (152-Ce) (Winter, 2005).

1.3.1 Uses of Cerium

In metallurgy cerium is used in making aluminum alloys and adding cerium to cast irons opposes graphitization and produces a malleable iron. In steels, cerium

degasifies and can help reduce sulfides and oxides. Cerium is used in stainless steel as a precipitation hardening agent. Cerium (IV) sulfate is used extensively as a volumetric oxidizing agent in quantitative analysis. Cerium compounds are used in the manufacture of glass, both as a component and as a decolorizer. Cerium compounds are used for the coloring of enamel. Cerium (III) and cerium (IV) compounds such as cerium(III) chloride have uses as catalysts in organic synthesis (Winter, 2005).

1.3.2 Environmental Effect of Cerium

Cerium, like all rare earth metals, is of low to moderate toxicity. Cerium is a strong reducing agent and ignites spontaneously in air at 65-80 ^{0}C. Cerium may react explosively with zinc, and its reactions with bismuth and antimony are very exothermic. Fumes from cerium fires are toxic. Water should not be used to stop cerium fires, as cerium reacts with water to produce hydrogen gas. Workers exposed to cerium have experienced itching, sensitivity to heat, and skin lesions. Animals injected with large doses of cerium have died due to cardiovascular collapse (Winter, 2005).

Cerium (IV) oxide is a powerful oxidizing agent at high temperatures and will react with combustible organic materials. While cerium is not radioactive, the impure commercial grade may contain traces of thorium, which is radioactive. Cerium serves no known biological function (Winter, 2005).

1.4 Separation Methods for Lanthanides

The determination of particular elements is usually preceded by their separation from the major components (matrix) of the sample and from other elements.

The most important methods for separating the rare-earth elements are based on precipitation, ion-exchange, liquid-liquid extraction (LLE) and solid phase extraction (SPE).

1.4.1 Precipitation

Precipitation methods for the separation of element are based on the differences in solubility of their compounds in aqueous solutions. Precipitation methods are used for separating trace elements alone, as well as for separating macro components from the traces. Trace elements are separated quantitatively from the solution by using collector (Marczenko, 1986).

Rare-earth elements (REE) may be isolated by precipitation as the oxalates, fluorides, or hydroxides. When the oxalates are precipitated from a weakly acidic medium (pH 1-4), calcium is used as a collector. Thorium is also precipitated with the REE, but can be masked with ethylenediaminetetraacetic acid (EDTA) at pH 3.2 (Gordon, Firsching, & Shaver, 1956).

1.4.2 Solvent Extraction

Solvent extraction separation is based on 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).

Rare-earth elements can be separated by extraction methods based on the thiocyanate, nitrate with tri-n-butyl phosphate and EDTA in the presence of

capriquat (trioctylmethylammonium chloride) complexes. The cerium-group elements have beeen extracted with di-isopentyl methyl-phosphonate (Fischer, Bramekamp, Klinge, & Pohlmann, 1964).

1.4.3 Ion-exchange

Separation and concentration of trace elements can be achieved by using synthetic organic ion-exchangers. Ion-exchange processes are based on the reversible exchange of ions between the solid ion-exchange resin and a liquid eluent. Separation depends on the differences in stability of complexes, and the associated differences in distribution coefficients. Generally, ion-exchangers consist of a matrix of cross-linked polymerized hydrocarbons, which contain ionizable functional groups. The functional groups in cation-exchangers are $–SO_3H$, -COOH, and –OH; those in anion-exchangers are $–NR_3^+$, $-NR_2$, -NHR, and NH_2 (Marczenko, 1986).

Rare-earth elements have been separated on the strongly basic anion-exchanger Amberlite IR-400 by taking advantage of the small differences in the stabilities of the EDTA complexes of the various elements. Trace amounts of lanthanides have been separated from uranium on Dowex 1 by using mixture of methanol with hydrochloric acid or acetic acid (Minczewski, & Dybczynski, 1962). Anion-exchange separation of REE in ortho-phosphoric acid medium has also been achieved (Polkowska-Motrenko, & Dybczynski, 1980).

Solvent extraction and ion exchange techniques have been mostly applied to the recovery and separation of metal ions. However, recovery and separation by solvent extraction requires multiuse extraction and back-extraction in order to get successful separation. Also, ion exchange resins have lower extraction selectivity for transition metals with respect to alkali metals.

1.4.4 Solid Phase Extraction

SPE is currently being used as a preconcentration or separation technique whenever complex matrices or low concentration analytes have to be analyzed. It is now the most common sampling technique in many areas of chemistry, including environmental, pharmaceutical, clinical food and industrial chemistry. The basic principle of SPE is the transfer of analytes from the aqueous phase to the active sites of the adjacent solid phase; it can also be termed solid-liquid extraction. The transfer is stimulated by the selection of appropriate optimal conditions in the system of three major components: water (liquid phase); analyte; and, sorbent. Either the analyte after sorption on the solid phase is desorbed with a suitable eluate or the analyte along with the sorbent is dissolved in a suitable solvent and further analyzed (Martinez, Cugat, Borrull, & Callul, 2000; Bruzzoniti, Sarzanini, & Mentássi, 2000).

Solid phase extraction is the presentation of an adsorbent in a convenient vehicle for the extraction of analytes from a matrix such as water. The adsorbent allows a fairly rapid flow through of the media. This is a solventless extraction and therefore reduces concentration requirements as well as solvent usage. Some solvent is required to flush the analytes from the adsorption bed unless SPE is used where the coated needle can be inserted directly into the injection port of the gas chromatography and the analytes desorbed there (Simpson, & Van Horne, 1993).

Over time, various sampling formats and sorbents have been developed to facilitate the convenient processing of different sample types and to extend the scope of the method. A high level of automation is also possible using robotics or on-line interfaces to separation and spectroscopic instruments. Full system integration for unattended extraction, separation and detection is possible, although flexible, inexpensive manual sample processing remains the more common practice in most laboratories (Pawliszyn, 2002; Simpson, 2000).

SPE is replacing LLE because of the several advantages that it offers, including: flexibility; low cost because of lower consumption of reagents; absence of emulsion;

speed and simplicity; sampling in the field; safety with respect to hazardous samples; and, ease of automation (Pyrzynska, & Trojanowicz, 1999).

1.4.4.1 Extraction Columns

SPE for liquid sample become a widely used laboratory technique in the early 1980s with the introduction of disposable cartridges containing silica based chemically bonded sorbents of a suitable size for sample processing by gentle suction. Typical cartridge devices consist of short columns (generally an open syringe barrel) containing a sorbent with a nominal particle size of 50-60 μm, packed between porous plastic or metal frits (Figure 1.1). Low-volume cartridge or pre-column devices are the basis of on-line hyphenated systems (SPE-LC, SPE-GC) for integrates sample processing and separation that matured into robust practical systems in the mid-1990s (Masque, Marce, & Borrull, 1998; Louter, Vreuls, & Brinkman, 1999).

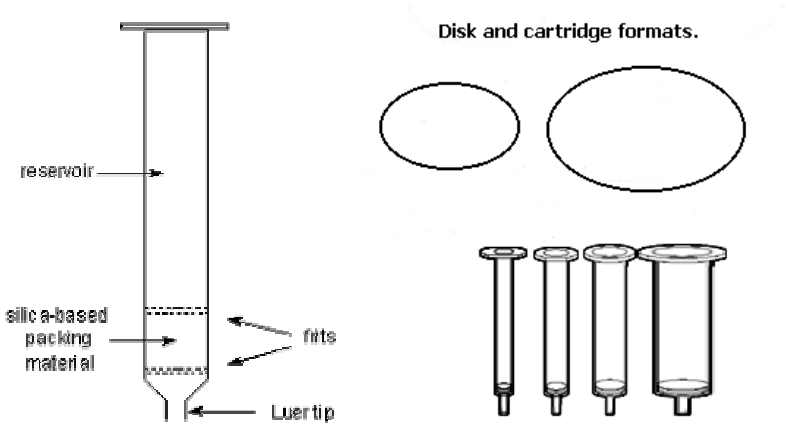


Figure 1.1 A solid-phase extraction column.

SPE discs were developed initially to provide higher sample processing rates for large sample volumes and to minimize plugging by suspended particles and matrix components. Since small-diameter discs are easily prepared, discs are also favored for handling small volume samples. At least three different disc formats are offered today. Particle-loaded membranes contain sorbent particles of 8—12 μm diameter

immobilized in a web of short poly tetrafluoroetylene (PTFE) fibrils. These are formed into 0.5 mm thick discs of various sizes containing about 90 % by weight of sorbent (Lingeman, & Hoekstra-Oussoren, 1997; Thurman, & Snavely, 2000; Fritz, & Masso, 2001).

1.4.4.2 Solid Sorbent

1.4.4.2.1 Selection of Solid Sorbent: The nature of properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for the solid sorbent are: (1) the possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions); (2) the fast and quantitative sorption and elution; (3) a high capacity; (4) regenerability; and (5) accessibility. In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacities. Hence, sorbents based on hydrophilic macroporous polymers and cellulose or on fibrous materials provide excellent kinetic properties (Camel, 2003).

Adsorption of trace elements on the solid sorbent is required for preconcentration. The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, chelation or ion-exchange. Also, for trace elements, ion-pair solid phase extraction may be used. Trace elements are usually adsorbed on solid phases through van der Waals forces or hydrophobic interactions. Hydrophobic interactions occur when the solid sorbent is highly non-polar (reversed phase). More recently, reversed polymeric phases have appeared especially the styrene-divinylbenzene copolymer that provides additional Π-Π interaction when Π-electrons are present in the analyte (Camel, 2003).

