STUDIES ON SUPRAMOLECULAR ASSEMBLES AND THEIR APPLICATION

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DEVARSHI N. THAKER

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LIST OF ABBREVIATIONS

FT-IR	Fourier Transform Infra Red
INAA	Instrumental Neutron Activation Analysis
NAA	Neutron Activation Analysis
PAA	Photon Activation Analysis
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectrometry
GF-AAS	Graphite Furance - Atomic Absorption Spectrometry
HG-AAS	Hydride Generation - Atomic Absorption Spectrometry
ARS	Alizarin Red S
NMR	Nuclear Magnetic Resonance
THF	Tetrahydrofyran
HPLC	High Performance Liquid Chromatography
PVC	Poly vinyl chloride
CMPO	Octyl phenyl *N*,*N*-diisobutyl carbamoylmethyl phosphine oxide
UV-VIS-NIR	Ultra Violet-Visible-Near Infra Red
dipy	Dipyridyl
nm	Nanometer
ml	Millilitre
mp	Melting Point
mg	Microgram
ng	Nanogram
ε	Molar Absorptivity
λ_{max}	Wavelength of Maximum Absorbance

LIST OF AUTHOR'S PUBLICATIONS

- "Studies on Supramolecular Assemblies and Their Applications", Y. K. Agrawal and D. N. Thaker, Reviews in Analytical Chemistry, 26(4), 2007, 229-311.
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- Selective supercritical fluid extraction of titanium(iv) using calixarene hydroxamic acid and simultaneous on-line determination by inductively-coupled plasma-mass spectrometry (ICP-MS), Y.K. Agrawal, D.N. Thaker, Anal. Chim. Acta (Communicated).
- Extraction, preconcentration, separation, transportation and recovery of niobium(v) and tantalum(v) and trace determination by inductively-coupled plasma-mass spectrometry, Y.K. Agrawal and D.N. Thaker, Anal. Lett. (Communicated).

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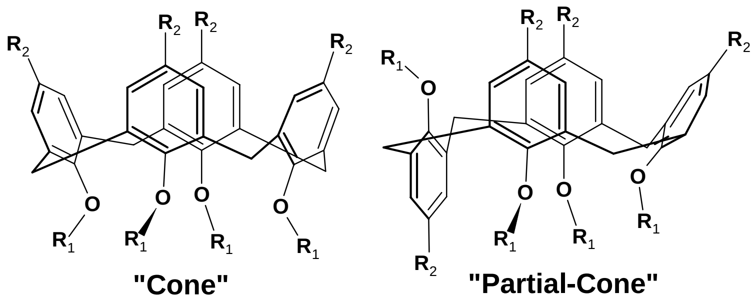
Chapter I

INTRODUCTION

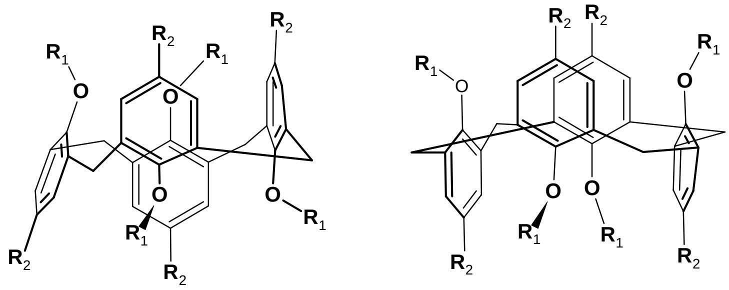
INTRODUCTION

A widely used module of supramolecular chemistry - Calixarene, has encouraged many research groups to work in this area because of its different structure and properties /1-8/. Lehn invented the term “supramolecule”, an organized, complex entity that is created from the association of two or more chemical species held together by intermolecular forces. Supramolecule structures are the result of not only additive but also cooperative interaction, including hydrogen bonding, hydrophobic interactions and coordination, and their properties are different (often better) than the sum of the properties of each individual component. Supramolecules offer numerous and diverse possibilities; as models for biological systems, synthetic ionophores or therapeutic reagents, selective extractive agents etc. The formation of new chemical structure by the assembly of molecular sub-units bound together by different forces such as hydrogen bond, ion-dipole and dipole-dipole interaction, Van der Wall’s interaction etc., have a major impact on current chemical research and will continue in the foreseeable future.

Calixarenes have been proved to be very important building blocks in supramolecular chemistry. Calixarenes have received special attention because their reparation and ability to undergo further synthetic elaboration. The easy chemical transformability of this molecule together with its “tunable” structure make calixarene an attractive candidate for molecular design strategies and has led to an increasing number of examples in the literature /1-23/. Calixarenes are cyclic oligomers of phenol units. Gutsche, a pioneer in calixarene chemistry coined the word “Calixarenes” in 1975, where “calix” means vase or chalice and “arene” indicated the number of aryl moieties in the macrocylic array. He explored these compounds as the potential candidates for new building blocks. The calixarenes are synthesized by acid catalyzed condensation of a variety of aromatic compounds. Among these, the aldehydes viz. formaldehyde, acetaldehyde, propionaldehyde etc. have been reported extensively. In the vicinity of metal complexes and analytical applications of calixarenes, lots of work has been done /9-23/. Calixarenes made up of phenol and methylene units have many conformational isomers because of two possible rotational modes of the phenol unit: the oxygen-through-the-annulus rotation and the para-substituent-through-the-annulus rotation. It has four different stable conformational isomers: “cone”, “partial-cone”, “1,2-alternate”, and “1,3-alternate” (Fig.1). These isomers give an enormous number of unique calixarenes with the different shape and the different size.



"Cone" "Partial-Cone"



"1,2-Alternate" "1,3-Alternate"

(Fig. 1) Four different stable conformational isomers of calix[4]arene

A synthetic chemist can synthesize calixarene based receptors according to the size of the metal cations, anions, neutral ions or molecules which he wants to isolate even with high selectivity.

A trace level concentration Mn(II) was quantitatively extracted at pH 6.0 with 1×10^{-4} M of hexaacetatocalix(6)arene in hexane /24/. Mn(II) from the organic phase was stripped with 2M sulfuric acid and determined as its iodo complex spectrophotometrically at 545 nm /24/.

Syntheses and binding characters with different metal of Calix[2]uracil[2]arene was studied /25/.

Syntheses, spectroscopic properties, molecular structures, and complexation of novel calix[4]arene imido compounds with molybdenum and tungsten are described. /26/.

Solvent extraction of Ag(I) and Pd(II) ions with 37,38,39,40,41,42-hexakis(acetomethoxy)-5,11,17,23,29,35-hexakis(1,1,3,3-tetramethyl-butyl)calix[6]-arene, 5,26,-27,28-tetrakis(acetomethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethyl-bu-tyl)calix[4]arene, *p*-(1,1,-3,3-tetramethylbutyl)-phenoxyacetone as a monomeric analog, from highly concentrated HCl or HNO_3 into chloroform was investigated. For comparison, the corresponding carboxylate derivatives and the unmodified calixarenes were also examined. Since both Ag and Pd ions strongly form complexes with chloride anions, the extraction of both metals was found to be suppressed in highly acidic media. Among the compound employed in the present work, tetrameric ketone was found to be capable of selectively extracting silver over palladium at about 1 mol dm^{-3} HNO_3 and was suitable for removing traces of silver from a large excess of palladium. It was suggested from the observation of the chemical shift of proton nuclear magnetic resonance that the ketonic derivative of calix[4]arene forms a complex with silver ion surrounded by phenoxy oxygen and carbonyl groups /27/.

The introduction of four carboxylate groups into calix[4]arenes made it possible to produce more selective complexone for the lanthanide ions as compared to complexones based on polycarboxylic acids /28-30/.

Preliminary binding properties of Schiff-base-p-tert-butylcalix[4]arenes were tested by solvent extraction of alkaline, alkaline earth metal, Mn, Fe, Co, Ni, Cu, Cd, Pb, Y, Pr, Nd, Eu, Gd, Yb picrates into dichloromethane in neutral conditions. Heavy metal cations are better extracted with higher preference for Pb(II) /31-32/.

A group of new calix[4]arenes with two *N*-(X)sulfonylcarboxamide groups of 'tunable' acidity that exhibit good extraction selectivity for Pb(II) over alkali and alkaline earth metal cations, as well as Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) /33/ with other which have different pendant functional groups [*N*-(X)sulfonylcarboxamide, carboxylic acid, ester, ether, phenol] were synthesized /34/.

1,3-Lower rim Se-bearing calix[4]arenes were synthesized and they showed high selectivity towards Ag(I)/35/.

The synthesis and physico-chemical characterization of three novel calixphyrin–ferrocene conjugates and a first insight into their electrochemical recognition properties was reported. The copper and zinc complexes of the porphodimethene were synthesized and characterized /36/.

New designer ligands calix[4]azacrown were synthesized and their solid state structure was determined. Complexation behaviour and their selectivity for Fe(III) and Cu(II) suggests that macrocycles based on a calixarene platform may act as versatile ligands for the selective recognition of metal cations /37/. Synthesis of a new fluorescent chemosensor for Hg(II) based on a dansyl amide-armed calix[4]-aza-crown was reported /38/. Fluorescence and complexation studies of calix[4]arene derivatives with zinc were carried out /39/.

A study of extraction of Ag(I) with different calixarene amine derivatives and distribution experiments in the absence and in the presence of calix(4)arene amine derivatives were carried out /40/.

Calixarene-based hyperbranched molecules with an N,S-multidentate ligand core was synthesized and its capability to bind with metal ions was also studied /41/.

A fluorogenic cone calix[4]triazacrown-5 bearing two pyrene amide groups and its structural analogue have been prepared. The fluorescence intensities of both monomer and excimer were also studied after complexation with Pb(II) and Co(II) /42/.

The synthesis of four diamide derivatives of the ***p***-tert-butylcalix[4]arenes from various primary amines were reported /43/. Their complexing properties of toward $Cr_2O_7^{2-}$ /HCr_2O^{7-} anions were also studied. Synthesis of three new bisazocalix[4]arene derivatives and their extraction properties was reported /44/.

A novel calix[4]arene derivative bearing two spirobenzopyran moieties in the lower rim, can recognize lanthanide ions. Alternating irradiation with ultraviolet and visible light controls the ligand-to-metal charge transfer (LMCT) and energy transfer of the host–Eu(III) complexes. Thus, fluorescence of Eu(III) can be switched on and off through light. The system may be applied as molecular logic switches /45/.

The influence of the concentration of dimethylaminomethylated calix[4]resorcinolarene, pH, supporting electrolyte, and additions of 1,10-phenanthroline to the organic phase on the distribution of Eu(III) and Am(III) between the aqueous and organic phases was studied /46/.

The first structural authentication of *p*-sulfonatocalix[8]arene shows the large host to adopt a 'pleated loop' conformation in the solid state was reported. Each resulting 'groove' in the macrocycle is occupied by a 4,4'-dipyridine-N,N'-dioxide molecule in an extended multicomponent La(III) 3D coordination polymer /47/. The nature of the reaction intermediate appearing during the transformation of the monometallic complex of europium and calixarene was reported /48/.

The ring inversion process was used as a probe of the mechanistic interactions of p-sulfonatocalix[4]arene with metallic cations /49/. The kinetics of the ring inversion interacting with Ca(II) and La(III) were investigated in water and water–acetone solutions following the exchange between the axial and the equatorial methylene protons by ^{1}H NMR.

Reaction of *p*-tert-butyloctahomotetraoxacalix[8]arene (LH_8) with uranyl nitrate hexahydrate in the presence of rubidium hydroxide to give a mixed complex that can be viewed as a tetrauranate dimer containing four disordered rubidium ions and water molecules. The resulting octanuclear complex presents an unprecedented geometry evidencing the assembling potential of uranyl ions /50/.

The separation of U(VI) from aqueous solution by textile bound uranophile calix[6]arenes is possible at pH ≥4. A maximum of 7.6×10^{-7} mol uranium per 1 g of the calixarene modified textile is bound at pH 5. The influence of competing ions on the uranium separation at pH 5 is very small. However, at pH 7 in carbonate rich waters calcium ions have a competing effect. Under environmentally relevant pH conditions the uranium is strongly bound to the calixarene modified textile. Under acidic conditions an almost complete regeneration of the calixarene modified textile is possible. The regenerated material can be utilized for further uranium separation cycles /51/.

A new series of the cone-shaped tetraalkoxycalix[4]arenes substituted at the wide rim with four phosphomethyl groups have been synthesized by the Arbuzov, Michaelis–Becker and Aterthon–Todd reactions of the chloromethyl or phenylhydrophosphinylmethylcalix[4]arenes /52/. Their binding properties towards Eu^{3+} and Am^{3+} cations were investigated by the liquid–liquid extraction method.

New mixed-ligand yttrium derivatives of calixarenes were synthesized, which could serve as the starting compounds for the synthesis of the corresponding alkyl derivatives stabilized by calixarene ligands and their structure and properties were established /53/.

The existence of a strong synergic effect in the extraction of europium in the title system using the cone conformation has been found /55/. After reviewing the results obtained from that extraction behavior prompted the present investigation of the influence of the type of the conformation of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis[(ethoxy-carbonyl)-methoxy]-2,8,14,20-tetrathiacalix-[4]arene on the distribution of metals in this synergic solvent extraction system. Three conformations have been synthesized: cone, partial cone and 1,3-alternate /56/. To study extraction results of modified cone conformation some typical nuclear fission products Eu, Sr and Cs and some other metals (e.g., radioactively spiked Ba and Co) were chosen /54/.

By preparing calixarene monolayers on gold electrodes a sensing mechanism for uranium has been developed /57/. The methodology has shown excellent response to laboratory generated uranium solutions and with real uranium containing wastes.

A self-assembled hydrophilic calix[6]arene monolayer was designed for uranyl ion detection. The uranyl ion recognition-function of the calix[6]arene monolayer was evaluated using surface plasmon resonance (SPR) at various concentrations of uranyl ions in 0.1 M Tris-HCl buffer solution. Calix[6]arene monolayer showed good sensitivity and selectivity to detect very low concentration of uranyl ions /58/.

Molecular Dynamics Simulations of *p*-sulfonatocalix[4]arene complexes with inorganic and organic cations in water and its structural and thermodynamic study were reported /59/.

New analogues of calix[4]arenetetrasulfonate were prepared, in which the methylene bridges are replaced by S and SO_2 . The complexation ability of these calixarene ligands toward Tb^{3+} ion and luminescence properties of the resulting complexes were examined. All the ligands formed complexes with lanthanide ions [Pr(III), Sm(III), Eu(III), Tb(III) and Dy(III)], among which the Tb(III) complex exhibited strong energy transfer luminescence /60/.

Magnetic silica particles with covalently attached CMPO [octyl phenyl N,N-diisobutyl carbamoylmethyl phosphine oxide] derivatives on the surface, which allow for the evaluation of the preorganization effect of chelating ligands through direct comparison of calixarene and single ligand CMPO derivatives. Efficient extraction of americium and europium from simulated nuclear waste conditions has been achieved by CMPO-calix[4]arenes together with surprisingly high levels of cerium extraction /61/.

The synthesis of two polymer supported calix[4]arenes, using TentaGel S NH_2 /62/ and aminomethyl polystyrene, have been significantly improved by the replacement of thionyl chloride and excessive amounts of solvents with carbodimide coupling reagents. The extraction efficiencies of uranium and cadmium by these polymer supported calix[4]arenas demonstrate an additional green aspect the work /63/.

A novel double-armed calix[4]arene derivative has been synthesized by the reaction of 1,3-alternately lower-rim-modified bis(2-

aminoethoxy)-substituted calix[4]arene with ***o***-vanillin in 90% yield and complexed with light lanthanoid(III) nitrates /64/.

The new narrow-rim functionalized calixarene based has been synthesized. Complexes with Ln = Eu, Gd, Tb, and Lu have been isolated and their crystal structure shows that metal ion encapsulated in the cavity formed by the four arms /65/.

The complexing properties of two lower rim calix(4)arene derivatives /66/ toward La, Sc and Yt cations in acetonitrile and in ***N***,***N***-dimethylformamide at 298.15 K were investigated.

The alkylaminomethylated calix[4]resorcinarene derivatives, modified by dimethylamino-, piperidyl- and trimethylammonium moieties, have been synthesized and their efficiency towards lanthanide ions was studied and compared with the calix[4]resorcinarene /67/. Both calix[4]resorcinarene and its derivatives have been shown synergistic affect to lanthanide ion extraction from neutral aqueous solutions by 1,10-phenanthroline through outer-sphere interaction of lanthanide bis-phenanthrolinate cations with deprotonated forms of calix[4]resorcinarene.

A dinuclear trivalent uranium complex and a mixed-valence U(III)/U(IV) complex have been prepared by using the $[(-CH_2-)_5]4$-calix[4]tetrapyrrole tetraanion /68/. Calix[4]arenes /69/ synthesized by Böhmer et al., containing four carbamoylphosphine oxide groups at the macrocyclic wide or narrow rims. These calixarenes exceed the CMPO extractant (i-$Bu_2NAC(O)ACH_2AP(O)Ph(Oct)$) developed for the

TRUEX (transuranic elements extraction process), by more than two orders of magnitude in the extraction of actinides (Np, Pu, Am). Calixarenes containing monodentate $Ph_2P(O)CH_2$ groups at the lower rim is also a better extractant for actinides than the ungrafted Oct_3PO or CMPO ligands do /70/. Calixarenes containing $Ph_2P(O)CH_2$ groups at the wide rim are less efficient than their analogues with the same groups at the narrow rim and surpass only slightly trioctylphosphine oxide /71/. However, modeling of an analogue of points to the 'possible cooperative participation of four phosphoryl groups of lignad in the complexation of hard metal cations, leading to a high ionophoric efficiency /72/.

Extractability, extraction equilibria and extraction constants of lanthanide and actinide ions was reported /73/. The ligands differ in the number and position of carboxylic acid and amide groups.

A method for speciation, preconcentration and separation of Fe(II) and Fe(III) in different matrices was developed using solvent extraction and flame atomic absorption spectrometry /74/.

Study of the electrostatic attraction between host *p*-sulfonatocalix[4]arene and seven rare-earth-metal cations representative of lanthanide series and two alkaline earth metal cations was reported /75/.

A new tri-anionic ligand was developed using a calix[4]arene as a shaping unit which binds lanthanide(III) cations to form 1:1 and 2:2 (M:L) complexes in a concentration-dependent equilibrium /76/.

The complexation of *p*-*tert*-butylcalix[4]arene tetraethanoate, *p*-*tert*-butylcalix[4]arene tetramethyl ketone, and *p*-*tert*-butylcalix[4]arene tetraacetamide and trivalent cations was investigated in acetonitrile and *N*,*N*-dimethylformamide at 298.15 K /77/.

Computing the distribution of radioactivity inside the nuclear plants bulk concrete needs techniques providing accurate element concentrations. In order to investigate the elements of interest for the decommissioning process, A. Gaudry ***et al.*** used four multielement analytical techniques: thermal neutron activation analysis, epithermal neutron activation analysis, ICP-AES and ICP-MS. INAA is the most useful technique for the analysis of metal iron in reinforcing bars /78/.

A very sensitive voltammetric procedure for the determination of trace zirconium is described, based on the adsorptive accumulation and the electrochemical oxidation of the zirconium(IV)-alizarin red S complex on the carbon paste electrode surface /79/.

The possibilities of instrumental PAA (Photon Activation Analysis) for multielement analysis using photoexitation and other photonuclear reactions were reviewed and compared with those of instrumental NAA (Neutron Activation Analysis), namely for geological materials. The need and usefulness of radiochemical PAA procedures are also discussed /80/.

Two different analytical techniques NAA and ICP-MS were used for multi-element analyses of the major and trace elements in environmental samples /81/. The concentrations of most elements determined by both methods are in good agreement, even if the concentrations of the elements in the samples have wide ranges of variation.

A quantitative analysis has been carried out to determine the concentration of Zr(IV) ion in aqueous solution by using alizarin red S (ARS) as reagent to form ARS-Zr complex /82/. Characterization of ARS-Zr complex gives a dynamic Zr(IV) concentration range of 5–35 mg/l. The use of artificial neural network (ANN) was able to extend the dynamic concentration range of Zr^{+4} to a larger range of 5–200 mg/l.

Membrane filtration equipment was used to evaluate zirconium and hafnium separation efficiency by a membrane separation process. High rejection of Zr and Hf species in aqueous solution were obtained with nanofiltration and ultrafiltration membranes. Enhanced transportation across the nanofiltration and ultrafiltration membranes was observed when aminocarboxylic ligands, like EDTA, were introduced in the solution /83/. The reported enhancement could be explained by a depolymerization process of the polynuclear complexes induced by the ligands.

The solid phase adsorbent, cross-linked chitosan-3,4-dihydroxy benzoic acid (CCTS-DHBA) resin, allows a rapid, precise, and relatively selective collection and enrichment of trace and ultra-trace amounts of uranium in tap water, river water and seawater samples /84/. This newly synthesized resin offers high adsorption capacity for the uranium(VI) of 330 $mg.g^{-1}$ resin.

A novel resin is reported for simultaneous preconcentration and determination of ultratrace Zr, Hf, Nb, Ta and W in seawater, both in the form of dissolved and acid-dissolvable species /85/. 8-Hydroxyquinoline bonded covalently to a vinyl polymer resin, was used in a chelating adsorbent column to concentrate the metals.

As metal levels in human specimens reflect the total exposure from all sources possible, their determination is a good way to estimate metal influences on health. For calculating risks resulting from environmental and/or occupational pollution, urinary reference concentrations for the normal population are needed to compare with data of exposed persons. The urinary levels of seven trace elements (Al, Co, Cr, Mo, Nb, Ni, Ti) were determined by atomic spectrometric methods (ICP-MS and GFAAS) in 100 urine samples of the Viennese population /86/.

A novel organic reagent 3-(8-quinolinylazo)-4-hydroxybenzoic acid (QAHBA) was synthesized for chemically modified nanometer-sized alumina, and it was characterized with infrared spectrum and ^1H NMR spectra. By using modified nanometer-sized alumina as micro-column packing material, a new method of flow injection (FI) on-line preconcentration coupled to ICP-OES was developed for simultaneous determination of trace metals (Ag, Pd, Au, Ga, In and Nb) in geological and environmental samples. The effects of pH, sample flow rate, sample volume, elution and interfering ions on the recovery of the analytes have been investigated /87/.

A niobium-selective Amberlite XAD-7 resin with a sulfinyl-type calix-ligand /88/ is reported and it allows the separation of niobium(V) and tantalum(V) without addition of a high concentration of hydrofluoric acid, which is preferable in terms of human-health safety. 18 partly commercially available samples of rock salt were investigated with respect to their content of trace elements using instrumental neutron activation analysis /89/.

Validation of an inductively coupled plasma mass spectrometry (ICP-MS) method for the determination of cerium, strontium, and titanium in ceramic materials used in radiological dispersal devices (RDDs) is reported /90/. This work demonstrates that, ICP-MS instrumentation is a good analytical alternative to INAA for the measurement of the aerosolized ceramic collected on air filters.

The new electrolytic dissolution in batch of aluminum alloys samples as grains or turns and the determination of Fe, Cu, Mn, Mg, Cr, Ni, Zn, Pb and Ti by ICP-OES was investigated /91/.

Laser-induced breakdown spectroscopy (LIBS) system was developed for determination of toxic metals in wastewater collected from paint manufacturing plant /92/.

Microwave-acid digestion(MW-AD) followed by ICP-AES, GFAAS, and HGAAS were examined for the determination of various elements in coal and coal fly ash (CFA) /93/.

First sequential injection (SI) method for the spectrophotometric determination of Ti(IV) is reported /94/. The method is based upon the reaction of Ti(IV) with chromotropic acid (CA) in acidic medium to form a water-soluble complex. The developed method proved to be adequately selective and applied successfully to the analysis of real samples (dental implant and natural Moroccan phosphate rock) giving accurate results based on recovery studies.

A new rapid decomposition and dissolution method with a mixture of sodium di-hydrogen orthophosphate and di-sodium hydrogen orthophosphate as a novel flux is described and ICP-OES is used for the determination of Al, Ca, Mg, Cr, V, Si, Fe and Ti /95/.

A methodology for bulk analysis of Al and Ti and for determination of soluble and total Al and Ti concentration in steel samples by laser ablation inductively coupled plasma mass spectrometry was developed /96/.

Micelle mediated extraction of titanium and its ultra-trace determination in silicate rocks is described. The reported method is highly sensitive and selective. The results obtained for titanium estimation in a host of silicate rock samples have been found to be highly reproducible, accurate and favourably comparable with certified values of reference materials and those obtained from standard methods /97/.

A robust microwave-assisted acid digestion procedure followed by ICP-MS was developed to quantify rare earth elements in fluidizedbed catalytic cracking catalysts and atmospheric fine particulate matter /98/.

The 37 trace elements were determined in 130 human blood samples from occupationally non-exposed volunteers living in the greater area of Bremen in northern Germany /99/. Trace metal determination was analysed by ICP–MS with an octopole-based collision/reaction cell. Mean values, geometric mean values, ranges and selected percentiles of all elemental concentrations in human blood are presented, which helps toxicologists and clinical chemists planning research about exposition to metals and health effects caused by exposition to metals.

A method for the determination of trace Fe, Hf, Mn, Na, Si and Ti in high-purity zirconium dioxide (ZrO_2) powders by ICP-AES is described. Standard addition method was used to compensate the depress effect of a high concentration of Zr on the analyte peaks. The wavelet transform was applied for correction of spectral interference of Zr on the analytes Three kinds of high-purity ZrO_2 powder were etermined using the proposed method /100/.

Calixarene Hydroxamic Acid

Calixarenes hydroxamic acid derivatives have been reported in literature for the selective binding of various metal cations, as extractants for alkali, alkaline earth metal ions and transition metal ions, as ion-selective electrodes for alkali, alkaline earth and heavy metal ions, as fluorogenic reagents, etc. /101-115/.

p-*t*-Butylcalix[6]arene derivative bearing six hydroxamate groups has been synthesized: it efficiently extracted UO_2^{2+} from the aqueous phase to the organic phase /116/.

The 4-tert-butylcalix[4]arene tetrahydroxamate have been sysnthesized and extraction studies have been performed using Th(IV) [as a surrogate for Pu(IV)], Fe(III), UO2(II) and Cu(II) to estimate the metal ion selectivity and extraction efficacy of these extractants /117/.

A very efficient extractant, calixarene hydroxamic acid, is synthesized and used for the extraction of zirconium. The extract is also determined by spectrophotometry and GFAAS (graphite furnace atomic absorption) spectrometry /118/.

A calix[4]arene bearing a bispyrenyl and two hydroxamic acid functional groups has been reported for the optical detection of Cu(II) and Ni(II) metal ions /119/.

Synthesis of calix[6]arene hydroxamic acid and its thermodynamic dissociation constant is discussed /120/.

Sequential separation and determination of Th(IV) with calixarene hydroxamic acids is reported which can be use for the analysis of the environmental samples /121/. New fluorescein calix[4]aryl hydroxamic acid derivative is reported and their lasing characteristics is studied /122/. A polycalix[6]arene hydroxamic acid is syntehsized and utilised for the selective column separation of Th(IV), Ce(IV) and U(IV). These rare elements were preconcentrated and determined in the presence of each other, monazite sand and environmental samples /123/.

Synthesis of polycalixarene hydroxamic acid is reported for the first time and separation of Ga(III), In(III) and Tl(III) is studied. The selectivity towards the metals ions was achieved by maintaining pH /124/.

Five different calix[4]resorcinarene hydroxamic acid has been synthesized by conventional as well as microwave irradiation /125/.

An experimental and theoretical study of calixarene hydroxamic acid has been carried out and cone confirmation of the calixarene in polar solvent was confirmed by NMR spectroscopy /126/.

For monitoring of workers exposed to a risk of internal contamination with actinides, a new procedure for analyzing Pu(IV) traces from urine media and in the presence of uranium is reported and calixarene hydroxamic acid is used as an extractant for this study /127/.

A extraction, preconcentration and transport study of La(III) with calix[4]resorcinarene hydroxamic acid has been reported /128/.

For the first time the single-step synthesis of methyl calix[6]arene and a novel bis-calix[6]arene hydroxamic acid is reported /129/.

The affinity of calix[6]-arenes bearing hydroxamic acid groups and carboxylic groups towards americium were studied by solvent extraction and the results proved that the ligands have a very good affinity for americium and enhance the possibility of separating Pu from U and Am /130/.

A new calixarene hydroxamic acid derivative has been synthesized which can be used for the determination of atenolol, propranolol hydrochloride and metoprolol tartarate in pharmaceutical tablets and urine /131/.