While elution of trace elements from the sorbent the same kind of interactions usually occurs during the elution step. This time, the type of solvent must be correctly chosen to ensure stronger affinity of the trace element for the solvent, to ensure disruption of its interaction with the sorbent (Camel, 2003).

Of prime importance is to selective elute only the target species. So, if they are more strongly retained on the sorbent than the interferent compounds, a washing step with a solvent of moderate elution strength is highly advisable before elution of the target species with the appropriate solvent (Camel, 2003).

1.4.4.2.2 Sorbent Types: It is convenient to divide sorbents for SPE into three groups: inorganic oxides; low-specificity sorbents; and, compound-specific and class-specific sorbents (Poole, 2003).

The most important inorganic oxides adsorbents for SPE are silica gel, alumina, Florisil (synthetic magnesium silicate) and diatomaceous earth (Barker, 2000).

Adsorbent properties that increase retention are a larger surface area and a high activity. Hydrogen-bonding functional groups are strongly retained (e.g. sulfonic acid, carboxylic acid, phenol and hydroxyl). Coating inorganic oxides with a complexing agent (e.g. silver nitrate, and caffeine) or an acid or base (an acid can be used for the selective isolation of bases and vice versa) can be used to modify selectivity for the isolation of target compound (Thurman, & Mills, 1998).

Low-specificity sorbents, which include chemically-bonded silicas, porous polymers and carbon, are commonly used for the isolation of contaminants from aqueous solution. Silica-based, siloxane-bonded sorbents can be prepares with a wide range of bonding density, pore size and functional group types. Silica gels of high surface area, 500-600 m^2 / g, are generally used to prepare sorbents for the isolation of small molecules. Siloxane-bonded sorbents with high surface areas, long alkyl chains and high phase loading maximize retention of small molecules from aqueous solution, while wide-pore materials with a low phase loading short alkyl chains are used to isolate macromolecules. Porous polymer sorbents are generally copolymers of styrene and divinylbenzene processed to enhance their properties for SPE. They are either similar in chemistry to porous polymers developed for HPLC and have moderate surface area (< 600 m^2 / g) or are biporous and highly crosslinked with surface areas of 700-1200 m^2/ g. The modern forms of carbon used for SPE are

graphitized carbon blacks and porous graphitic carbon. Graphitized carbon blacks are (largely) non-porous with moderate surface area of 100-210 m^2 / g (Poole, 2003).

Various selective sorbents based on ion exchange, bioaffinity, molecular recognition, and restricted access material are used. Ion-exchange sorbents are usually classified as weak or strong, depending on the identity of the ionic group and whether its charge is independent of the sample pH (strong ion exchanger) or can be manipulated by changing pH (weak ion exchanger) (Poole, 2003).

Restricted access sorbents were initially developed for the isolation of low-molecular-mass drugs from biological fluids with minimum sample pretreatment and now also find use in the isolation of herbicides from surface waters containing high levels of humic substance (Simpson, 2000).

Immunosorbents (or immunoaffinity sorbents) have long been used for sample pretreatment in medicine, biology and food science, but more general applications, such as to environmental samples. Immunosorbents are prepared by covalently bonding a suitable antibody to an appropriate sorbent (Delaunay, Pichon, & Hennion, 2000).

Molecular imprinting is a technique used for preparing polymers with synthetic recognition sites having a predetermined selectivity for a specified analyte (or group of similar analytes). The imprint is obtained by the polymerization of functional and crosslinking monomers in the presence of a template molecule (the analyte). The template-monomer system is chosen such that in solution the imprint molecule complexes one or several of the functional monomers, which then become spatially fixed in a solid polymer by the polymerization reaction. The resultant imprints possess a steric (size and shape) and chemical (spatial arrangement of complementary functional groups) memory for the template molecule (Simpson, 2000).

Polymeric adsorbents, which are sub-groups of low-specificity sorbents, are highly porous structures whose internal surfaces can adsorb and then desorb a wide variety of different species depending on the environment in which they are used. For example, in polar solvents such as water, polymeric adsorbents exhibit non-polar or hydrophobic behaviour and so can adsorb organic species that are sparingly soluble. This hydrophobicity is most pronounced with the styrenic adsorbents. In non-polar solvents, such as hydrocarbons, etc. most adsorbents exhibit slightly polar or hydrophilic properties and so will adsorb species with some degree of polarity. This polarity is most pronounced with the acrylic adsorbents and the phenolic adsorbents.

The efficiency of the polymeric sorbents depends on various physico-chemical parameters such as particle size, surface area, pore diameter, pore volume, degree of crosslinking and particle size distribution. The highly porous materials have higher real activity surface available which allows higher Π-Π interactions and so higher adsorption capacity. The band broadening with highly porous sorbents is only slightly greater than with other sorbents because porosity minimizes band dispersion. Band broadening is also minimized when working with sorbents with a narrower particle size distribution (Puig, & Barceló, 1996).

Macroporous hydrophobic resins of the Amberlite XAD series are good supports for developing chelating matrices. Amberlite XAD-1, XAD-2, XAD-4 and XAD-16 (Table 1.1) are polystyrene-divinylbenzene (PS-DVB) resins with a high hydrophobic character and no ion-exchange capacity. The broader range of pH stability of these resins increases the flexibility of the method, and they have no silanol groups (Bouvier, Martin, Iraneta, Capparella, Cheng, & Phillips, 1997).

XAD-1, XAD-2 and XAD-4 are PS-DVB with a highly hydrophobic character. XAD-7 and XAD-8 are acrylic ester resin with a higher affinity for solutes. XADs based on PS-DVB have some drawbacks including lack of selectivity, low breakthrough volumes for very polar compounds, and sampling rate, and they require extensive cleaning before use (Åkerblom, 1995).

Table 1.1 Some properties of Amberlite resins

Amberlite	**Chemistry**	**Surface area (m^2/g)**	**Av. pore diameter (Å)**	**Mean diameter (µ)**	**Applications**
XAD4	pStyDVB*	750	100	640	Removal of solvents and low MW species
XAD16	pStyDVB	800	150	700	Small molecules, antibiotic recovery
XAD1180	pStyDVB	500	400	530	Plant extracts, large MW product recovery
XAD1600	pStyDVB	800	150	400	Antibiotic recovery, chromatography
XAD7HP	Aliphatic ester	500	450	560	Plant extract, enzyme purification, peptides

*pStyDVB: polystyrene divinylbenzene

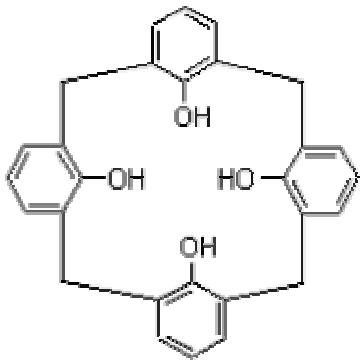
1.4.4.3 Chelating Agents

Several functional group atoms are capable of chelating trace elements. The atoms most frequently used are nitrogen, oxygen (e.g. O present in carboxylic, hydroxyl,

phenolic, ether, carbonyl, phosphoryl groups) and sulfur. The nature of the functional group will give an idea of the selectivity of the ligand towards trace elements (Camel, 2003).

Chelating agents may be directly added to the sample for chelating trace elements, the being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For that purpose, three different means are available: (1) the synthesis of new sorbents containing such groups; (2) the chemical bonding of such groups on existing sorbents; and (3) the physical binding of the groups on the sorbent by impregnation the solid matrix with a solution containing the chelating ligand (impregnated, coated or loaded sorbents). The latter remains the most simple to be used in practice. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent (Camel, 2003).

Different ligands (dithizone, thiocarbamate, calixarene, resorcinarene, chromotropic acid, etc.) immobilized or impregnated on a variety of solid matrices have been successfully used for preconcentration, separation and determination of trace metal ions.



Calixarenes have been extensively used as hosts for the complexation of lanthanide ions. Recently, it was described that calixarene derivatives substituted with three carboxylic acid groups form neutral complexes with lanthanide ions.

Calixarenes are popular building blocks in supramolecular chemistry. (Jun-Min, Chuan-Feng, Qi-Yu, & Zhi-Tang, 2004).

Recently, calixarenes, which are macrocyclic products of phenol-formaldehyde condensations, are amenable to chemical modifications at the upper or lower rim to yield new macromolecules and are effective ionophores that can selectively bind a range of metals. The use of calixarenes as extractants for many kinds of metal ions has been reported. The calixarene compounds, having a cone-type configuration, are found to be suitable as selective extracting agents for actinides. Solvent extraction of uranium(VI) and thorium(IV) ions using calix[4]arenes with phenolic functional groups have been reported. Ramkumar and his co-workers have studied the transport of uranyl ion across a bulk liquid membrane using calixarene and synergistic agents as carriers.

In addition to calixarenes, structurally related resorcinarenes, which are the macrocyclic products of resorcinol with aldehydes (except formaldehyde), form complexes with both cations and polar organic molecules. Until now, few reports on using these resorcin[n]arenes for extraction of metals have appeared. Several groups have studied the novel resorcin[4]arenes and their complexation with alkali metal ions especially potassium ions (Demirel, Merdivan, Pirinccioglu, & Hamamci, 2003).

1.5 Determination of Lanthanides

Determination of lanthanides is important from the point of view of their technological applications especially in metallurgy, ceramic, nuclear industry, geological materials and soils and sediments. Their determination in geological materials is helpful in mineral exploration program. Knowledge of geochemistry of these elements is also necessary for understanding different geological processes such as chemical fractionation, terrestrial evolution, etc. For all these purposes, the development of analytical methodologies for the separation and determination of these elements becomes essential (Raut, Jaison, & Aggarwal, 2004).

A lot of determinations of lanthanides in geological materials have been reported using mainly instrumental neutron activation analysis (NAA), X-ray fluorescence analysis (XRF), inductively coupled plasma source atomic emission spectrometry (ICP-AES) and lately inductively coupled plasma source mass spectrometry (ICP-MS) and spectrophotometric analyses using colored reagents (Ivanova, Djingova, Korhammer, & Markert, 2000).

The reagents which give color reaction upon which spectrophotometric methods are called spectrophotometric reagents. They can be grouped into two categories: organic and inorganic. The most important spectrophotometric reagents are dithizone and related reagents, azo reagents, triphenylmathane reagents, xanthene reagents, non-chelating organic reagents, dithiocarbamates, 8-hydroxyquinoline and derivatives, thiocyanate (Holzbecher, Divis, Kral, Sucha, & Vlacil, 1976).

The lanthanides in the +3 oxidation state have only very slight chromophoric properties, but, more sensitive spectrophotometric methods utilize colored many organic reagents. Arsenazo III method is the most important commonly used, but Arsenazo I and Xylenol Orange methods are also important (Eremin, & Bondarenko, 1972).

The absorbance of free Arsenazo III (λ_{max}=520-530 nm) at the absorption maxima of the metal complexes (λ=655-665 nm) is very slight. The large difference ($\Delta\lambda$) between the wavelengths of the absorption maxima of the complexes and free reagent is important (Marczenko, 1986).

Arsenazo III forms 1:1 complexes with bivalent or tervalent cation (e.g. UO_2^{2+}, Pb^{2+}, La^{3+}, and Ce^{3+}) and 1:1 or 1:2 complexes with quadrivalent cation (e.g. Th^{4+} and U^{4+}), depending on the pH and the excess of the reagent (Marczenko, 1986).

One half of the symmetrical Arsenazo III molecule complexes with a metal ion. The metal ion bonds to the nitrogen atom of the azo group, the oxygen atom of the arsenic acid group, and the oxygen atom of the hydroxyl group. The distortion of the

symmetry of the reagent molecule gives rise to two neighbouring absorption maxima in the visible spectra of the Arsenazo III metal complexes (Marczenko, 1986).

In weakly acidic media the lanthanides react with Arsenazo III to colored complexes which are the basis of this sensitive method. In weakly acidic solution, the reagent is violet, whereas its complexes with the rare-earth elements are green. The maximum absorbance for cerium (III) is obtained at pH 2.3-2.7. The optimum pH values for the various REE differ slightly (Marczenko, 1986).

The method has the advantage that the reagent does not absorb at the wavelength of the absorption maximum of the complex (650 nm). The molar absorptivity of the Arsenazo III complex with cerium is 5.6×10^4 (specific absorptivity 0.40). The other REE complexes have similar molar absorptivity (Marczenko, 1986).

Chloride, sulphate, and phosphate do not interfere in the determination of rare-earth elements with Arsenazo III. Neither do small amounts (less than 1 mg per 50 ml of solution) of titanium, aluminum, calcium, and iron [reduced to Fe (II) with ascorbic acid], but larger quantities of these metals and certain other metals (Th, Zr, U, Bi, Cu) should be removed. Many interfering metals can be masked with EDTA (Vdovenko, & Lisichenok, 1967).

1.6 Use of Factorial Design for Optimization

Experimental methods are widely used in research as well as in industrial settings, however, sometimes for very different purposes. The primary goal in scientific research is usually to show the statistical significance of an effect that a particular factor exerts on the dependent variable of interest.

Procedures for optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical and effective and allow more than one variable to be optimized simultaneously. This optimization can be accomplished using experimental designs, which can be of first or second order. The second order

designs have advantages, because they not only determine the influence of thevariables to be optimized on the response, but also enable the response function to be obtained and optimized (Araujo and Brrereton, 1996).

The Doehlert matrix is an optimization system, defined as a second order design for a process involving two variables (A and B) and an experimental response /Y), the model is described as:

$$Y = a + bA + cB + dA^2 + eB^2 + fAB$$

Where Y is the experimental response, A and B represent the variables to be optimized, a is an independent term, b and c are coefficients of the linear terms, d and e are coefficients of the quadratic terms and f is the coefficient of the interaction term. The identification of the critical points (maximum, minimum or saddle point) the Lagrange critierion in the equations obtained during the optimization process using experimental data (Lundstedt et al., 1998).

One of the problems with the preconcentration techniques has been optimization of the several factors that affect an extraction procedure. In most cases, a classical one-at-a-time method is applied, which may result in wrong conclusions if there are interactions between different factors. On the other hand, use of a method such as factorial design can reduce the number of experiments or provide much more information about the effect of different variables. The interest in the use of such optimization methods has substantially increased in recent years, such as: development of a procedure for preconcentration and determination of Ni with ICP-OES (Lemos et al., 2005); optimization process for simultaneous solvent extraction of several methods (Gazquez et al., 1998); extraction process using microwaves (Dagnac et al., 1998); optimization of adsorption conditions (Mobed and Chang, 1988).

1. 7 Related Studies

In 1998, Vicente and coworkers used flow injection–ICP-AES to determine lanthanum in urine by on-line preconcentration system. For the retention of lanthanum, quinolin-8-ol and Amberlite XAD-7 were used at pH 9.5. The lanthanum complex was removed from the micro-column with nitric acid. The value of detection limit for the preconcentration of 100 ml of aqueous solution was 0.09 ng ml^{-1} with a relative standard deviation (RSD) of 1.5%. The calibration graph using the preconcentration system for lanthanum was linear with a correlation coefficient of 0.9993 at levels near the detection limits up to at least 100 ng ml^{-1} (Vicente, Masi, Martinez, Olsina, & Marchevsky, 1998).

In 2002, Jain and coworkers used polymer supported calix[4]arene-semicarbazone derivative for separation and preconcentration of La(III), Ce(III), Th(IV) and U(VI). The resin exhibits good separating ability with maximum sorption between pH 2.5–4.5 for Th(IV) and between pH 5.5–7.0 for U(VI) whereas La(III) and Ce(III) were found to have maximum sorption between pH 6.5–8.5. The preconcentration factors for La(III), Ce(III), Th(IV) and U(VI) were 125, 130, 102 and 108, respectively. The relative standard deviation was between 96 and 98% with good analytical reliability (Jain, Handa, Pandya, Shrivastav,& Agrawal, 2002).

In 1998, Bruzzoniti and coworkers used ion chromatography to determine lanthanides. As an extension of our previous studies, in this work, an ion exchange method for the determination of rare earths in YbF_3 matrix, used for optical fibres manufacture, was improved. The separation has been performed on a mixed bed column, IonPac CS5 containing both anion and cation exchange sites, by oxalic and diglycolic acids eluents and post-column spectrophotometric detection (Bruzzoniti, Mentasti, & Sarzanini, 1998).

In 2005, Bahramifar and coworker studied the on-line column preconcentration technique with ICP-OES has been developed using a cartridge filled with octadecyl silica modified by 1-(2-pyridylazo) 2-naphtol to determine some rare earth elements

(Ce, Dy, La, Sm, and Y) and uranium in water samples. Detection limits based on three times of standard deviations of blank by 10 replicates were in the range of 11 ng l^{-1} for Dy to 69 ng l^{-1} for U. Recoveries of the REEs from natural water samples were between 95 and 106% with percent relative standard deviation of 1.0-7.9% (Bahramifar, & Yamini, 2005).

In 2005, Liang and coworker used ICP-AES after solid phase extraction to determination of La, Eu and Yb in water samples. Preconcentration of La, Eu, and Yb was achieved by sorption of their 1-phenyl-3-methyl-4-benzoylpyrazol-5-one complexes on a silica gel column at pH 5 and then eluting with 1.0 mol L^{-1} HNO_3. For the preconcentration of 100mL of aqueous solution, an enrichment of 100 was obtained for all analytes, and the detection limits for La, Eu and Yb were 82, 34 and 45 ng l^{-1}, respectively. The method has been successfully applied to the determination of La, Eu and Yb in lake water and synthetic seawater (Liang, & Fa, 2005).

In 2001, Jain and coworkers study pre-concentration, separation and trace determination of La(III), Ce(III), Th(IV) and U(VI) on polymer supported *o*-vanillinsemicarbazone. A nonionic polymeric adsorbent styrene divinylbenzene, Amberlite XAD-4 was functionalized with o-vanillinsemicarbazone and its analytical properties have been studied. The resin exhibits good chemical stability, reusability and faster rate of equilibrium for their determination by spectrophotometry and their simultaneous confirmation of the results by ICP-AES and graphite furnace-atomic absorption spectrometry. The detection limit of these metal ions on the resin is 100 ng cm^{-3} with recovery up to 96–98% (Jain, Handa, Sait, Shrivastav, & Agrawal, 2001).

In 2001, Jain and coworkers used polymer supported calix[4]arene-semicarbazone derivative for separation and preconcentration of La(III), Ce(III), Th(IV) and U(VI). The resin exhibits good separating ability with maximum sorption between pH 2.5–4.5 for Th(IV) and between pH 5.5–7.0 for U(VI) whereas La(III) and Ce(III) were found to have maximum sorption between pH 6.5–8.5. The preconcentration factors for La(III), Ce(III), Th(IV) and U(VI) were 125, 130, 102 and 108, respectively. The

relative standard deviation was between 96 and 98% with good analytical reliability (Jain, Handa, Pandya, Shrivastav, & Agrawal, 2001).