A conventional and microwave assisted synthesis of novel calixarene hydroxamic acid and thiacalixarene hydroxamic acid derivatives has been reported /132-133/.

Synthesis of six novel tetra-functionalized calix[4]pyrrole hydroxamic acids and their preliminary analytical application for the liquid–liquid extraction and determination of V(V) by UV–Vis spectroscopy and ICP-AES is reported /134/.

A theoretical study on the complexation of UO_2(II) with calix[6]arene cage, hydroxamic and carboxylic acid functional groups has been carried out using density functional theory calculations /135/.

A spectrophotometric method is proposed for the extractive determination of vanadium(V) in an acidic medium in the presence of diversified matrix by using calixresorcinarene hydroxamic acid derivative /136/.

New 1,3-alternate thiacalix[4]arene hydroxamic acid scaffold is synthesized and their affinity toward vanadate ions is investigated. Proposed structures and complexation behavior of the receptors were explained by critical examination of FTIR, UV–visible, mass, and ^{1}H NMR data /137/.

Synthesis and application of calix[4]pyrrole hydroxamic acid has been reported for vanadium and Spectrophotometric results were compared with ICP-OES /138/.

AIM & SCOPE

A review of the literature reveals that a little work has been reported /101-138/ on hydroxamic acid substituted calixarenes and their metal complexation study. Starting from this considerations, it was decided to carry out a series of studies arrived at synthesizing the calixarene hydroxamic acids, which, fully meeting the requirements for extraction, separation, preconcentration, recovery, transport and trace determination of selected metal ions by sensitive, selective, simple, rapid, low cost and environmental friendly techniques.

Niobium and tantalum have very similar chemical properties and their determination in various matrices is important in both industrial and geological applications. Tantalum is found with niobium in tantalite or columbite. It is used in electronics, in cutting alloys, in chemical manufacturing as a catalyst and acid resistant materials. Most of the methods available for the extraction and determination of tantalum and niobium are either time consuming or show the interference of large number of diverse ions /138-141/.

Titanium is often alloyed with aluminum, vanadium, copper, iron, manganese, molybdenum and with other metals. It is known for its durability, light weight, dent- and corrosion- resistance. About 95% of titanium ore extracted from the Earth is destined for refinement into titanium dioxide, an intensely white pigment used in paints, paper, toothpaste and plastics. Zirconium and hafnium are strategical elements and their separation is difficult due to the similarity of their behavior. Zirconium is used in nuclear reactors and chemical plants /142-143/. Continuous efforts are made to develop new extractants viz. Alizarine Red S /144/, 2-hydroxy-5-nonylaceto-phenoneoxime /145/, Cyanex 302 /146/, 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester(PC-88A) /147/, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)/148/, LIX 84-IC (2-hydroxy-5-nonylaceto-phenone-oxime)/149/, Quinaliza-rin /150-151/, bis(diphenylphosphino)ferrocene /152/, 4-(2-pyridylazo)-resorcinol (PAR) /153-154/, sulfinyl-calix[4]arene /155/, tributyl phosphate (TBP) /156/, for the extraction and possible separation of titanium, zirconium, hafnium, niobium and tantalum. But the treatments with some extractants are time consuming, laborious, expensive and originated from the cost of their materials associated with the removal process. Many of previously reported methods usually need tedious and complicate chemical separation processes that make the procedure of the operation difficult to control and time-consuming.

The aims of this work are to present a chemical system, which is sensitive, selective, simple in operation, rapid, low cost, environmental friendly and having high enrichment factor, for determination of niobium, tantalum, titanium, zirconium and hafnium metal ions on one hand, and to compare the applicability of developed techniques for analysis of standard samples and natural samples.

PRESENT INVESTIGATION

The elimination of volatile organic solvents in organic syntheses is the most important need in 'green' chemistry. Microwave irradiated organic reactions make syntheses simpler, save energy and prevent, solvent wastes, hazards and toxicity. By keeping this in view, in present investigation the microwave assisted syntheses of tetranitrocalix[4]arene(TNC4A), hexacarboxycalix[6]-arene (HCC6A), pyridinium bearing calix[4]arenehydroxamic acid(PC4AHA), coumarin-calix[4]arenehydro-xamic acid(CC4AHA) and tetracarboxycalix[6]-crownhydroxamic acid (TCC6CHA) is reported and characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Solvent extraction, separation, preconcentration and recovery of niobium and tantalum is reported. Niobium and tantalum are extracted effectively with 5,17-dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[pyridyl hydroxamic acid] (pyridine-calix[4]arene hydroxamic acid) (PC4AHA) from 8M and 10M acidic aqueous solutions, respectively. The transport study of niobium and tantalum ions through a supported liquid membrane has been carried out. Factors affecting extraction viz., influence of molarity of acid, extractant concentration, diverse ions is discussed. The final extracts of niobium and tantalum complex were directly inserted in the plasma for ICP-MS measurement which enhances the sensitivity. Niobium and tantalum were determined in certified samples.

A solvent extraction and separation of titanium, zirconium and hafnium with coumarin-calix[4]arene hydroxamic acid (CC4AHA) is described. Quantitative extraction of titanium, zirconium and hafnium is possible in dichloromethane solution of CC4AHA at 6, 8 and 0.6 molarity. The binding ratio of titanium, zirconium and hafnium with CC4AHA is 1:1. The trace determination was achieved by directly aspirating the extract for ICP-MS measurements. A liquid membrane transport study of titanium, zirconium and hafnium was carried out from source to the receiving phase under controlled conditions. The synthesized chelating extractant was tested for simultaneous separation of titanium, zirconium and hafnium mixtures. The validation of the procedure was performed by the analysis of certified standard reference materials.

Titanium(IV) is extracted with coumarin-calix[4]arene hydroxamic acid (CC4AHA), in dichloromethane by supercritical carbon dioxide (SC-CO_2)-dichloromethane (modifier) medium. An aliquot of aqueous titanium solution of is extracted accurately. Influence of six experimental factors: pressure, temperature, extraction times, molarity of aqueous solution, solvent and interference of ions were studied and optimized. Quantitative analysis of the extracts was performed online by inductively coupled plasma mass spectrometry (ICP-MS). The results showed that Ti(IV) could be quantitatively extracted from the matrix at 50°C temprature, 17 MPa pressure, at 8.0 molarity, 6 min of extraction time. To check the validity of the proposed method for titanium extraction, the metal ions are determined in standard geological samples.

REFERENCES

1. C.D. Gutsche, J.F. Stoddart, Editors, Calixarenes Revisited, The Royal Society of Chemistry, England, Cambridge, **1998**.
2. Calixarenes. A Versatile Class of Macrocyclic Compounds, ed. J. Vicens, V. Böhmer, Kluwer, Dordrecht, **1991**.
3. C. D. Gutsche, Calixarenes Revisited, Royal Society of Chemistry, Cambridge, UK, **1998**.
4. V. Böhmer, A. Shivanyuk, in: L. Mandolini, R. Ungaro (Eds), Calixarenes Action, Imperial College Press, London, **2000**, 203.
5. V. Böhmer, Angew. Chem., Int. Ed. Engl., **1995**, 34, 713.
6. A. D. Cort, L. Mandolini, in: L. Mandolini, R. Ungaro (Eds), Calixarenes Action, Imperial College Press, London, **2000**, 85.
7. A. Pochini, R. Ungaro, Calixarenes and Related Hosts, in Comprehensive Supramolecular Chemistry, ed. J. L. Atwood, J. E. D. Davies, D. D. Macnicol, F. Vögtle, J.-M. Lehn, Pergamon, Tarrytown, N.Y., **1996**, 2, 103.
8. J. Rebek Jr., Chem. Commun., **2000**, 637.
9. D. M. Roundhill, in Progress in Inorganic Chemistry, ed. K. D. Karlin, Wiley, New York, **1995**, 43, 533.
10. M. A. McKervey, M.-J. Schwing-Weill, F. Arnaud-Neu, in Comprehensive Supramolecular Chemistry, ed. G. W. Gokel, Elsevier, New York, **1996**, 1, 537.
11. A. Ikeda, S. Shinkai, Chem. Rev., **1997**, 97, 1713.
12. C. Wieser, C. B. Dieleman, D. Matt, Coord. Chem. Rev., **1997**, 165, 93.
13. P. Molenveld, J. Engbersen, D. Reinhoudt, Chem. Soc. Rev., **2000**, 29, 75.
14. W. Sliwa, Croat. Chem. Acta, **2002**, 75, 131.
15. R. Ludwig, Fresenius J. Anal. Chem., **2000**, 367, 103.

16. D. Diamond, J Inclusion Phenom. Mol. Recognit. Chem, **1994**, 19, 49.
17. J. C. Lockhart, Chem. Sensors, **1996**, 6, 605.
18. D. Diamond, M. A. McKervey, Chem. Soc. Rev., **1996**, 25, 15.
19. R. Ludwig, JAERI-Review 95–022, JAERI, Japan, **1999**.
20. A. Ikeda, S. Shinkai, Chem. Rev., **1997**, 97, 1713.
21. A. T. Yordanov, D. M. Roundhill, Coord. Chem. Rev., **1998**, 170, 93.
22. C. Floriani, Chem. Eur. J., **1999**, 5, 19.
23. I. S. Antipin, E. K. Kazakova, W. D. Habicher, A. I. Konovalov, Russ. Chem. Rev., **1998**, 67, 905.
24. D. Malkhede, P. M. Dhadke, S. M. Khopkar, Anal. Sci., **1999**, 15, 781.
25. S. Kumar, G. Hundal, D. Paul, M. S. Hundal,, H. Singh, J. Org. Chem. **1999**, 64, 7717.
26. U. Radius, I. Attner, Eur. J. Inorg. Chem., **1999**, 12, 2221.
27. K. Ohto, E. Murakami, T. Shinohara, K. Shiratsuchi, K. Inoue, M. Iwasaki, Anal. Chim. Acta, **1997**, 341, 275.
28. K. Ohto, M. Yano, K. Inoue, et al., Anal. Sci., **1995**, 11, 893.
29. K. Ohto, M. Yano, K. Inoue, et al., Polyhedron, **1997**, 16, 1655.
30. M. H. B., Grote Gansey, W. Verboom, F. C. J. M., van Veggel, et al., J. Chem. Soc., Perkin Trans. 2, **1998**, 12, 2351.
31. R. Seangprasertkij, Z. Asfari, F. Arnaud, J. Vicens, Pure Appl. Chem.,**1995**, 67, 1037.
32. R. Seangprasertkij, Z. Asfari, F. Arnaud, J. Vicens, J. Org. Chem., **1994**, 59, 1741.
33. G. G. Talanova, H.-S. Hwang, V. S. Talanov, R. A. Bartsch, Chem. Commun., **1998**, 419.
34. G. G. Talanova, H -S Hwang, V. S. Talanov, R. A. Bartsch, Chem. Commun., **1998**, 1329.
35. X. Hu, Y. Chen, Z. Tiana, J. Xuea, J. Chem. Res., **1999**, 332.
36. C. Bucher, C. H. Devillers, J.C. Moutet, J. Pécaut, G. Royal, E.

Saint-Aman, F. Thomas, J. Chem. Soc. Dalton Trans., **2005**, 22, 3620.

37. S. Banthia, A, Samanta, Org. Biomol. Chem., **2005**, 3, 1428.
38. Q.-Y. Chena, C.-F. Chen, Tetrahedron Lett., **2005,** 46, 165.
39. J. Dessingou, R. Joseph, C. P. Rao, Tetrahedron Lett., **2005**, 46, 7967.
40. A. F. Danil de Namor, M. T. Goitia, A. R. Casal, J. Villanueva-Salas, Phys. Chem. Chem. Phys., **2001**, 3, 5242.
41. M. Mahouachi, Y. KIM, S. HO LEE, R. Abid, J. Harrowfield, J. Vicens, Supramol. Chem., **2005**, 17, 323.
42. J. Y. Lee, S. K. Kim, J. H. Jung, J. S. Kim, J. Org. Chem., **2005**, 70, 1463.
43. S. Bozkurt, A. Karakucuk, A. Sirit, M. Yilmaz, Tetrahedron, **2005**, 61, 10443.
44. T. Tilki, I. Şener, F. Karc, A. Gülce, H. Deligöz, Tetrahedron, **2005**, 61, 9624.
45. Z. Liu, L. Jiang, Z. Lianga, Y. Gao, Tetrahedron Lett., **2005**, 46, 885.
46. L. S. Kuznetsova, G. A. Pribylova, A. R. Mustafina, I. G. Tananaev, B. F. Myasoedov, A. I. Konovalov, Radiochemistry, **2004**, 46, 277.
47. S. J. Dalgarno, M. J. Hardie, J. L. Atwood, J. E. Warrenc, C. L. Raston, New J. Chem., **2005**, 29, 649.
48. J. G. Bünzli, F. Besançon, Phys. Chem. Chem. Phys., **2005**, 7, 2191.
49. Y. Israëliz, C. Detellier, Phys. Chem. Chem. Phys., **2004**, 6, 1253.
50. P. Thuéry, B. Masci, Supramol. Chem., **2004**, 16, 81.
51. K. Schmeide, K. H. Heise, G. Bernhard, D. Keil, K. Jansen, D. Praschak, J. Radioanal. Nucl. Chem., **2004**, 261, 61.
52. O. Klimchuk, L. Atamas, S. Miroschnichenko, V. Kalchenko, I. Smirnov, V. Babain, A. Varnek, G. Wippf, J. Incl. Phen., **2004**, 49, 47.
53. A. A. Trifonov, E. A. Fedorova, G. K. Fukin, S. Dechert, H. Schuman, M. N. Bochkareva, Russ. Chem. Bull., Int. Ed., **2003**, 52, 2683.

54. M. Kyr., K. Svoboda, P. Lhoták, J. Alexová, J. Radioanal. Nucl. Chem., **2003**, 258, 497.

55. M. Kyr., K. Svoboda, P. Lhoták, J. Alexová, J. Radioanal. Nucl. Chem., **2002**, 254, 455.

56. P. Lhoták, V. Tastnỳ, P. Zlatušková, I. Stibor, V. Michlová, M. Tkadlecová, J. Havlĭček, J. Sỳkora, Collect. Czech. Chem. Commun., **2000**, 65, 757.

57. C. Evans-Thompson, S. E. Field, A. H Jones, M. J. Kan, C. W. Hall, G. P. Nicholson, WM'02 Conference, February 24-28, **2002**, Tucson, AZ.