Jon and his group used a micro-column packed with immobilized 1-phenyl-3-methyl-4-bonzoil-5- pyrazone on nanometer Al_2O_3 powder as the adsorption material, the adsorption and elution behaviors of rare earth ions (Sc^{3+}, Y^{3+} and La^{3+}) on the above material under dynamic conditions were studied with ICP-AES. The detection limits of the method for Sc, Y and La were 0.16 mu g/L, 0.19 mu g/L and 0.39 mu g/L, respectively; and the relative standard deviation were 2.7%, 3.2% and 1.6%, respectively(n =9, C =0. 5 mg/L) (Jon, Pu, Jiang, & Hub, 2005)

Maheswari and Subramanian has developed a new extraction chromatographic method by grafting chloromethylated polymer support with 4-ethoxy-N,N-dihexylbutanamide, for the selective extraction of U(VI), Th(IV), La(III) and Nd(III) from highly acidic matrices. The developed amide grafted polymeric matrix shows good distribution ratio values even at high acidities, with the maximum metal sorption capacity values being 0.36, 0.69, 0.32 and 0.42 mmol g^{-1} for U(VI), Th(IV), La(III) and Nd(III), respectively, at 6 M HNO_3 mediumThe limits of analyte quantification using the developed method are in the range of 15-30 mg l^{-1}. The analytical data are within 3.8% relative standard deviation, reflecting the reproducibility and reliability of the developed method (Maheswari, & Subramanian, 2005) .

A method of glow discharge atomic emission spectroscopy is described for the determination of rare earth elements after separation and preconcentration by micro-column packed with immobilized 1-phenyl-3-methyl-4-benzoyl-5-pyrazone on microcrystalline naphthalene by Huang and coworkers. Under the experimental conditions selected, the detection limits for the determination of La, Nd, Eu, Dy and Y are 0.24, 0.32, 0.01, 0.07 and 0.06 μg/mL, respectively, with relative standard deviations in the range of 5-10% (Huang , Hu, Xiong, & Jiang, 2000).

8-Hydroxyquinoline immobilized on silica gel and RE-Spec, a supported organophosphorus extractant, were used to preconcentrate and purify rare earth elements from natural waters prior to their determination by isotope-dilution inductively coupled plasma mass spectrometry (Esser, Volpe, Kenneally, & Smith, 1994).

Takeshita and Nakano progressed a mathematical model for the breakthrough curve of metal ion on an extraction chromatographic column was proposed. Styrene-divinylbenzene copolymer gels impregnated with dihexyl-N,N'-diethylcarbamoyl methylphosphonate, octyl(phenyl)-N,N'-diisobutylcarbamoylmethylphosphine oxide and the equimolar mixture of CMP and CMPO were prepared. The column experiments for the extraction of Ce(III) from an aqueous solution containing nitrate ion were carried out. The predicted breakthrough curves of Ce(III) for the gels impregnated with CMP and the mixture of CMP and CMPO were in good agreement with the experimental ones. That for the gel impregnated with CMPO, however, overestimated the experimental data. The results suggest that the proposed model is applicable to the prediction of breakthrough curve and available as a design tool of extraction chromatographic column (Takeshita, & Nakano, 2000).

1.8 Objective of This Work

Determination of lanthanides is important from the point of view of their technological applications and industrial applications, especially in metallurgy, ceramic and nuclear industry. For all these purposes, the development of analytical methodologies for the separation and determination of these elements becomes essential.

The aim of this study was to develop a solid phase extraction method with chelating agent impregnated resin for enrichment and separation of La(III) and Ce(III) from solution samples applying factorial design in optimization. To achieve this goal we aimed at: (1) preparing of octacarboxymethyl-C-methylcalix[4]resorcinarene impregnated Amberlite XAD-16 resin; (2)

characterizing of octacarboxymethyl-C-methylcalix[4]resorcinarene impregnated Amberlite XAD-16 resin using FT-IR; (3) applying a factorial design to identify the effects of variables for recovery of La(III) and Ce(III); (4) controlling the effects of electrolytes and diverse ions; (5) applying the proposed method to synthetic and water samples.

CHAPTER TWO
EXPERIMENTAL METHODS AND MATERIALS

2.1 Preparation of Solid Phase by Impregnation

Octacarboxymethyl-C-methylcalix[4] resorcinarene synthesized by Demirel was used in this study (Demirel et al., 2003). The Amberlite XAD-16 resin (styrene-divinyl-benzene copolymer, surface area: 800 m^2 g^{-1}, pore diameter: 10 nm and bead size: 20-60 mesh) was supplied by Sigma. It was purified with 4 M HCl solution, after elimination of chlorides by washing with distilled water, with an ethanol-water (1:1) solution and finally with water again. Then the resin was dired in vacuum oven at 60 ^{0}C and stored in a polyethylene bottle.

Synthesis of octacarboxymethyl-C-methylcalix[4] resorcinarene (Figure 2.1) on Amberlite XAD-16: 1 g portion of dry Amberlite XAD-16 was placed in 50 ml of methanol (Merck) containing $0.6x10^{-3}$ mol octacarboxymethyl-C-methylcalix[4] resorcinarene and stirred for 24 hours. The resin was separated by filtration through a sintered glass funnel and was washed with a water to remove the solvent. The resin was used as an air-dried product.

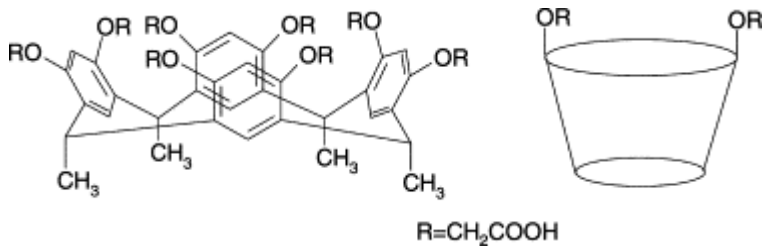


Figure 2.1 Chemical structures of octacarboxymethyl-*C*-methylcalix[4]resorcinarene.

2.2 Characterization of Solid Phase

The ligand content in the impreganated solution was determined by spectrophotometric measurement at 282 nm and also gravimetrically, by weighing

the dry ligand residue after removing the resin and evaporation of the solution. The amount of impreganated resin was calculated from the material balance.

The structural characterization of resorcinarene impregnated resin has been conducted with FT-IR. A Perkin Elmer Spectrum BX FT-IR spectrometer in the 4000-700 cm^{-1} range for group and finger print region, 30 coadded interferograms scanned at 2 cm^{-1} resolution was used. 1 mg of finely ground sample was intimately mixed with about 100 mg of dried potassium bromide (Merck, spectroscopy grade) powder by using an agate mortar. The mixture was then pressed in a special die at 700-800 kgf/cm^2. The pellet was investigated by FT-IR.

2.3 Preparation of Column

A Varian cartridge (polyethylene, 1.0 cm x 6.0 cm) equipped with 20 μm polypropylene frits was used for solid phase experiments.

0.1 g of Octacarboxymethyl-C-methylcalix[4] resorcinarene on Amberlite XAD-16 was firstly wetted with 5 ml methanol and stirred for 10 min, then 5 ml of doubly deionized water was added and stirred for 10 min again. Lastly, The mixture is transferred to the polyethylene column and 25 ml of methanol:water (10:90) is passed through the column. Before passing metal solution, column was washed with 20 ml of suitable pH solution.

2.4 Preconcentration Procedure of Optimization

The column technique was used to concentrate the investigated ions. For the sorption of these ions, the parameters were optimized using factorial design.

2.4.1 The Factorial Design Test

For performing the factorial design test, three parameters were chosen as variables and tested at two levels. The parameters were pH, concentration metal ion and

sorption flow rate. The high and low levels defined for them are listed in Table 2.1 and 2.2. Maximum and minimum levels of each factor were chosen according to data from previous experiments. For three variables with two levels for each variable, there are 2^3 or 8 possible combinations in a full factorial design.

Table 2.1 The factors included in the factorial design for La(III)

Variable	Low (-)	High (+)
pH	3	5
c_{La} (μg ml^{-1})	0.250	4.00
Flow Rate (ml min^{-1})	0.5	2

Table 2.2 The factors included in the factorial design for Ce(III)

Variable	Low (-)	High (+)
pH	3	6
c_{Ce} (μg ml^{-1})	0.250	4.00
Flow Rate (ml min^{-1})	0.5	2

An analysis of variance (ANOVA) test was used in order to identify the effect of individual factors and their second-order interactions. The full factorial designs were randomly performed in duplicate by fixing the amount of impregnated resin as 0.1 g. Experimental data were processed using SPSS 13.0 and Minitab statistical programs.

2.5 Optimization of the Stripping Procedure for Loaded Ions

After the sorption step the column was washed with 25 ml of doubly deionized water to remove any uncomplexed La(III) or Ce(III) from the resin bed. For the complete desorption of studied ions, type of desorption solution, its concentration and volume and desorption flow rate were tested.

For this purpose, different concentration of HCl and HNO_3 solutions varying from 0.001 to 0.02 mol l^{-1} were used. Additionally, the flow rate in the range of 0.5 to 2 ml min^{-1} and the volume required for the stripping solution were examined.

2.6 Procedure for the Determination of Lanthanum and Cerium

UV-1601 model Shimadzu uv-vis spectrophotometer in the range of 500-700 nm with 30 mm quartz cells. was used to determine La(III) and Ce(III) as M(III)–arsenazo III complex. pH measurements were made Ino Lab WTW model digital pH-meter.

0.1 % (w/v) Arsenazo III {3,6-bis[(2-arsonophenyl)-azo]-4,5-dihydroxy-2,7-nphthtalenedisulphonic acid} solution was prepared from an Aldrich sample. Standard stock solutions (1000 μg ml^{-1}) of lanthanum and cerium were prepared by dissolving the required amount of their nitrate salts ($La(NO_3)_3.6H_2O$, $Ce(NO_3)_3.6H_2O$, Aldrich) in doubly distilled water. Calibration standard solutions of La(III) from 1 to 5 μg ml^{-1} and Ce(III) from 1 to 8 μg ml^{-1} were prepared. KCl/HCl buffer solution having pH 2 was prepared by mixing 8.1 ml of 0.2 mol l^{-1} HCl and 41.9 ml of 0.2 mol l^{-1} KCl solutions and diluting to 100 ml with doubly distilled water. Reagent blank solution containing Arsenazo III and buffer solution was freshly prepared at each measurement.

Calibration solutions and sample solutions containing 1 ml of standard/sample solution + 0.2 ml of Arsenazo III solution + 1 ml of buffer solution were diluted to 5 ml with distilled water and measured at 653.5 nm for Ln(III).

Calibration curves of La(III) and Ce(III) were linear and the correlation coefficients were 0.9991 and 0.9978, respectively. At each measurement, fresh calibration curve was used.

2.7 Preparation of Electrolyte and Diverse Ion Solutions

The effects of common electrolytes and diverse ions on the recovery of La(III) and Ce(III) were studied. For this purpose, NaCl, $NaNO_3$, Na_2SO_4, $CaCl_2$, NaSCN, KCl, EDTA, NH_4Cl, Na_3PO_4, and Na_2CO_3 (0.001–1 mol l^{-1}, Merck/Riedel) and

$UO_2(C_2H_5O_2)_2.2H_2O$, $Th(NO_3)_4.6H_2O$, $FeSO_4.7H_2O$, $NiSO_4.6H_2O$, $CuSO_4$, $NiCl_2.6H_2O$, $Pb(NO_3)_2$ (5 – 50 μg ml^{-1}, Merck/Riedel) were used to prepare their working solutions.

2.8 Analysis of Synthetic Solutions and Water Samples

To check the applicability of the proposed method for preconcentration and determination of lanthanum and cerium, the impregnated resin was subjected to various synthetic solutions and water samples.

2.8.1 Preparation of Synthetic Solution

Fifty ml of 6 different synthetic aqueous solutions (Table 2.3) were prepared.

Table 2.3 Compositions of synthetic aqueous solutions

Composition of synthetic sample (μg ml^{-1})	**Added**	
	La(III) (μg ml^{-1})	Ce(III) (μg ml^{-1})
Fe (30), Ni (20), Th (2)	1	1
Th (1), U (2), Cu (40), Ni (40)	2	1
Fe (20), Pb (40), Zn (40), Cu (30), U (1)	2	2
Ni (30), Th (2), Zn (30), Pb (40), Cu (40)	2	3
Th(5), U(5)	5	-
Th(5), U(5)	-	5

2.8.2 Sampling of Water Samples

Seawater samples and well water samples were taken from Datça, Muğla. They were stored in refrigerator until analysis at 4 ^{0}C in polyethylene bottles by acidifying with 4 M HNO_3.

CHAPTER THREE
RESULTS AND DISCUSSIONS

3.1 Characterization of Solid Phase

The characterization and the sorption ability of octacarboxymethyl-C-methylcalix[4]resorcinarene impregnated Amberlite XAD-16 resin was controlled gravimetrically and taking UVand IR spectra.

By using UV absorption data of the clelating agent of resorcinarene before and after the impregnation on XAD-16 and also weighing the amount of filtrate having the unused resorcinarene after evaporation of the methanol, the maximum sorption of resorcinarene in the resin was found as 0.42 mmol g^{-1} dry XAD-16 resin.

Table 3.1 Some fundamental frequencies (in cm^{-1}) of Amberlite XAD-16 and resorcinarene impregnated resin

XAD-16	XAD-16-resorsinarene	Assignments
-	3445	OH-stretching
3086,3047,3019	3087,3054,3021	Aromatic CH-stretching
2921,2857	2965, 2926,2851	Aliphatic CH-stretching
-	1733	C=O stretching
1510,1485,1448	1509,1487,1447	C=C ring stretching
-	1409	OH bending
-	1122, 1080	C-O stretching

The IR absorption frequencies of XAD-16 and octacarboxymethyl-C-methylcalix[4]resorcinarene impreganated resin were given in Table 3.1. The IR spectrum of the loaded Amberlite XAD-16 was compared with that of free Amberlite

XAD-16. The carbonyl stretching vibration at 1733 cm^{-1} and the OH stretching vibration at 3445 cm^{-1} are observed sharply in the resorcinarene loaded resin. Additional bands observed are at 1409 and 1122 and 1080 cm^{-1} which belong to OH bending and C-O stretching groups, respectively.

3.2 Factorial Design Results

The proposed enrichment method is based on the solid phase extraction of lanthanum (III) and cerium(III) using resorcinarene impregnated XAD-16 resin. The flowing factors were evaluated: pH, concentration of metal ion and adsorption flow rate. Table 3.2 and 3.3 show the design matrix for eight experiments for La(III) and Ce(III). The recovery was defined as the dependent variable and the three selected factors as independent variables in these tests.

Table 3.2 Design matrix and the results of La(III) extraction

Runs	**pH**	**La(III) concentration**	**Sorption flow rate**	**Recovery (%)** R_1	R_2
1	+	+	+	94	91
2	+	+	-	99	98
3	+	-	+	96	98
4	+	-	-	100	99
5	-	+	+	60	63
6	-	+	-	66	65
7	-	-	+	69	68
8	-	-	-	71	73

Table 3.3 Design matrix and the results of Ce(III) extraction

Runs	pH	Ce(III) concentration	Sorption flow rate	Recovery (%) R_1	R_2
1	+	+	+	79	80
2	+	+	-	83	80
3	+	-	+	88	90
4	+	-	-	94	95
5	-	+	+	55	55
6	-	+	-	57	58
7	-	-	+	68	68
8	-	-	-	71	72

The ANOVA results for lanthanum produced the Pareto chart of main effects shown in Figure 3.1. Bar lengths are proportional to the absolute value of estimated effects, which helps in comparing the relative importance of effects. The interpretation of this chart demonstrates that the pH is only and highly significant. An increase in pH increases the extraction efficiency. The other factors have an insignificant effect. The effects of interactions can be also showed geometrically by analysis of the graph present in Figure 3.2. For three variables, corners of a cube can describe the eight experiments necessary to design application. The corner, which presents the recovery percent value of 99.5, is corresponding at levels combination (+,-,-) for all studied variables. In the opposite corner, the worst recovery can be found, which possesses a value of 61.5 %. This response corresponds at follow level combination (-,+,+). But similar high recovery percentage are seen at these level combinations (+,+,-), (+,-,+) and (+,+,+). So, two-level factorial design indicates that optimum procedure values to develop solid phase extraction procedure for lanthanum are 5 for pH, 0.25-4.0 μg ml^{-1} and 2 ml min^{-1} for flow rate.

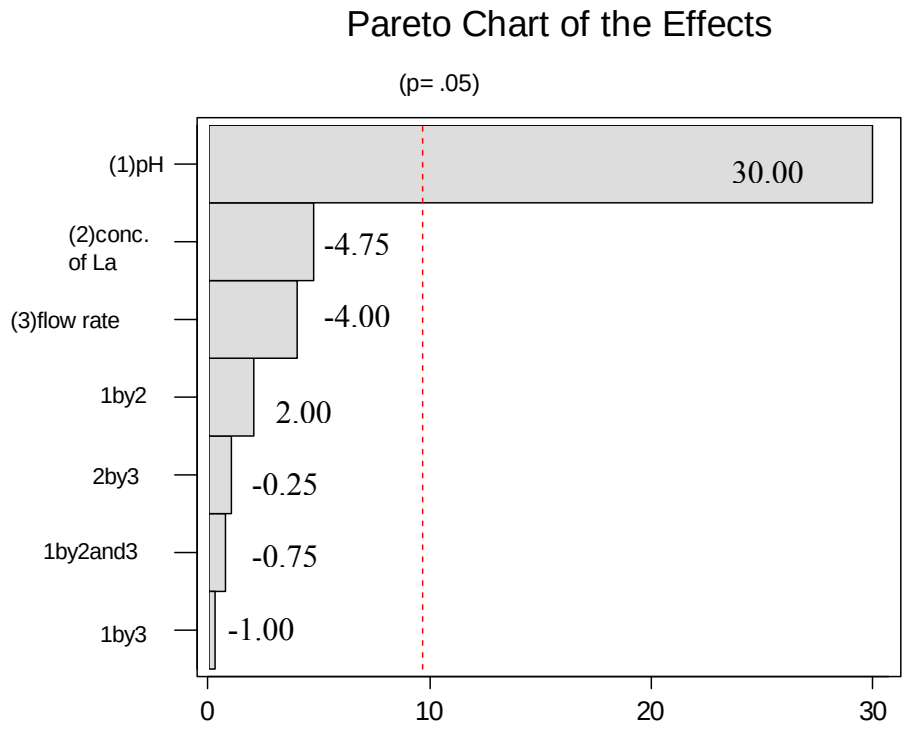


Figure 3.1 Pareto chart of standardized effects for variables in the lanthanum extraction.