58. M. Lee, Y. Hura, J. Kim, H. Choi, K. Koh, Mol. Cryst. Liq. Cryst, **2002**, 377, 237.

59. A. Mendes, C. Bonal, N. Morel-Desrosiers, J. P. Morel, P. Malfreyt, J. Phys. Chem. B, **2002**, 106, 4516.

60. N. Iki, T. Horiuchi, H. Oka, K. Koyama, N. Morohashi, C. Kabuto, S. Miyano, J. Chem. Soc., Perkin Trans. 2, **2001**, 2219.

61. C. Grüttner, S. Rudershausen, S. E. Matthews, P. Wang, V. Böhmer, J.–F. Dozol, Eur. Cells & Materials, **2002**, 2, 48.

62. TentaGel is a trademark of Rapp polymer.

63. C. W. Hall, J. S. Cockayne, M. J. Kan, G. P. Nicholson, Green Chem., **2001**, 3, 114.

64. Y. Liu, B. Zhao, H. Zhang, T. Wada, Y. Inoue, J. Chem. Soc., Perkin Trans. 2, **2001**, 1219.

65. F. de M. Ramírez, L. Charbonnière, G. Muller, R. Scopelliti, J. G. Bünzli, J. Chem. Soc., Dalton Trans., **2001**, 3205.

66. A. F. Danil de Namor, O. Jafou, J. Phys. Chem. B, **2001**, 105, 8018.

67. L. S. Kuznetsova, A. R. Mustafina, A. Y. Ziganshina, E. K. Kazakova, A. I. Konovalov, J. Incl. Phen., **2001**, 39, 65.

68. I. Korobkov, S. Gambarotta, G. P. A. Yap, Organometallics, **2001**, 20, 5440.

69. (a) F. Arnaud-Neu, V. Böhmer, J. F. Dozol, C. Grüttner, R.A. Jakobi,

D. Kraft, H. Mauprivez Rouquette, M.J. Schwing-Weill, N. Simon, W. Vogt, J. Chem. Soc., Perkin Trans. 2, **1996**, 1175; (b) L. H. Demau, N. Simon, M. J. Schwing-Weill, F. Arnaud-Neu, J. F.Dozol, S. Eymard, B. Tournois, V. Böhmer, C. Grüttner, C. Musigmann, A. Tunayar, Chem. Commun., **1998**, 1627; (c) S. E. Matthews, M. Saadioui, V. Böhmer, S. Barboso, F. Arnaud-Neu, M.J. Schwing-Weill, A.G. Carrera, J. F. Dozol, J. Prakt. Chem.,**1999**, 341, 264; (d) A. Arduini, V. Böhmer, L. Delmau, J.F. Desreux, J. F. Dozol, M.A.G. Carrera, B. Lambert, C.Musigmann, A. Pochini, A. Shivanyuk, F. Ugozzoli, Chem. Eur. J., **2000**, 6, 2135.

70. F. Arnaud-Neu, J. K. Browne, D. Byrne, D. J. Marrs, M. A. McKervey, P. O'Hagan, M. J. Schwing-Weill, A. Walker, Chem. Eur. J., **1999**, 5, 175; J. F. Malone, D. J. Marrs, M. A. McKervey, P. O'Hagan, N. Thomson, A. Walker, F. Arnaud-Neu, O. Mauprivez, M. J. Schwing-Weill, J. F. Dozol, H. Rouquette, N. Simon, J. Chem. Soc., Chem. Commun., **1995**, 2151.

71. M.J. Schwing-Weill, F. Arnaud-Neu, Gazz. Chim. Ital., **1997**, 127, 687; J. F. Dozol, V. Boehmer, M. A. McKervey, F. Lopez-Calahorra, D.

Reinhoudt, M. J. Schwing-Weill, R. Ungaro, G. Wip.: Report EUR. 17615EN, Eur. Com., Nuclear Science and Technology (**1997**).

72. A. V. Solovyov, L. I. Atamas, O. V. Klimchuk, V. L. Rudzevich, A. B. Drapailo, V. I. Kalchenko, A. A. Varnek, G. Wip., In C. Davies (ed.), EURADWASTE **1999**. Radioactive Waste Management Strategies and Issues, Eur. Com., Luxembourg, **2000**, 523.

73. N. T. K. Dzung, K. Kunogi, R. Ludwig, ISEC **1999**, Barcelona.

74. Şerife Sacmacı, Şenol Kartal, Anal. Chimica Acta, **2008**, 623, 46.

75. C. Bonal, Y. Israëli, J-P Morel, N. Morel-Desrosoers, J. Chem. Soc., Perkin Trans. 2, **2001**, 1075.

76. R. F. Ziessel, L. J. Charbonnière, M. Cesario, T. Prangé, M. Guardigli, A. Roda, A. V. Dorsselaer, H. Nierengraten, Supramol.

Chem., **2003**, 15, 277.

77. A. F. Danil de Namor, K. Baron, S. Chahine, O. Jafou, J. Phys. Chem. A, **2004**, 108, 1082.

78. A. Gaudry, R. Delmas, J. Radioanal. Nucl. Chem., **2007**, 271(1), 159.

79. Y. Li, Q. Zhao, M. Huang, Microchim Acta, **2007**, 157, 245.

80. Z. Randa, J. Kučera, J. Mizera, J. Frána, J. Radioanal. Nucl. Chem., **2007**, 271(3), 589.

81. H. Tsukada, A. Takeda, H. Hasegawa, S. Ueda, T. Iyogi, J. Radioanal. Nucl. Chem., **2005**, 263(3), 773.

82. H. C. Loh, S. M. Ng, M. Ahmad, Anal. Lett., **2005**, 38, 1305.

83. L. Poriel, F. Chitry, S. Pellet-Rostaing, M. Lemaire, Sep. Sci. Technol., **2006**, 41, 2883.

84. A. Sabarudin, M. Oshimaa, T. Takayanagi, L. Hakima, K. Oshita, Y. Gaoc, S. Motomizu, Anal. Chim. Acta, **2007**, 581, 214.

85. M. L. Firdaus, K. Norisuye, T. Sato, S. Urushihara, Y. Nakagawa, S. Umetani, Y. Sohrin, Anal. Chim. Acta, **2007**, 583, 296.

86. M. Zeiner, M. Ovari, G. Zaray, I. Steffan, J. Trace Elem. Med Biol., **2006**, 20, 240.

87. C. Hang, B. Hu, Z. Jiang, N. Zhang, Talanta, **2007**, 71, 1239.

88. H. Matsumiya, S. Yasuno, N. Iki, S. Miyano, J. Chromatogr. A, **2005**, 1090, 197.

89. G. Steinhauser, J. H. Sterba, K. Poljanc, M. Bichler, K. Buchtela, J. Trace Elem. Med Biol., **2006**, 20, 143.

90. A. P. Packer, D. Larivi`ere, C. Li, M. Chen, A. Fawcett, K. Nielsen, K. Mattson, A. Chatt, C. Scriver, L. S. Erhardt, Anal. Chim. Acta, **2007**, 588, 166.

91. T. Grigoletto, E. de Oliveira, I. G. R. Gutz, Talanta, **2005**, 67, 791.

92. M. A. Gondal, T. Hussain, Talanta, **2007**, 71, 73.

93. A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Y. Fujita, T. Yamashita, Talanta, **2007**, 71, 251.

94. F. S. Kika, D. G. Themelis, Talanta, **2007**, 71, 1405.

95. R. Radhamani, P. Murugesan, A. Premadas, P. Srivastava, Talanta, **2007**, 71, 1932.

96. A. G. Coedoa, T. Dorado, I. Padilla, J. C. Farinas, Talanta, **2007**, 71, 2108.

97. P. K. Tarafder, R. Thakur, Talanta, **2008**, 75, 326.

98. P. Kulkarni, S. Chellam, D. W. Mittlefehldt, Anal. Chim. Acta, **2007**, 581, 247.

99. P. Heitland, H. D. Köster, J. Trace Elem. Med Biol., **2006**, 20, 253.

100. X. Ma, Y. Li, Anal. Chim. Acta, 579, **2006**, 47.

101. M. J. Miller, Chem. Rev., **1989**, 89, 1563.

102. Y. K. Agrawal, S. K. Menon, Rev Inorg Chem, **1996**, 16, 1.

103. Y. K. Agrawal, S. Kunji, S. K. Menon, Rev. Anal. Chem., **1998**, 17, 69.

104. Y. K. Agrawal, K. R. Sharma, Rev. Anal. Chem., **2004**, 23, 133.

105. Y. K. Agrawal, V. S. Mishra, Rev. Inorg. Chem., **2004**, 24, 1.

106. Y. K. Agrawal, D. N. Thaker, Rev. Anal. Chem., **2007**, 26, 229.

107. Y. K. Agrawal, J. P. Pancholi, Indian J. Chem. A, **2007**, 46A, 1373.

108. Y. K. Agrawal, S. K. Bhatt, Rev. Anal. Chem., **2008**, 27, 5.

109. Y. K.Agrawal, J.P.Pancholi and J.M.Vyas, J. Sci. Ind. Res., 2009, 68, 745.

110. Y.K. Agrawal, R. N. Patadia, Rev. Anal. Chem., **2006**, 25, 155.

111. S. K. Menon, M. Sewani, Rev. Anal. Chem., **2006**, 25, 49.

112. N. Dallali, A. Darabi, Y. K. Agrawal, Rev. Anal. Chem., **2005**, 24, 263.

113. Y. K. Agrawal, C. R. Sharma, Rev. Anal. Chem., **2005**, 24, 35.

114. S. K. Menon, M. S. Gidwani, Y. K. Agrawal, Rev. Anal. Chem., **2003**, 22, 35.

115. Y. K. Agrawal, H. Kaur, Rev. Anal. Chem., **2001**, 20, 185.

116. T. Nagasaki, S. Shinkai, T. Matsuda, J. Chem. Soc. Perkin Trans. 1, **1990**, 2617.

117. L. Dasaradhi, P. C. Stark, V. J. Huber, P. H. Smith, G. D. Jarvinen, A.

S. Gopalan, J. Chem. Soc. Perkin Trans. 2, **1997**, 1187 .

118. Y. K. Agrawal, M. Sanyal, P. Shrivastav, S. K. Menon, Talanta, **1998**, 46(5)**,** 1041.

119. B. Bodenant, T. Weil, M. B. Pourcel, F. Fages, B. Barbe, I. Pianet, M. Laguerre, J. Org. Chem., **1999**, 64, 7034.

120. Y. K. Agrawal, S. Kunji, S. K. Menon, Iran. J. Sci. Technol., **2005**, 29(A1), 1.

121. Y. K. Agrawal and M. Sanyal, Analyst, **1995**, 120, 2729.

122. M.S. Gidwani, S. K. Menon, Y. K. Agrawal, Indian J. Chem. Tech., **2003**, 10, 519.

123. U. V. Trivedi, S. K. Menon, Y. K. Agrawal, React. Funct. Polym., **2002**, 50, 205.

124. M. S. Gidwani, S. K. Menon, Y. K. Agrawal, React. Funct. Polym., **2002**, 53, 143.

125. Y. K. Agrawal, R. N. Patadia, Synth. Comm., **2006**, 36, 1083.

126. B. Boulet, L. Joubert, G. Cote, C. B. Capely, C. Cossonnet, C. Adamo, J. Phys. Chem. A, **2006**, 110, 5782.

127. B. Boulet, C. C. Bouvier, G. Cote, L. Poriel, C. Cossonnet, J. Alloys Compd, **2007**, 444, 526.

128. V. K. Jain, S. G. Pillai, H. C. Mandalia, J. Chil. Chem. Soc., **2007**, 52(2), 1177.

129. Y. K. Agrawal, S. K. Bhatt, Synth. Comm., **2007**, 37, 551.

130. L. Poriel, B. Boulet, C. Cossonnet, C. B.Capely, Radiat. Prot. Dosimetry, **2007**, 127(1-4), 273.

131. S. K. Menon, P. Jose, U. Harikrishnan, U. Pal, Indian J. Chem. A, **2008**, 47(A), 246.

132. Y. K. Agrawal, D. N. Thaker, Synth. Comm., **2008**, 38, 2437.

133. Y. K. Agrawal, J. P. Pancholi, Synth. Comm., **2008**, 38, 2446.

134. V. K. Jain, H. C. Mandalia, S. Eringathodi, J. Inclusion Phenom Macrocyclic Chem., **2008**, 62, 167.

135. B. Boulet, L. Joubert, G. Cote, C. B. Capely, C. Cossonnet, C.

Adamo, Inorg. Chem., **2008**, 47,7983.

136. V. K. Jain, S. G. Pillai, H. S. Gupte, J. Iran. Chem. Soc., **2008**, 5(4), 646.
137. M. H. Patel, V. B. Patel, P. S. Shrivastav, Tetrahedron, **2008**, 64(9), 2057.
138. Z. Marczenko, Spectrophotometric Determination of Elements, Ellis-Horwood Ltd, Chichester, **1976**, 516.
139. Y.K. Agrawal, K.T. John, Analyst, **1985**, 101, 1041.
140. J.M. Mathur, G.R. Choppin, Solvent Extr. Ion Exch., **1993**, 11, 1.
141. C.K. Friese, V. Krivan, Fresenius, J. Anal. Chem., **1999**, 364, 72.
142. P. Peralta-Zamora and J.W. Martins, Talanta, **1999**, 49, 937.
143. A. Abbaspour and L. Baramakeh, Anal. Sci., **2002**, 18, 1127.
144. M. M. Hassanien, Sep. Sci. Technol, **2005**, 40, 1621.
145. B. R. Reddy, J. R. Kumar, Sep. Pur. Technol., **2005**, 42, 169.
146. B. R. Reddy, J. R. Kumar, K. P. Raja, A. V. Reddy, Miner. Eng., **2004**, 17, 939.
147. B. R. Reddy, J. R. Kumar, A. V. Reddy, D. N. Priya, Hydrometallurgy, **2004**, 72, 303.
148. S. O. Dowski, J. Jakubowska, Talanta, **2003**, 60, 643.
149. B. R. Reddy, J. R. Kumar, A. V. Reddy, Hydrometallurgy, **2004**, 74, 173.
150. H. Karami, M. F. Mousavi, Y. Yamini, M. Shamsipur, Microchim. Acta, **2006**, 154, 221.
151. S. Shariati, Y. Yamini, J. Colloid. Interface Sci., **2006**, 298, 419.
152. M.B. Gholivand, A. Babakhanian, M. Joshaghani, Anal. Chim. Acta, **2007**, 584, 302.
153. E. B. Liu, Y. M. Liu, J. K. Cheng, Anal. Chim. Acta, **2001**, 434, 301.
154. O. M. El Hussaini, N. M. Rice, Hydrometallurgy, **2004**, 72, 259.
155. H. Matsumiya, S. Yasuno, N. Iki, S. Miyano, J. Chromatogr. A, **2005**, 1090, 197.
156. M. E. Campderrós, J. Marchese, J. Membr. Sci., **2000**, 164, 205.