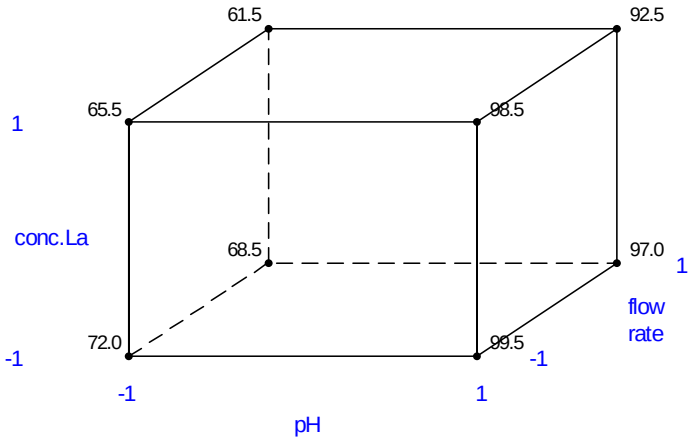
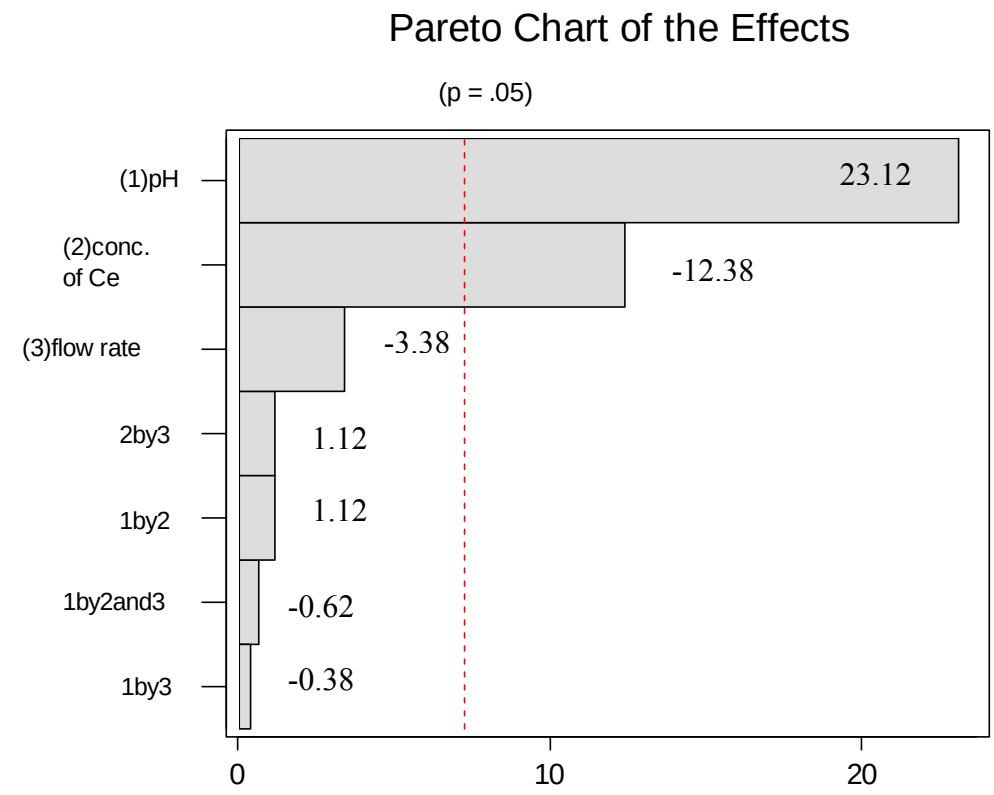


Figure 3.2 Cubic representation of the factorial design for the sorption of La(III).

The Pareto chart in Figure 3.3 demonstrates that pH and concentration of cerium provides a more significant effect for cerium extraction. An increase in pH and a decrease in concentration of cerium lead to higher extraction efficiency. The flow rate in the 0.5 – 2 ml min^{-1} range has no significant effect on the cerium extraction.

The effects of interactions for cerium are shown geometrically by analysis of the graph present in Figure 3.4. The corner, which presents the recovery percent value of 94.5, is corresponding at levels combination (+,-,-) for all studied variables. In the opposite corner, the worst recovery can be found, which possesses a value of 55 %. This response corresponds at follow level combination (-,+,+). The next high recovery percentages are seen at these level combinations (+,-,+), (+,+,-) and (+,+,+). So, two-level factorial design indicates that optimum procedure values to develop solid phase extraction procedure for lanthanum are 6 for pH, >4.0 μg ml^{-1} and 2 ml min^{-1} for flow rate for fast extraction.



”

Figure 3.3 Pareto chart of standardized effects for variables in the cerium extraction.

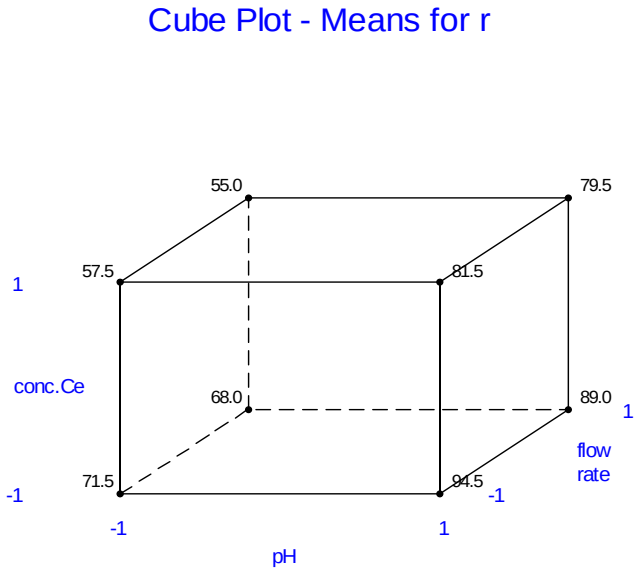


Figure 3.4 Cubic representation of the factorial design for the sorption of Ce(III).

3.3 Optimization of the Stripping Procedure for Loaded Ions

For desorption of La(III) and Ce(III) ions from the loaded impregnated XAD-16 resin, HCl and HNO_3 solutions at different concentrations from 0.001 to 0.02 mol l^{-1} were tested and the results were tabulated in Table 3.4. The better stripping was achieved by 0.005 mol l^{-1} HCl and HNO_3 solutions for La(III). In Ce(III) experiments, 0.015 mol l^{-1} HCl showed the highest recovery. In all desorption experiments, 0.005 mol l^{-1} HCl for La(III) because of its slightly higher effect and 0.015 mol l^{-1} HCl for Ce(III) were used. For complete recovery of loaded ions, the optimum volume of stripping solutions of 0.005 mol l^{-1} HCl for La(III) and 0.015 mol l^{-1} HCl for Ce(III) were controlled. Experimental conditions for optimization of stripping volume and flow rate were same as given in Table 3.5 and 3.6, respectively. The optimum stripping volume for La(III) and Ce(III) were found as 2 and 5 ml, respectively. After the optimization studies of desorption flow rate, 1.5 ml min^{-1} was used in all experiments for two ions.

Table 3.4 Results of stripping solutions for La(III) and Ce(III) loaded on impreganated resin

HCl concentration (mol l^{-1})	**HNO_3 concentration (mol l^{-1})**	**Recovery with HCl (%)**	**Recovery with HNO_3 (%)**
For La(III)			
0.001	0.001	76	57
0.002	0.002	97	88
0.005	0.005	99	98
0.01	0,01	98	93
For Ce(III)			
0.001	0.001	58	49
0.005	0.002	83	55
0.01	0.01	96	76
0.015	0.015	98	81
0.02		89	

Exp. conditions: c_{La} = 1 μg ml^{-1}, c_{Ce} = 2 μg ml^{-1}, 100 ml; pH 5 for La, pH 6 for Ce; 0.1 g resin

Table 3.5 Stripping volume of desorption solutions for La(III) and Ce(III)

Stripping volume (ml)	**Recovery (%)**	**Total recovery (%)**
For La(III)		
1	52	99
2	47	
For Ce(III)		
1	37	
2	30	
3	24	98
4	5	
5	2	

Table 3.6 Optimization of desorption flow rate of La(III) and Ce(III)

Desorption flow rate of La(III)		**Desorption flow rate of Ce(III)**	
Flow rate	Recovery (%)	Flow rate	Recovery (%)
0.5	98	0.5	98
1	97	1	97
1.5	98	1.5	98
2	89	2	92

3.4 Sorption Capacity and Distribution Coefficient

The sorption capacity of the resin was determined by a batch technique by equilibrating 0.1 g of the resin sample with 25 ml of 50 μg ml^{-1} La(III) or Ce(III) solution for 2 h at their optimum pH at room temperature. The loading capacity for lanthanum and cerium on the resin was calculated from the difference between the metal ion concentration before and after desorption. The metal sorption capacities of impregnated resin were 0.37 mmol g^{-1} for La(III) and 0.41 mmol g^{-1} for Ce(III). The distribution coefficients (K_D) of the metal ions, defined by the equation were determined by using the batch equilibration method. In the equilibration experiment,

25 ml of solution containing 400 μg of the metal ion in question at the optimum pH was treated with 0.1 g of fresh resin. The solution was stirred for 2 h at room temperature, filtered to remove the resin, and the metal ion content of the filtrate was determined spectrophotometrically. The distribution coefficients for lanthanum and cerium are 3687 and 3536, respectively.

$$K_D = \frac{\text{Amount of metal ion taken by the resin}}{\text{Amount of metal ion remaining in the solution}} X \frac{\text{Volume of solution}}{\text{Amount of resin taken}}$$

3.5 Exchange Kinetics

To determine the rate of loading of lanthanum and cerium on the resin, batch experiments were carried out under the following conditions: 0.1 g of resin was stirred with 10 ml of feed solution containing lanthanum or cerium at room temperature. The studied contact times are: 10, 30, 60, 120, 240 and 360 min. The concentration of metal ion in the filtrate solution and the amount of metal ion loaded on the resin phase was calculated by mass balance as μg g^{-1} resin. The loading half time $t_{1/2}$, defined as the time required to reach 50% of the resin's total loading capacity, was estimated from the curves (Figure 3.5). From the kinetics of lanthanum and cerium exchange, it was observed that an equilibrium time of about 1 h for La(III) and 30 min for Ce(III) were required for 96-98 % sorption. However, the time required for 50% sorption of lanthanum and cerium was 15 and 12 min. The faster uptake of these metal ions on Amberlite XAD-16-octacarboxymethyl-C-methylcalix[4]resorcinarene reflects a beter accessibility of the metal ions to the chelating sites in the resin.

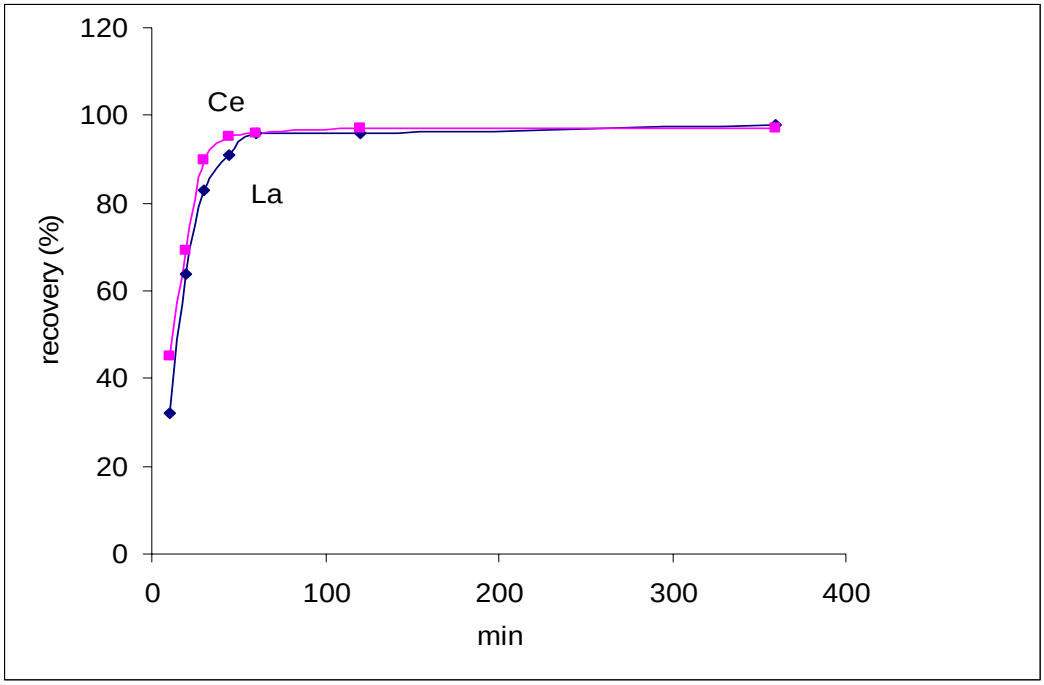


Figure 3.5 Kinetics of La(III) and Ce(III) binding by resorcinarene impregnated XAD-16: 2 μg ml^{-1}, 10 ml, pH: 6 for La(III) and 5 for Ce(III).

3.6 Stability and Reusability of the Resin

The La(III) and Ce(III) was sorbed and desorbed on 0.1 g of the resin several times. It was found that sorption capacity of octacarboxymethyl-C-methylcalix[4]resorcinarene impregnated resin after 40 cycles of equilibration changes by less than 2.5% indicating the possible reuse of resin for several cycles. The sorption capacity of the resin stored for more than 2 mounths under ambient conditions has been found to be practically unchanged.

3.7 Preconcentration of La(III) and Ce(III) on Amberlite-XAD-16-octacarboxymethyl-C-methylcalix[4]resorcinarene

The performance of the resin in column concentration of La(III) and Ce(III) may be assessed from their elution. The column concentration behaviour for studied two ions was evaluated in terms of the preconcentration factor (PF).

$$PF = \frac{\text{Concentration of metal in the stripping solution}}{\text{Initial concentration of metal in the feed solution}}$$

Quantitative collection of lanthanum and cerium was possible from a solution concentration order of 100 ng ml^{-1} with recovery up to 96-99%. The preconcentration factors for lanthanum and cerium were found to be 125 and 83, respectively. The results are also given in Table 3.7.

Table 3.7 Preconcentration factor for La (III) and Ce (III)

Feed solution (ml)	Concentration (ng ml^{-1})	Stripping solution (ml)	Recovery (%)	Preconcentration factor
500	100	4	99	125 (La)
500	100	6	96	83 (Ce)

Exp. conditions: pH 5 (La),pH 6 (Ce), resin 0.1 g, flow rate 1.5 ml min^{-1}, strip. soln 0.005 M HCl(La), 0.0015 M HCl (Ce).

3.8 Effect of Electrolytes and Diverse Ions

The effect of various electrolytes like NaCl, $NaNO_3$, Na_2SO_4, $CaCl_2$, NaSCN, KCl, EDTA, NH_4Cl, Na_3PO_4, and Na_2CO_3 on the sorption of La(III) and Ce(III) with Amberlite XAD-16-octacarboxymethyl-C-methylcalix[4]resorcinarene resin was studied. It was found that all the electrolytes were tolerable in the 0.1 – 0.75 mol l^{-1} concentration range except for sodium carbonate where it was only 0.001 mol l^{-1} for both metal ions. Their limit of tolerance was defined as the amount of electrolyte anion/foreign ion (cation) that caused an error of 2-3% in the recovery of metal ions. The results are given in Table 3.8.

The effects of commonly occurring cations in water samples like Ni(II), Pb(II), Fe(III), Cu(II), Zn(II) and some actinides Th(IV) and U(VI) by impregnated resin have been studied. In the sorption of 50 μg of lanthanum or cerium at their optimum pH, the tolerance limits of studied cations were summarized in Table 3.9. However, the separation of lanthanum(III) or cerium(III) from uranium(VI) or thorium(IV) was

achieved by sequential acid elution when taken in the same concentration ratio (125 μg, 25ml^{-1}) and measured spectrophotometrically using Arsenazo III. At higher concentrations the sorption was not quantitative and with low recoveries.

Table 3.8 Tolerance limits of electrolytes on the sorption of La(III) and Ce(III)on the resin.

	Electrolytes (mol l^{-1})							
Metal ion								
(50μg/50 ml)	NaSCN	NaCl	Na_2SO_4	Na_3PO_4	$NaNO_3$	Na_2CO_3	KCl	NH_4Cl
La (III)	0.225	0.25	0.25	0.10	0.25	0.001	0.75	0.25
Ce (III)	0.25	0.25	0.25	0.15	0.25	0.001	0.1	0.5

Table 3.9 Tolerance limits of cation on the sorption of La (III) and Ce (III) on the resin[a]

Cation	**Metal ion (50 μg / ml^{-1})**	
	La(III)	**Ce (III)**
Ni (II)	35*	25
Pb (II)	45	40
Fe (III)	40	35
Cu (II)	35	40
Zn (II)	35	30

[a] Experimental conditions: resin: 0.1 g; 50 ml, for La (III) pH 5, for Ce (III) pH 6.
* μg / ml^{-1}

3.9 Application to Analysis of Synthetic Aqueous Solutions and Water Samples

The proposed method has been applied to the determination of lanthanum and cerium from synthetic solutions. The results of synthetic aqueous sample solutions were tabulated in Table 3.10. The synthetic samples were prepared taking multiple mixtures of metal ions based upon their possible interference effect. The synthetic samples containing lanthanum, cerium and other metal ions were prepared in 50 ml solution. The separation and analysis of lanthanum and cerium was achieved successfully by a degree of 87-97%.

Further, the column effluents were analyzed for Lanthanum or cerium with common actinides such as uranium(VI) and thorium(IV). Quantitative separations were successfully achieved by sequential elution as shown in their separation patterns in Figure 3.6 and 3.7.

Table 3.10 Determination of La (III) and Ce (III) in synthetic samples

Composite of synthetic sample (mg / 50 ml)	**Concentration of La (III) and Ce (III) (µg ml^{-1})**			
	Added		Found[a]	
	La (III)	Ce (III)	La (III)	Ce (III)
Fe (1.5), Ni (1.0), Th (0.1)	1.0	1.0	0.97±0.01	0.93±0.02
Th (0.05), U (0.1), Cu (2.0), Ni (2.0)	2.0	1.0	1.92±0.03	0.92±0.01
Fe (1.0), Pb (2.0), Zn (2.0), Cu (1.5), U (0.05)	2.0	2.0	1.94±0.02	1.92±0.01
Ni (1.5), Th (0.1), Zn (1.5), Pb (2.0), Cu (2.0)	2.0	3.0	1.95±0.02	2.92±0.03
Th (5), U(5)	5	-	4.35±0.04	-
Th (5), U(5)	-	5	-	4.40±0.05

[a] Average and standart deviation from triplicate run.