Chapter - II

Environmentally benign syntheses of calixarene derivatives

ABSTRACT

New hydroxamic acid derivatives of calixarene has been synthesized by conventional and microwave method. Calixarene hydroxamic acids were synthesized by reacting corresponding hydroxyl amine with acid chlorides at low temperature in an aqueous suspension of sodium bicarbonate. The comparison of conventional and microwave-assisted synthesis methods have been discussed. These hydroxamic acids were characterized by elemental analysis, FT-IR, ^{1}H NMR & ^{13}C NMR.

INTRODUCTION

Calixarenes were developed later than crown ether and cyclodextrins but have still been extensively researched /1-2/. Macrocycles of calix[n]arenes are constructed by linking a number of phenol residues via methyene moieties. Like crown ethers, the name "calixarene" reflects the structures of these molecules, since a calix is a chalice. Different conformations of calixarene are described in chapter 1. As part of the continuing investigation of calixarene ligands, one of my research objectives is to synthesize a group of highly lipophilic calixarene hydroxamic acid derivatives.

A promising series of reagents, hydroxamic acids, is the versatile chelating agent and extensively studied for separation, preconcentration and recovery of several metal ions. Introduction of coumarin, pyridine and aza crown along with hydroxamic acid can enhance the complexing ability, extraction efficiency and stability of calixarene based lignad with the metal ions /11-17/.

Coumarin, pyridine and aza crown derivatives have been reported for analytical applications /18-26/. With this in view a new series of calixarene hydroxamic acids containing the coumarin, pyridine and aza crown moiety are synthesized for better chromogenic reagent.

The use of microwaves in organic synthesis has increased dramatically in the last few years, receiving widespread acceptance and becoming an indispensable tool /3/. Microwave radiation is converted into heat with high efficiency, so that "superheating" becomes possible at ambient pressure. Enormous accelerations in reaction time can be achieved, if superheating is performed in closed vessels under high pressure; a reaction that takes several hours under conventional conditions can be completed over the course of minutes. Microwave technology has become a powerful tool in organic synthesis, since by employing this technique it is generally possible to prepare organic compounds very fast, with high purity and better yields compared to other more conventional methods /4-6/. Here, conventional as well as microwave assisted methods have been developed for the synthesis of new calixarene hydroxamic acid derivatives.

EXPERIMENTAL

Apparatus

Melting points were determined in capillaries and are uncorrected. KENSTAR 20 OM DGQ domestic oven has been used for the microwave-irradiated synthesis. IR spectra were recorded on JASCO FT/IR 6100 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on DRX 300.

Chemicals

All the chemicals used were of A.R. grade of Fluka, BDH or E. Merck unless otherwise specified. The solvents were purified as described elsewhere /10/.

SYNTHESIS

Synthesis of 5,17-dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[pyridyl hydroxamic acid] and 5,17-Dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[coumarin hydroxamic acid]

Synthesis of compound (3)

Conventional method

Compound 3 was synthesized by previously reported method /7/.

Microwave method

A mixture of *p*-nitrophenol (1g, 0.0073M), 37% formaldehyde (0.6ml, 0.0073M) and conc. hydrochloric acid (1 ml.) was placed into to the Kenstar domestic microwave at 20% power out put for 180 sec. to obtain white solid, washed with hot water and finally with hot alcohol to get compound 3.

Synthesis of compound (6)

Conventional Method

Nitrocalix[4]arene (10 g, 0.015 M), hydrazine hydrate (10 ml, 0.205 M) and Raney-Ni (W-2) (2-2.5 g) in 1,4-dioxane were stirred at 0-10°C for 1 h to get compound 6. Filtered immediately and used *in-situ* for the preparation of hydroxamic acid derivatives.

Microwave Method

Nitrocalix[4]arene (1g, 0.0015 M), hydrazine hydrate (1 ml, 0.0205 M) and Raney-Ni (W-2) (0.2–0.3 g) were placed into to the Kenstar domestic microwave at 0% power output for 120 sec to get compound 6.

Synthesis of compound (9)

Conventional method

Thionyl chloride (15 ml) slowly added to a stirred mixture of isonicotinic acid 7 (10g, 0.0813M) and dimethylformamide (1 ml). Mixture was stirred at 75-80°C for 3 hours. The isonicotinoylchloride hydrochloride 8 was precipitated as white powder by adding 50 ml of dried petroleum ether.

The acid chloride 8 (2.3g, 0.0016M) was condensed with compound 6 (3.60g, 0.0064M) in the presence of an aqueous suspension of sodium bicarbonate (2g) at 0-10°C for 2 h to get compound 9.

Microwave method

A mixture of isonicotinic acid (7) (1g, 0.0081M), dimethylformamide (0.1ml) and thionyl chloride (1.5ml) placed into to the Kenstar domestic microwave at 40% power out put for 120 sec. The isonicotinoylchloride hydrochloride was precipitated as white powder by adding 50 ml of dried petroleum ether.

The acid chloride 8 (1.5g, 0.0011M) was condensed with compound 6 (1g, 0.0015M) in the presence of an aqueous suspension of sodium bicarbonate (2g) in the oven at 0% power output for 120 sec. to get compound 9.

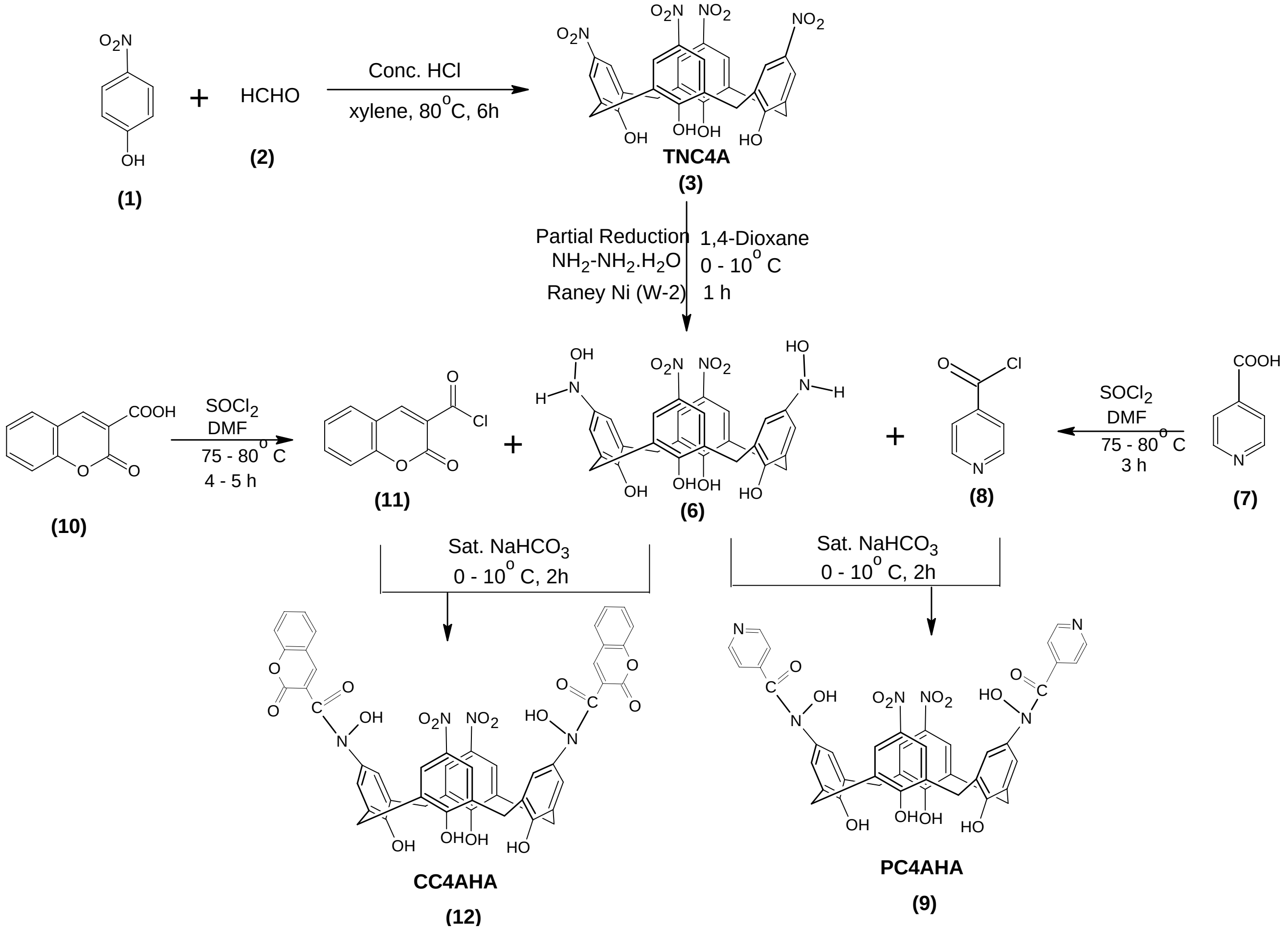


Figure 1. Synthetic route for compound 9 and 12.

Synthesis of compound (12)

Conventional method:

Thionyl chloride (10 ml) slowly added to a stirred mixture of coumarin-3-carboxylic acid /9/ (3g, 0.015M) and dimethylformamide (0.8 ml). Mixture was stirred at 75-80°C for 4-5 hours. The coumarin-3-carbonylchloride was precipitated as white powder by adding 40 ml of dried petroleum ether. The acid chloride was condensed with freshly prepared compound 6 (3.60g, 0.0064M) in the presence of an aqueous suspension of sodium bicarbonate (2g) at 0-10°C for 2 h to obtain compound 12.

Microwave method:

A mixture of coumarin-3-carboxylic acid /9/ (1g, 0.05M), dimethylformamide (0.3 ml) and thionyl chloride (3.35ml) was placed into to the Kenstar domestic microwave at 40% power output for 120 sec. The coumarin-3-carboylchloride was precipitated as white powder by adding 40 ml of dried petroleum ether.

The acid chloride was condensed with compound 6 (1g, 0.0015M) in the presence of an aqueous suspension of sodium bicarbonate (2g) in the oven at 0% power output for 120 sec. to get compound 12.

Synthesis of 5,11,23,29-tetracarboxy-38,39,41,42-tetrahydroxycalix[6] crown-17,35-*bis*-[*N*-phenylbenzo hydroxamic acid]

Synthesis of compound (5)

Conventional method:

Compound 5 was synthesized by previously reported method /8/.

Microwave method:

A mixture of *p*-hydroxybenzoic acid (1 g, 0.0072M), 37% formaldehyde (4 ml, 0.0015M) and conc. hydrochloric acid (2.5 ml.) was placed into to the Kenstar domestic microwave at 40% power out put for 120 sec to obtain white solid, washed with hot distilled water to remove acidic impurities and recrystallised from acetone-petroleum ether (60°-80° C) to get compound 5.

Synthesis of compound (16)

Conventional method:

To a suspension of compound 5 (5g, 0.005 M) and 1,4-dibromopropane (2.7g, 0.0125 M) in acetonitrile (100 ml) was added anhydrous K_2CO_3 (0.7g, 0.005 M) and the reaction mixture was stirred under reflux for 24 h. After the solvent was removed under reduced pressure, the residue was then purified by crystallization form chloroform to get compound 13.

To a solution of compound 13 (2g, 0.00179 M) in acetonitrile (25 ml) were added anhydrous K_2CO_3 (0.5g, 0.00358 M) and diethylene triamine (2.0g, 0.002M). The mixture was refluxed about 7 h. The solvent was removed by rotary evaporator. Then CH_2Cl_2 (10 ml) was added. Organic layer was then washed with distilled water (2 X 5 ml), organic

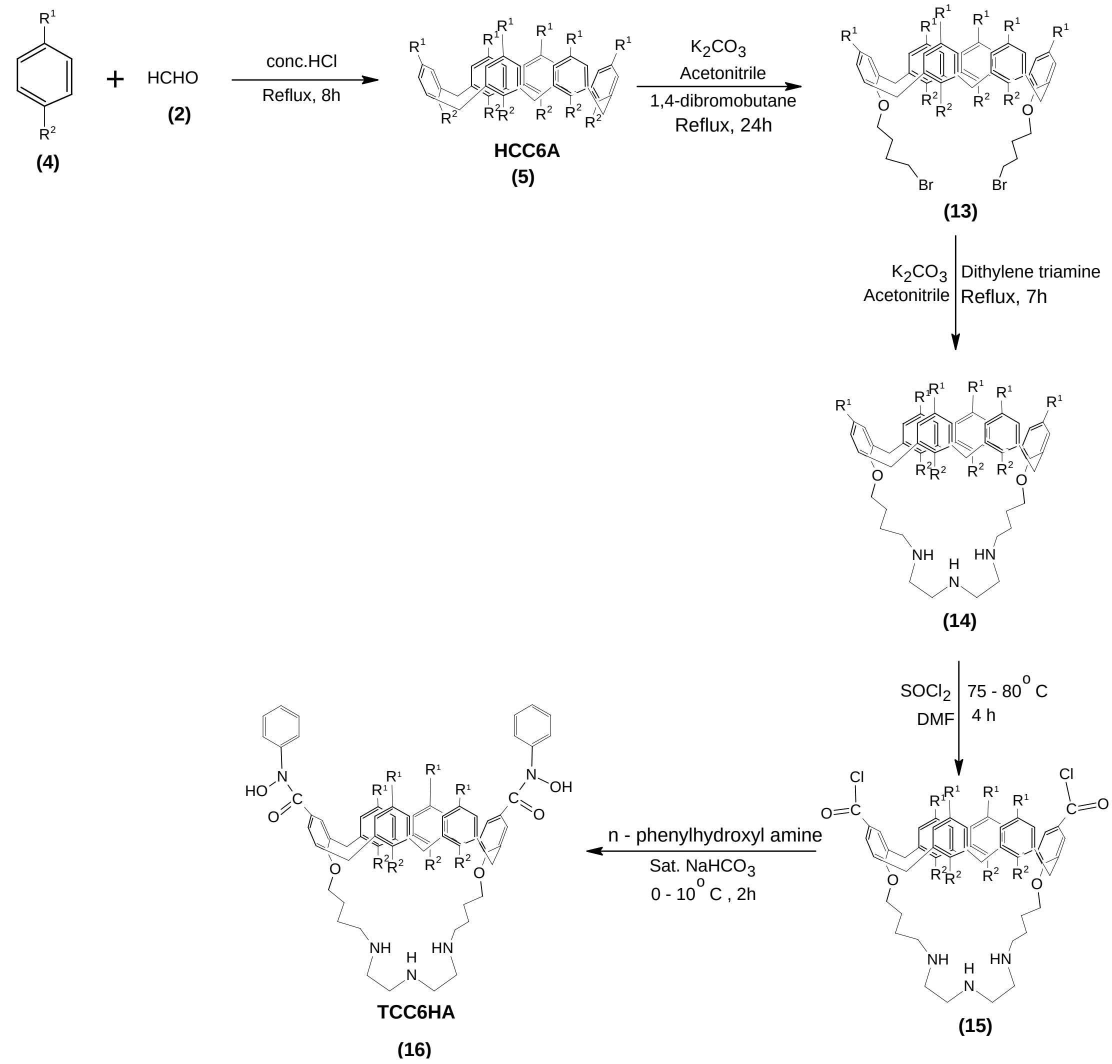


Figure 2. Synthetic route for compound 16 (R^1=COOH, R^2=OH).

phase was evaporated under reduced pressure to dryness. Residue purified by crystallization from chloroform to get compound 14.

Compound 14 was refluxed with thionyl chloride in the presence of dimethylformamide for 4 h and excess thionyl chloride was removed under reduced pressure to get compound 15. Which was added to a mixture of N-phenyl hydroxyl amine and sodium bicarbonate in 1,4-dioxane at O-10°C within 1 h. Reaction mixture was further stirred for 1 h more, then filtered. Solid was washed with water and purified by crystallization from chloroform to get compound 16.

Microwave method

A mixture of compound 5 (1g, 0.001M), 1,4-dibromobutane (0.6g, 0.0025M) in and anhydrous K_2CO_3 (0.15g, 0.001M) was placed into to the Kenstar domestic microwave at 20% power out put for 240 sec to get compound 13.

A mixture of 13 (0.5g, 0.0005M), anhydrous K_2CO_3 (0.13g, 0.00090M) and diethylene triamine (0.5g, 0.0005M) was placed into to the Kenstar domestic microwave at 20% power out put for 180 sec to get compound 14.

Compound 14 (2g, 0.0017M), dimethylformamide (0.3 ml) and thionyl chloride (2.5 ml) was placed into to the Kenstar domestic microwave at 40% power output for 120 sec to get compound 15, which was condensed with N-phenyl hydroxyl amine in the presence of sodium bicarbonate (2g) in the microwave oven at 0% output for 120 sec to get compound 16.

RESULTS AND DISCUSSION

The elimination of volatile organic solvents in organic syntheses is the most important need in 'green' chemistry. Microwave irradiated organic reactions make syntheses simpler, save energy and prevent, solvent wastes, hazards and toxicity. By keeping this in view, in present investigation the microwave assisted syntheses of tetranitrocalix[4]arene (TNC4A) (3), hexacarboxycalix[6]arene (HCC6A) (5), pyridine-calix[4]arenehydroxamic acid (PC4AHA) (9), coumarin-calix[4]arenehydroxamic acid (CC4AHA) (12) and tetracarboxycalix[6]crown hydroxamic acid (TCC6CHA) (16) is reported.

Compound (3) and (5) (Figure 1) were synthesized by the acid catalyzed condensation of formaldehyde with *p*-nitrophenol and *p*-hydroxy benzoic acid respectively /7,8/. Compound (3) was partially reduced with hydrazine hydrate in the presence of Raney Ni (W-2) at 0-10°C for 1 h to obtain corresponding hydroxylamine (6) was condensed with isonicotinoyl chloride (8) and coumarin-3-carbonyl chloride (11) in the presence of an aqueous suspension of sodium bicarbonate at 0°-10°C to yield PC4AHA (9) and CC4AHA (12) (Figure 1), respectively. The products were purified by crystallization from chloroform.

Compound (5) was refluxed with 1,4-dibromo butane in the presence of K_2CO_3 using acetonitrile as a solvent at 80°C for 24 h to yield compound (13). Then further reacted with diethylene triamine in the presence of K_2CO_3 to obtain compound (14). Compound (14) was refluxed with thionyl chloride in the presence of dimethylformamide for 4 h and condensed with N-phenylhydroxylamine in the presence of an aqueous suspension of sodium bicarbonate at 0°-10°C to get TCC6CHA (16) (Figure 2).

The FT-IR (KBr) spectrum of compounds 3, 5, 9, 12 and 16 displayed three sharp bands at 3185, 1635, and 920 cm^{-1} confirms the υ_{OH}, $\upsilon_{C=O}$ and υ_{N-O} of the hydroxamic acid functional group. The band at 3600-3200 due to the O-H of phenolic calixarene. The band at 3185 cm^{-1} is due to O–H stretching vibration. It is known that O–H stretching vibrations bands occur at around 3600 cm^{-1}; hydrogen bonding shifts these bands to lower frequencies. In hydroxamic acids, the –OH group is placed very close to the polar carbonyl C=O group. The band at 1635 cm^{-1} is assigned for the C=O of the hydroxamic acid group. A sharp band at 920 cm^{-1} is attributed to N-O stretching vibrations. Compounds 3, 9 and 12 displayed a sharp band at 1350 cm^{-1} for $-NO_2$ stretching vibrations.

The structures of compounds 3, 5, 9, 12 and 16 were established by elemental analysis, ^1H NMR and ^{13}C NMR spectra. These compounds display singlet around 7.82, 7.70, 7.60, 7.51, 7.45 and 6.82 for aromatic protons. A pair of doublets appears at δ 4.50 and 3.90 for $ArCH_2Ar$ protons in the ^{1}H NMR. Prominent signals appeared at δ 9.00, 9.20 and 9.90 for aromatic hydroxyl protons and δ 10.27, 10.28 and 10.70 for hydroxamic group. In compound 3, 9 and 12 a prominent downfield shift in the position of hydroxyl signal suggested that nitro groups were present at positions *para* to the hydroxyl groups.

A singlet appears at δ 10.32 is for each carboxyl hydrogen present in compound 5 and 16. Notice that this peak is not sharp; it has broadened by hydrogen bonding and exchange. Two singlets appear at 8.01 and 3.40 for NH and CH_2CH_2OAr respectively.

The ^{13}C NMR (DMSO) spectrum of compounds 3, 5, 9, 12 and 16 displayed singlet at δ 116-125 and 128-137 for aromatic protons and one singlet near δ 167 and 166 for ketone groups. In addition compound 5 and 16 displayed singlet at 166.86 for carboxylic acid group and doublet at δ 35.12 and 34.63 for bridged methane groups. Compound 16 displayed one triplet at δ 51.48 for crown moiety.

The results obtained from elemental analysis of compound 3, 5, 9, 12 and 16 confirm the presence of hydroxamic acid groups.

Table – 1 Comparison of yields and reaction time of conventional and Microwave-Irradiation technique

Compounds	**Conventional method**		**Microwave method**	
	Melting Point (ºC)	**Yield (%)**	**Melting Point (ºC)**	**Yield (%)**
TNC4A	140-142	70	140-142	93
HCC6A	110-111	80	110-111	95
PC4AHA	239-241	58	239-241	91
CC4AHA	186-188	61	186-188	93
TCC6CHA	219-222	66	219-222	89

Table 2 Physico-chemical properties of calix[4]arene hydroxamic acids

Compounds	Molecular Formula	Molecular Weight	Melting Point (°C)	Elemental Analysis, %		
				C	H	N
PC4AHA	$C_{40}H_{30}N_6O_{12}$	786	186-188	61.07 (61.48)	3.84 (3.55)	10.68 (10.72)
CC4AHA	$C_{48}H_{32}N_4O_{16}$	920	239-241	62.61 (62.75)	3.50 (3.45)	6.08 (6.01)
TCC6CHA	$C_{72}H_{71}N_{18}O_5$	1267	219-222	66.81 (66.75)	5.53 (5.60)	5.41 (5.57)

The experimental values are given in parenthesis

TNC4A

mp 140-142° C, IR (KBr): υ = 3185, 1635, 1350, 920 cm^{-1}. ^1H NMR (DMSO): δ = 9.20 (s, 4H, ArOH), 4.50 (d, 4H, $ArCH_2Ar$), 3.90 (d, 4H, $ArCH_2Ar$), 7.82 (s, 8H, ArH). $^{13}CNMR$ (DMSO): δ = 35.12 (d, $Ar-CH_2-Ar$), 119.05-132.10 (s, ArC).

HCC6A

mp 110-111°C IR (KBr): υ = 3185, 1635, 920 cm^{-1}. ^1H NMR (DMSO): δ = 9.90 (s, 6H, ArOH), 4.44 (d, 6H, $ArCH_2Ar$), 3.85 (d, 6H, $ArCH_2Ar$), 7.45 (s, 12H, ArH), 10.32 (s, 6H, COOH). $^{13}CNMR$ (DMSO): δ = 34.63 (d, $Ar-CH_2-Ar$), 120.20-125.52 (s, ArC), 127.26-134.94 (s, ArC), 166.86 (s, COOH). Anal. calcd. for $C_{48}H_{36}O_{18}$: C, 64.0%; H, 4.03%, Found: C, 63.91%; H, 4.10%.

PC4AHA

mp 186-188° C, IR (KBr): υ = 3185, 1635, 1350, 920 cm^{-1}. ^1H NMR (DMSO): δ = 10.27 (s, 2H, NOH), 9.20 (s, 4H, ArOH), 4.50 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.90 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 7.70 (s, 4H, ArH), 7.82 (s, 4H, ArH), 6.82-7.45 (s, 8H, ArH) $^{13}CNMR$ (DMSO): δ = 35.12 (d, $Ar-CH_2-Ar$), 119.05-126.62 (s, ArC), 128.21-137.48 (s, ArC), 167.12 (s, C=O). Anal. calcd. for $C_{40}H_{30}N_6O_{12}$: C, 61.07%; H, 3.84%; N,10.68%. Found: C, 61.48%; H, 3.55%; N, 10.72%

CC4AHA

mp 239-241°C, IR (KBr): υ = 3185, 1635, 1350, 920 cm^{-1}. ^1H NMR (DMSO): δ = 10.70 (s, 2H, NOH), 9.00 (s, 4H, ArOH), 4.26 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.82

(d, 4H, J=12.9 Hz, $ArCH_2Ar$), 7.70 (s, 4H, ArH), 7.82 (s, 4H, ArH), 6.82-7.40 (s, 10H, ArH) ^{13}CNMR (DMSO):

δ = 35.12 (d, Ar-CH_2-Ar), 116.05-120.62 (s, ArC), 127.18-134.80 (s, ArC), 166.07 (s, C=O). Anal. calcd. for $C_{48}H_{32}N_4O_{16}$: C, 62.61%; H, 3.50%; N, 6.08%. Found: C, 62.75%; H, 3.45%; N, 6.01%

TCC6HA

mp 219-222° C, IR (KBr): υ = 3185, 1635, 1350, 920 cm^{-1}. ^{1}H NMR (DMSO): δ = 10.28 (s, 2H, NOH), 9.90 (s, 4H, ArOH), 4.44 (d, 6H, J=13.5 Hz, $ArCH_2Ar$), 3.85 (d, 6H, J=13.5 Hz, $ArCH_2Ar$), 7.45 (s, 8H, ArH), 7.51 (s, 4H, ArH), 7.60 (s, 4H, ArH), 7.17 (s, 6H, ArH), 10.32 (s, 4H, COOH), 8.01 (br s, 3H, NH), 3.40 (s, 4H, CH_2CH_2OAr), ^{13}CNMR (DMSO): δ = 34.63 (d, Ar-CH_2-Ar), 120.20-125.52 (s, ArC), 127.26-134.94 (s, ArC), 166.86 (s, COOH), 167.73 (s, C=O). Anal. calcd. for $C_{72}H_{71}O_5N_{18}$: C, 66.81%; H, 5.53%; N, 5.41%. Found: C, 66.75%; H, 5.60%; N, 5.57%.

CONCLUSION

The microwave assisted synthetic procedures is developed for calixarene derivatives which gives better yield, purity and time saving. It is also solvent free and preventing the waste.

REFERENCES

1. C. D. Gutsche, Calixarenes Revisited. Cambridge: Royal Society of Chemistry, **1998**.
2. Z. Asfari, V. Böhmer, J. Harrowfield, J. Vivens, Kluwer Academic Publishers, **2001**.
3. J. P. Thierney, P. Lidstrm (Eds): Microwave Assisted Organic Synthesis. Blackwell Publishing Ltd; **2005,** 296.
4. A. Loupy (Eds): Microwaves in Organic Synthesis. Wiley-VCH, Weinheim; **2002**.
5. B. L. Hayes, Microwave Synthesis: Chemistry at the Speed of Light. CEM Publishing, N. C. Matthews; **2002**.
6. C. O. Kappe, A. Stadler, Microwaves in Organic and Medicinal Chemistry. Wiley-VCH, Weinheim; **2005**.
7. S. K. Jogani, S. K. Menon, Y. K. Agrawal, Synth. React. Inorg. Met.-Org. Chem., **2002**, 32(3), 603.
8. M. S. Gidwani, S. K. Menon, Y. K. Agrawal, React. Funct. Polym., **2002**, 53, 143.
9. L. C. Wood, S. John, J. Org. Chem., **1965**, 30(1), 312.
10. W. Armrego, C. Chai, “Purification of Laboratory Chemicals”, Elsevier, **2003**.

11. Y. K. Agrawal, S. K. Bhatt, Rev. Anal. Chem., **2008**, 27(1), 1.

12. Y. K. Agrawal, D. N. Thaker, Rev. Anal. Chem., **2007**, 26(4), 229.

13. Y. K. Agrawal, J. P. Pancholi, Indian J. Chem. Sect A, **2007**, 46A, 1373.

14. Y. K. Agrawal, C. R. Sharma, Rev. Anal. Chem., **2005**, 24(1), 35.

15. N. Dallali, A. Darabi, Y. K. Agrawal, Rev. Anal. Chem., **2005**, 24(4), 263.

16. K. R. Sharma, Y. K. Agrawal, Rev. Anal. Chem., **2004**, 23(2), 133

17. S. K. Menon, M. S. Gidwani, Y. K. Agrawal, Rev. Anal. Chem., **2003**, 22(1), 35.

18. B. J. Ryu, E. J. Cho, K. C. Nam, Bull. Korean Chem. Soc., **2007**, 28(9), 1585.

19. L. F. Capitán-Vallvey, M. D. Fernández-Ramos, A. Lapresta-Fernández, E. Brunet, J. C. Rodriguez-Ubis, O. Juanes, Talanta, **2006**, 68, 1663.