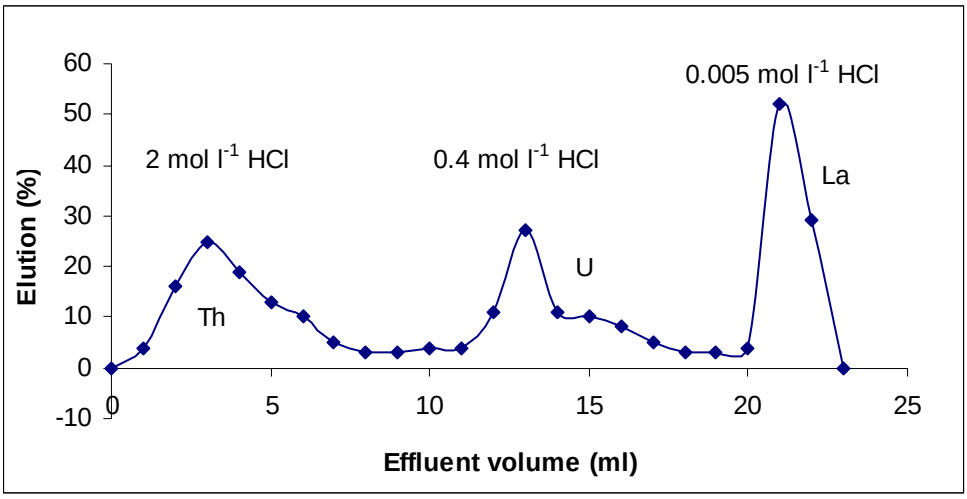


Figure 3.6 The elution profiles of La(III), Th(IV) and U(VI).

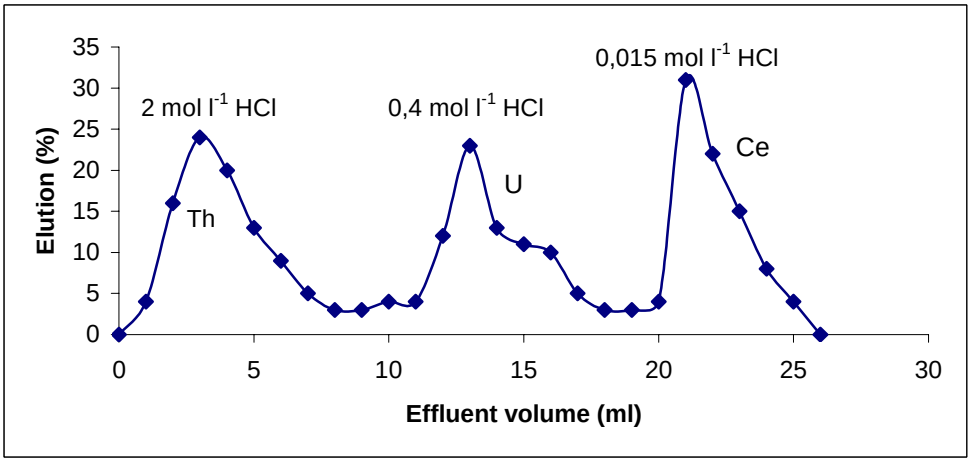


Figure 3.7 The elution profiles of Ce(III), Th(IV) and U(VI).

The accuracy of the developed preconcentration procedure was tested by a applying of standard addition technique to seawater and well-water samples.1 μg ml^{-1} of La(III) or Ce(III) was added to water samples and the recovery percentages were found within 88-97 % (Table 3.11). The recovery obtained displayed that the proposed procedure has good accuracy for both ions.

Table 3.11 Determination of La(III) and Ce(III) in seawater and well-water samples

	Concentration of La (III) and Ce (III) (μg ml^{-1})			
	La (III)		Ce (III)	
	Added	Found[a]	Added	Found[a]
Seawater*	-	0	-	0
	1.0	0.89±0.04	1.0	0.88±0.03
Well water*	-	0	-	0
	1.0	0.97±0.02	1.0	0.95±0.01

[a] Average and standart deviation from triplicate run.
*50 ml sample solution.

3.10 Analytical Figures of Merit

Under the optimum conditions, calibration range, relative standard deviation (RSD), detection limit and linear working equation found for the progressed preconcentration method for lanthanum and cerium were summarized in Table 3.12. The calibration curves were linear over the concentration ranges 1.0-7.5 and 0.5-10.0 μg $ml^{-1}$of La(III) and Ce(III), respectively. The precision of the 25 ml of 1 μg ml^{-1} of La(III) and Ce(III) in the proposed procedure was given as a relative standard deviation of 2.27 and 1.97%, respectively. The detection limit corresponding to three times the standard deviation of the blank as found to be 0.83 μg l^{-1} for La(III) and 0.25 μg l^{-1} for Ce(III). 10 replicates for precision calculation and 20 replicates for detection limit calculation was done. All statistical calculations are based on the average of triplicate readings except for each standard solution in the given range for each ion.

Table 3.12 Summary of analytical statistical data

	Lanthanum	**Cerium**
Linear working range (μg ml^{-1})	1.0-7.5	0.50-10.0
Detection limit (μg l^{-1})	0.83	0.25
RSD % (1 μg ml^{-1})	2.27	1.97
Linear working equation	A=0.1463C-0.0919	A=0.1083C-0.0074
Correlation coefficient (r^2)	0.997	0.998

3.11 Comparison with Other Methods

The octacarboxymethyl-C-methylcalix[4] resorcinarene impregnated XAD-16 resin exhibits highest, equal or sometimes lower preconcentration factor (PF) , higher sorption capacity (SC) and higher or equal detection limits (DL) and $t_{1/2}$ for La(III) and Ce(III) compared to other studies as seen in Table 3.13.

Table 3.13 Comparison of SPE preconcentraton procedures developed for La(III) and Ce(III)

Resin	**PF**		**SC (mmol g^{-1})**		**DL (ng l^{-1})**		**$t_{1/2}$ (min)**	
	La(III)	Ce(III)	La(III)	Ce(III)	La(III)	Ce(III)	La(III)	Ce(III)
This work	125	83	0.37	0.41	830	250	15	12
XAD-4-bicin resin (Dev, Pathak and Rao, 1999)			0.35					
PS-DVB-CH2-calix[4]-arene-semicarbazone (Jain et al., 2002)	125	130	0.0135	0.0103			10	12.5
Polymer supported calix[6]arene hydroxamic acid (Trivedi, Menon, Agrawal, 2002)		107		0.395				12
XAD-4-o-vanilinsemicarbazone (Jain et al., 2001)	95	97	0.016	0.018			9	8.5
XAD-7-quinolin-8-ol (Vicente, Masi, Martinez, Olsina, & Marchevsky, 1998)					90			
chloromethylated polymer support with 4-ethoxy-N,N-dihexylbutanamide (Mahesvari, & Subramanian, 2004)	225		0,32				3.7	

CHAPTER FOUR
CONCLUSION

One of the aims of this work was to develop the preconcentration and separation method for La(III) and Ce(III) ions using solid phase extraction.

Octacarboxymethyl-C-methylcalix[4]resorcinarene as chelating agent was used. It was impreganated on Amberlite XAD-16 resin. By IR analysis, the resulting resin was characterized. The sorption capacity of the ligand loaded resin was found as 0.42 mmol resorcinarene g^{-1} resin.

To get optimum preconcentration conditions, two-level full factorial design was carried out. Three variables (pH, metal concentration and sorption flow rate) were regarded as factors in the optimization. Results of the two-level full factorial design with 8 runs for lanthanum extraction, based on the variance analysis, demonstrated that the factor pH was statistically significant. For cerium extraction, the variance analysis revealed that pH and concentration of cerium was statistically significant.

Parameters optimized for sorption and desorption of lanthanum and cerium ions in aqueous samples using resorcinarene impregnated Amberlite XAD-16 resin were pH, flow rate, concentration of acid for desorption, sorption capacity, preconcentration factor, recovery percentage, distribution coefficient, relative standard deviation, $t_{1/2}$ for exchange, detection limit and linear working range. These are summarized in Table 4.1.

The octacarboxymethyl-C-methylcalix[4]resorcinarene impreganated on Amberlite XAD-16 resin shows good potential for the enrichment of lanthanum and cerium as evident from the preconcentration factors. This impregnated resin has good potential for trace enrichment of these ions from the column studies as compared to the earlier studies reported in Table 3.13.

Table 4.1 Parameters optimized for sorption and desorption of La(III) and Ce(III) on Amberlite XAD-16-resorcinarene resin

Parameters	**Metal ions**	
	La(III)	Ce(III)
pH	5	6
Sorption flow rate (ml min^{-1})	2	2
Desorption flow rate (ml min^{-1})	1.5	1.5
Conc. of acid desorption	0.005 mol l^{-1} HCl/HNO_3	0.015 mol l^{-1} HCl
Sorption capacity (mmol g^{-1})	0.37	0.41
Preconcentration factor	125	83
Average recovery (%)	99	96
RSD(%)[a]	2.27	1.97
Distribution coefficient	3687	3536
$t_{1/2}$ for exchange (min)	15	12
Linear range (μg ml^{-1})	1.0-7.5	0.50-10.0
Linear working equation	A=0.1463C-0.0919	A=0.1083C-0.0074
Detection limit (ng l^{-1})	830	250

[a]10 determination of 1.0 μg ml^{-1}

The solid phase extraction method has a good potential for the separation of lanthanum or cerium form host of co-existing alkali metals, common anions and some heavy metal ions.

The separation of lanthanum and cerium and also from common actinides such as uranium and thorium was achieved by sequential elution system using the resorcinarene impregnated resin.

The results obtained from the analysis of synthetic solutions and seawater and well water samples prove the reliability of the proposed preconcentration method for its application to various kinds of analytical matrix samples.

The resin has the advantage of faster rate of equilibrium, high stability and preconcentration factors. The loaded resin was recylcled many times without affecting its sorption capacity.

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