20. E. Brunet, P. Garcia-Losada, J. C. Rodriguez-Ubis, O. Juanes, Can. J. Chem., **2002**, 80, 169.

21. M. Wiśniewski, A. Jakubiak, J. Szymanowski, J. Chem. Technol. Biotechnol., **1994**, 63(3), 209.

22. D. Singh, J. M. Singh, O. V. Singh, S. N. Tandon, J. Radioanal. Chem., **1979**, 54(1-2), 69.

23. H. Higuchi, T. Matsufuji, T. Oshima, K. Ohto, K. Inoue, T. Tsend-Ayush, K. Gloe, Chem. Lett., **2005**, 1, 80.

24. C. Ümit, C. Baki, Transition Met. Chem., **2004**, 29(3), 263.

25. U. K. Gülderen, S. Memon , M. Sezgin, M. Yilmaz, J. Macromol. Sci., Pure Appl. Chem., **2003**, 40(2), 95.

26. L. G. Water, W. L. Driessen, J. Reedijk, D. C. Sherrington, Eur. J. Inorg. Chem., **2002**, 1, 221.

Chapter III

Extraction, Preconcentration, Separation, Transportation and Recovery of Niobium(V) and Tantalum(V) and their Trace Determination by Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS)

ABSTRACT

Solvent extraction, separation, preconcentration and recovery of niobium and tantalum is reported. Niobium and tantalum are extracted effectively with 5,17-dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[pyridyl hydroxamic acid] (pyridine-calix[4]arene hydroxamic acid) (PC4AHA) from 8M and 10M acidic aqueous solutions, respectively. The transport study of niobium and tantalum ions through a supported liquid membrane has been carried out. Factors affecting extraction viz., influence of molarity of acid, extractant concentration, diverse ions is discussed. The final extracts of niobium and tantalum complex were directly inserted in the plasma for ICP-MS measurement which enhances the sensitivity. Niobium and tantalum were determined in certified samples.

INTRODUCTION

Niobium and tantalum have very similar chemical properties, radii, and they occur in the same oxidation state /1/. Both metals are important components in alloys, semiconductors and superalloys. Niobium is an important because it has a low neutron cross section and is used in fuel element cladding. Addition of niobium to low chromium steels improves the toughness, weld ability, ductility and resistance to oxidation. Niobium in the form of ferroniobium is used worldwide, mostly as an alloying element in steels and in superalloys for such applications as jet engine components, rocket subassemblies, and heat-resisting and combustion equipment /2/. Tantalum is ductile, easily fabricated, highly resistant to corrosion by acids (used in the manufacture of hydrochloric acid), a good conductor of heat, electricity and has a high melting point. Major uses for tantalum capacitors include portable telephones, pagers, personal computers, and automotive electronics. It finds usage in tools for dentistry and surgery /3/.

There are number of analytical techniques reported for determination of trace amounts of niobium and tantalum viz., inductively coupled plasma–mass spectrometry (ICP–MS) /4-9/, inductively coupled plasma-atomic emission spectrometry (ICP–AES) /10-11/, reversed-phase high performance liquid chromatography (RP–HPLC) /12-15/, graphite furnace atomic absorption spectrometry (GFAAS) /16/, flow injection combined with inductively coupled plasma optical emission spectroscopy (FI-ICP-OES) /17/, instrumental neutron activation analysis (INAA) /18/, laser ablation inductively coupled plasma time of flight mass spectrometry (LA-ICP-TOF-MS) /19/, capillary electrophoresis /20-22/. The most common reagents 4-(2-pyridylazo)resorcinol (PAR) /22/, *N*-benzoyl-*N*-phenylhydroxylamine /9/, 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol (5-Br-PADAP) /23/, Alamine 336 /24,30/, sulfinylcalix[4]arene /25/, 2-(2-Thiazolylazo)-5-diethylaminophenol (TA-DAP) /26/, tetrabutylammonium bromide /27/, dibenzo-18-crown-6 /28/, tri-butylphosphate /29-32/, *N*-cinnamoyl-*N*-2,3-xylylhydroxylamine and thiocyanate /33/, *N*-a-phenylstyrylacrylohydroxamic acid /34/, octanol /35-37/ and 2-(5-nitro-2-pyridylazo)-5-diethylamino phenol (5-NO_2-PADAP) and tartaric acid /38/, dowex 1X8 resin /39/ and 4-(5-nitro-pyridylazo)resorcinol (5-NO_2-PAR) /12/ have been reported for the determination of niobium and tantalum.

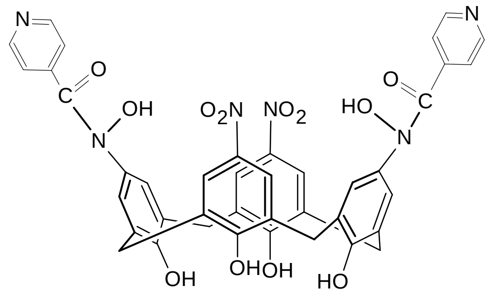
It seems that the allowance amounts of potential interference metal ions was not discussed in detail in a better sensitivity which used to analyze trace amounts of niobium and tantalum in geological material. Therefore, it is necessary that the further study for the determination of trace amounts of niobium and tantalum in different samples should be carried out.

Calixarene have achieved considerable importance as analytical reagents of the separation and determination of several metal ions /40-53/. The introduction of hydroxamic acid groups into the calixarene may enhance the extraction efficiency of the reagent. The method is required UV-Vis spectrophotomter instead of a costly instrument. The sample preparation is simple. So there is no requirement to establish a sophisticated laboratory. This method is better than the other methods because it is low cost, low maintenance and very simple.

EXPERIMENTAL

Standard Solutions & Reagents

All the chemicals used were of analytical grade obtained from Sigma-Aldrich or Merck. Deionised double distilled water was used, which was further purified by a Milipore Milli-Q water purification system. A 2.88×10^{-5} M standard niobium solution was prepared by fusing niobium pentoxide with potassium bisulphate and dissolving the fused mass in 1 M tartaric acid. A standard 2.42×10^{-5} M tantalum solution was prepared by fusing tantalum pentoxide with potassium bisulphate and finally dissolving the fused mass in 1 M ammonium oxalate. Final concentration of solutions determined spectrophotometrically /12/. 5,17-dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[pyridyl hydrox-amic acid] (pyridine-calix[4]arene hydroxamic acid) (PC4AHA) (Figure 1) was synthesized as described in Chapter 2. 1.27×10^{-3} M stock solution of PC4AHA was prepared in n-octanol for niobium and in dichloromethane for tantalum.



PC4AHA

Figure 1 Pyridine-calix[4]arenehydroxamic acid (PC4AHA)

Apparatus

Spectra were recorded on a JASCO-980 UV-Vis-NIR spectrophotometer with matching 10 mm quartz cells. A Plasma Scan Model 710 sequential Inductively Coupled Plasma with Plasma Scan multitasking computer and peristaltic pump was used. Thermo Jarrell-Ash Corporation, Franklin, MA, USA, POEMS mass spectrophotometer with a Fassel torch, a concentric glass nebulizer and cryogenic spray chamber was used. The optimized instrumental conditions are summarized in Table 1.

Table 1 Optimized instrumental conditions for ICP-MS

Instrumental parameters	**ICP-MS**
ICP Plasma	Argon
Forward Power	1.35 KW
Reflected Power	<10 W
Gas flow (L/min)	
Coolant	16
Carrier	0.70
Auxiliary	0.30
Nebuliser Pressure	2 bar
Solution uptake rate	0.8 mL/min
Sampler cone aperture	1 mm
Skimmer cone aperture	0.7 mm
Mass No.	
Nb	93
Ta	181

Extraction Procedure for Niobium

An aliquot of the 2.95-53.19 µg niobium(V) was transferred into a 60 ml separatory funnel. Molarity of aqueous phase was maintained at 10 M for niobium by adding appropriate amount of acid solution. The mixture was there after shaken with 8 ml of 0.1 % (w/v) n-octanol solution of PC4AHA reagent for 2 min. The organic phase was separated, dried over anhydrous sodium sulphate and transferred into a 25 ml volumetric flask. To ensure the complete recovery of the metal ions, the extraction was repeated with 2 ml of PC4AHA reagent solution. The sodium sulphate was washed with 2 × 2 ml of n-octanol and the combined extracts and washing were diluted to the mark with n-octanol. The absorbance of the extract was measured against the reagent blank. The organic extract was also directly inserted to plasma for ICP-MS measurements.

Extraction Procedure for Tantalum

An aliquot of the 5.35-26.75 μg tantalum(V) were transferred into a 60 ml separatory funnel. Molarity of aqueous phase was maintained at 8 M for tantalum by adding appropriate amount of acid solution. The mixture was there after shaken with 2 ml of 0.1 % (w/v) dichloromethane solution of PC4AHA reagent for 5 min. The organic phase was separated, dried over anhydrous sodium sulphate and transferred into a 25 ml volumetric flask. To ensure the complete recovery of the metal ions, the extraction was repeated with 2 ml of PC4AHA reagent solution. The sodium sulphate was washed with 2 × 2 ml of dichloromethane. Then add 5.0 ml of 0.01% crystal violet solution to the combined extracts and washing. The solution was diluted to the mark with dichloromethane. The absorbance of the extract was measured against the reagent-crystal violet blank. The organic extract was also directly inserted to plasma for ICP-MS measurements.

Transport Condition

Source phase aqueous 10 ml of 10M niobium solution, 10ml of 8M tantalum solution and 20ml membrane phase with 1.27×10^{-3} M PC4AHA solution as carrier were taken in a specially fabricated glass membrane assembly and stirred with teflon coated magnetic and mechanical stirrer. The receiving phase was 20 ml of 0.1 N HCl.

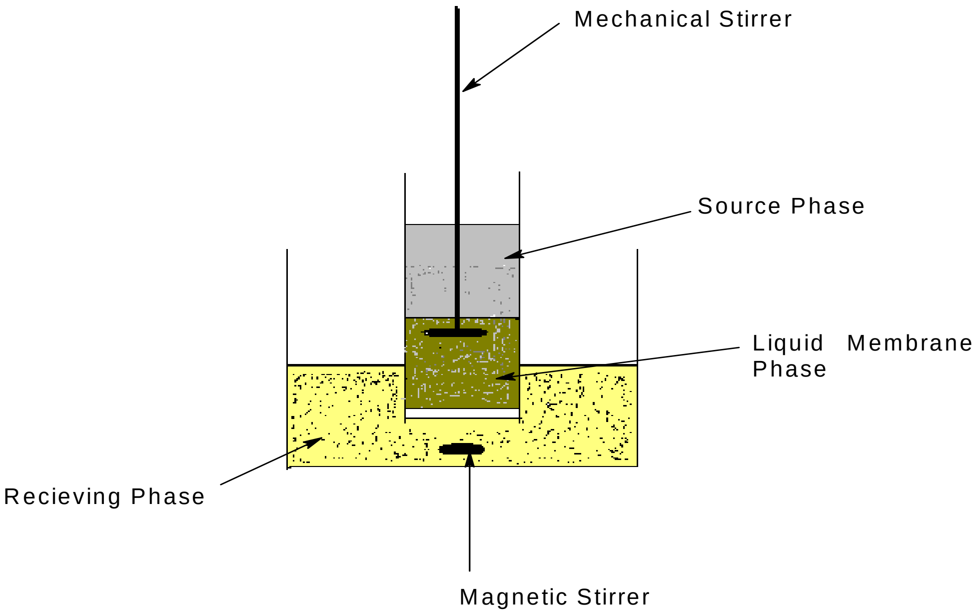


Figure 2 Membrane cell for the transport of niobium & tantalum

RESULT AND DISCUSSION

The niobium(V)-PC4AHA complex is colorless and has a maximum absorbance at 352 nm with molar absorptivity 1.90×10^5 L min^{-1} cm^{-1}. Violet colored tantalum(V)-PC4AHA-Crystal Violet complex has maximum absorbance at 579 nm with molar absorptivity 8.74×10^5 L mol^{-1} cm^{-1}. The reagent blanks do not absorb at these wavelengths. Under the optimum conditions, the calibration curves are linear over the concentration range of 2.95-53.19 μg ml^{-1} for niobium(V) and 5.35-26.75 μg ml^{-1} for tantalum(V). For the trace determination, the extracts were directly inserted into plasma for ICP-MS measurements which enhances the sensitivity to several times having the determination limits of 2.0 ng ml^{-1} for niobium and tantalum.

Influence of molarity

Niobium(V) and tantalum(V) were extracted with PC4AHA at different molarity (Table 2-3). It was observed that maximum extraction (%E) was found for niobium(V) and tantalum(V) at 9.5-10.5 M and 7.5-8.5 M, respectively. (Table 2-3). It was found that 4 min. of shaking time is sufficient for the quantitative extraction of niobium(V) and tantalum(V). The extracted complexes were stable for 15-20 h. For further extraction study is carried out at 10M and 8M for niobium and tantalum respectively.

Table 2 Influence of molarity on the extraction of Niobium(V)-PC4AHA complex

Niobium(V) : 5.91 µg ml^{-1} PC4AHA : 10 ml (1.27×10^{-3} M)

Solvent : n-Octanol λ_{max} : 352 nm

Molarity	Extraction %	ε* (L mol^{-1} cm^{-1})
5.0	NE	NE
6.0	22.45	4.26×10^4
7.0	41.96	7.97×10^4
8.5	68.23	1.29×10^5
9.5	99.99	1.90×10^5
10.0	99.99	1.90×10^5
10.5	99.99	1.90×10^5
11.0	82.37	1.54×10^5

Note: ε* = molar absorptivity; NE= no extraction

Table 3 Influence of molarity of acid on the extraction of tantalum(V)-PC4AHA-Crystal violet complex

Tantalum(V)	:	10.7 μg ml^{-1}	PC4AHA	:	4 ml (1.27 × 10^{-3} M)
Solvent	:	Dichloromethane	Crystal Violet	:	5 ml (0.01%)
			λ_{max}	:	579 nm

Molarity	**Extraction %**	**ε* (L mol^{-1} cm^{-1})**
6.0	53.85	1.71 × 10^4
7.5	99.99	8.73 × 10^5
8.0	99.99	8.73 × 10^5
8.5	99.99	8.74 × 10^5
9.0	74.83	6.47 × 10^5
10.0	62.49	5.58 × 10^5
11.0	37.22	2.89 × 10^5

Note: ε* = molar absorptivity; NE = no extraction

Influence of reagent concentration

The influence of the PC4AHA concentration was studied by extracting a fixed amount of niobium(V) and tantalum(V) with varying concentration of PC4AHA (Table 4-5). It was found that 10 ml and 3 ml of 1.27 × 10^{-3} M PC4AHA was adequate for the complete extraction of niobium(V) and tantalum(V). The lower concentration of PC4AHA gives incomplete extraction while a large excess of the reagent can be used without any difficulty.

Table 4 Influence of reagent concentration on Niobium(V)-PC4AHA complex

Niobium(V) : 5.91 μg ml^{-1} Solvent : n-Octanol

Molarity : 10 M λ_{max} : 352 nm

PC4AHA (10^{-4} M)	**-log [PC4AHA]**	**Niobium Conc. (M)**		**log D_{Nb}**
		$[Nb]_{org} \times 10^{-5}$	**$[Nb]_{aq} \times 10^{-6}$**	
1.01	3.99	2.70	4.82	0.74
2.03	3.69	2.93	2.52	1.06
3.05	3.51	3.01	1.72	1.24
4.06	3.39	3.05	1.32	1.36
5.08	3.29	3.08	1.02	1.47

Table 5 Influence of reagent concentration on tantalum(V)-PC4AHA-Crystal Violet complex

Tantalum(V) : 10.7 μg ml^{-1} Solvent : Dichloromethane

Molarity : 8 M λ_{max} : 579 nm

PC4AHA (10^{-4} M)	**-log [PC4AHA]**	**Tantalum Conc. (M)**		**log D_{Ta}**
		$[Ta]_{org} \times 10^{-5}$	**$[Ta]_{aq} \times 10^{-6}$**	
0.51	4.29	1.71	7.13	0.38
1.02	3.99	2.03	3.88	0.72
1.52	3.81	2.14	2.76	0.89
2.03	3.69	2.21	2.07	1.03

Influence of solvent

The extraction was carried out with different solvents viz. chloroform, dichloromethane, benzene, toluene, iso-amyl alcohol and n-octanol. Amongst the solvent used, n-octanol and dichloromethane are found to be the most adequate solvent for the quantitative analysis of niobium(V) and tantalum(V), respectively (Table 6-7).

Table 6 Influence of Solvent on the extraction of Niobium(V) with PC4AHA-Crystal Violet

Niobium(V) : 5.91 µg ml^{-1} Molarity : 10 M

Solvent	**Extraction %**	**ε* (L mol^{-1} cm^{-1})**
	Nb(V)	**Nb(V)**
Benzene	NE	NE
Toluene	NE	NE
Dichloromethane	56.39	1.07×10^5
Chloroform	60.72	1.15×10^5
Iso-amyl alcohol	69.84	1.32×10^5
n-Octanol	100.00	1.90×10^5

Note: ε* = molar absorptivity; NE = No Extraction

Table 7 Influence of Solvent on the extraction of Tantalum(V) with PC4AHA-Crystal Violet

Tantalum(V) : 10.7 µg ml^{-1} Molarity : 8 M

Solvent	**Extraction %**	**ε* (L mol^{-1} cm^{-1})**
	Ta(V)	**Ta(V)**
Benzene	NE	NE
Toluene	NE	NE
Dichloromethane	100.00	8.74×10^5
Chloroform	85.23	7.21×10^5
Iso-amyl alcohol	78.83	8.85×10^5
n-Octanol	87.21	7.15×10^5

Note: ε* = molar absorptivity; NE = No Extraction

Stoichiometry of the complex

The stoichiometry of the complex was established slope ratio method was employed viz. by plotting a graph of logarithm of metal distribution ratio (log D_M) against the negative logarithm of the concentration of ligand (-log C), which shows the formation of 1:1 Metal : PC4AHA complex for niobium(V) and tantalum(V) with a slope 1.00 (Figure 3-4). Above method confirms that one molecule of ligand is required for one mole of niobium(V) and tantalum(V).

The extraction of niobium(V) and tantalum(V) with PC4AHA can be represented as,

$$NbOCl_{3[aq]} + 2\ HA_{[org]} \Leftrightarrow [(NbOA_2)Cl]_{[org]} + 2\ HCl_{[aq]} \quad .....(1)$$

$$TaOCl_{3[aq]} + 2\,HA_{[org]} \Leftrightarrow [(TaOA_2)Cl]_{[org]} + 2\ HCl_{[aq]} \qquad .....(2)$$

Where, 2 HA stand for one PC4AHA molecule.

The extraction constant K_{ex} can be given

$$K_{ex} = \frac{[MA_2]Cl_{[org]} \times [H^+]^2_{[aq]}}{[M]^{3+}_{[aq]} \times [HA]^2_{[org]}} \qquad .....(3)$$

D_M is metal distribution ratio between organic and aqueous phases given as,

$$D_M = \frac{[MA_2]Cl_{[org]}}{[M]^{3+}_{[aq]}} \qquad .....(4)$$

Where, the subscripts [aq] and [org] are aqueous and organic phases, respectively.

The distribution constant of the PC4AHA can determined by shaking mechanically for 10 min. a series of solution of PC4AHA with the same volume of aqueous phase of optimum molarity. After phase separation, the absorbance of the organic phase can be measured at the λ_{max}.

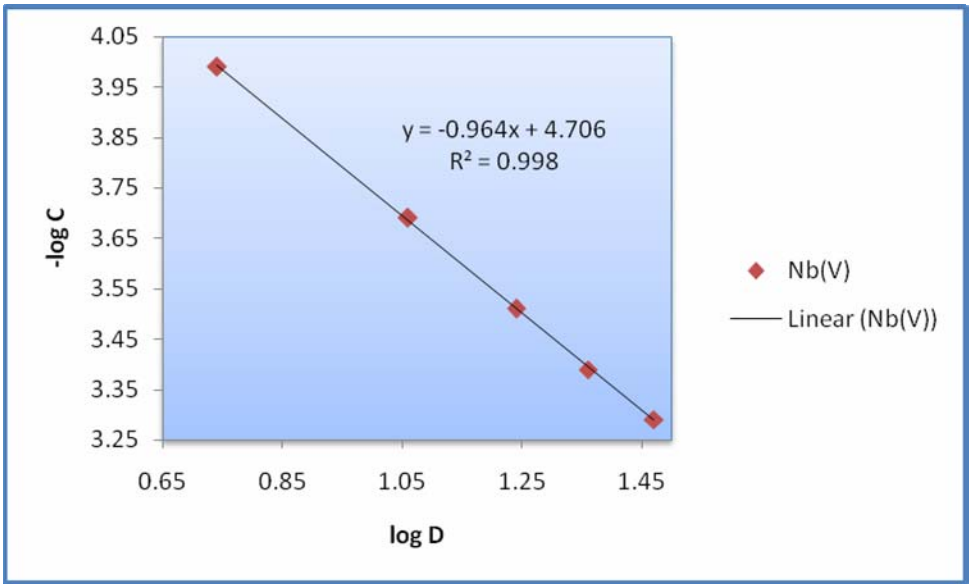


Figure 3 Influence of reagent concentration on the stoichiometry of niobium(V)-PC4AHA complex

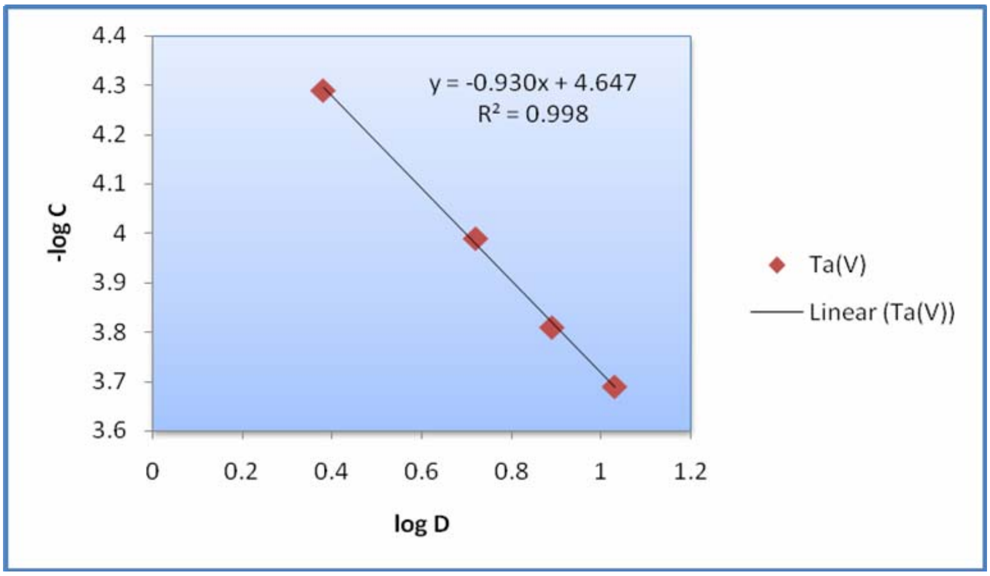


Figure 4 Influence of reagent concentration on the stoichiometry of tantalum(V)-PC4AHA complex

Influence of diverse ions

In order to examine the utility of the present method the effect of various cations and anions in the separation and determination of niobium and tantalum was studied. Interference studies were made by measuring the absorbance of the extracted organic phase and also by making the measurements by ICP-MS of both the extract as well as aqueous phase. The tolerance limit was set as the amount of foreign ion causing a change of absorbance of 0.020% on absorbance or 2.1% error in the recovery of titanium, zirconium and hafnium.

Table 8 Influence of diverse ions on niobium(V)-PC4AHA complex

Niobium(V) : 10 µg ml^{-1} Solvent : n-Octanol
Molarity : 10 M λ_{max} : 352 nm

Foreign ion	Amount added (mg)	Niobium found (µg ml^{-1})	
		Spectrophotometry	ICP-MS
Nb^{5+}	-	-	-
Ag^{+}	40	9.98 ± 0.03	10.002 ± 0.002
Co^{+}	40	9.97 ± 0.04	10.000 ± 0.005
Ca^{2+}	40	10.02 ± 0.01	9.997 ± 0.001
Cd^{2+}	35	10.03 ± 0.03	9.999 ± 0.003
Zn^{2+}	40	9.98 ± 0.05	10.003 ± 0.002
Mn^{2+}	30	10.02 ± 0.04	10.002 ± 0.002
Cu^{2+}	40	9.97 ± 0.02	9.998 ± 0.004
Hg^{2+}	40	9.99 ± 0.04	10.005 ± 0.001
Sn^{2+}	30	10.02 ± 0.01	10.003 ± 0.003
Al^{3+}	40	9.95 ± 0.01	9.998 ± 0.001

Fe^{3+}	35	9.99 ± 0.02	9.997 ± 0.002
As^{3+}	45	10.03 ± 0.04	10.001 ± 0.002
Fe^{2+}	40	9.96 ± 0.05	10.004 ± 0.003
Ni^{2+}	40	9.99 ± 0.02	10.004 ± 0.004
Ti^{4+}	40	10.01 ± 0.01	10.003 ± 0.005
Zr^{4+}	35	10.00 ± 0.03	10.005 ± 0.005
V^{5+}	35	9.98 ± 0.02	9.997 ± 0.003
Cl^{-}	45	9.97 ± 0.05	9.999 ± 0.002
NO_3^{-}	45	9.99 ± 0.05	10.000 ± 0.003
I^{-}	45	9.96 ± 0.05	9.998 ± 0.003
SO_4^{2-}	45	9.99 ± 0.04	10.001 ± 0.003

Niobium added 10 $\mu g\ ml^{-1}$

Table 9 Influence of diverse ions on tantalum(V)-PC4AHA-Crystal Violet complex

Tantalum(V) : 10 $\mu g\ ml^{-1}$ Solvent : Dichloromethane

Molarity : 8 M λ_{max} : 579 nm

Foreign ion	**Amount added (mg)**	**Tantalum found ($\mu g\ ml^{-1}$)**	
		Spectrophotometry	**ICP-MS**
Ta	-	-	-
Ag^{+}	35	10.01 ± 0.04	9.997 ± 0.003
As^{3+}	40	9.98 ± 0.02	9.999 ± 0.002
Be^{2+}	30	9.98 ± 0.05	9.998 ± 0.002
Mg^{2+}	40	9.97 ± 0.03	10.002 ± 0.002
Ca^{2+}	45	10.03 ± 0.03	10.003 ± 0.003

Sn^{2+}	40	9.99 ± 0.01	10.001 ± 0.003
Cd^{2+}	40	10.00 ± 0.03	10.002 ± 0.004
Co^{2+}	35	10.05 ± 0.04	9.998 ± 0.001
Cu^{2+}	35	9.96 ± 0.02	9.999 ± 0.003
Cr^{3+}	35	10.03 ± 0.05	9.997 ± 0.002
Hg^{2+}	40	10.01 ± 0.03	9.998 ± 0.002
Ni^{2+}	40	9.97 ± 0.01	10.003 ± 0.003
Fe^{3+}	50	9.98 ± 0.02	10.002 ± 0.004
Mn^{2+}	50	10.01 ± 0.01	9.997 ± 0.004
Zn^{2+}	50	10.05 ± 0.05	10.001 ± 0.002
Ti^{4+}	40	10.02 ± 0.04	10.003 ± 0.002
V^{5+}	40	9.99 ± 0.01	9.997 ± 0.003
Mo^{6+}	40	9.96 ± 0.03	9.998 ± 0.002
Nb^{5+}	40	9.97 ± 0.04	9.999 ± 0.005
Zr^{4+}	40	10.03 ± 0.03	10.003 ± 0.005
Hf^{4+}	40	10.04 ± 0.02	10.002 ± 0.005
Cl^-	50	9.97 ± 0.04	9.997 ± 0.005
Br^-	50	9.98 ± 0.05	9.998 ± 0.004
PO_4^{3-}	50	9.98 ± 0.02	10.002 ± 0.002

Separation and determination of niobium(V) and tantalum(V)

Generally, niobium interferes in the determination of tantalum. In order to check the accuracy and applicability of the proposed method, niobium(V) and tantalum(V) have been separated from their mixture. The separation of niobium(V) and tantalum(V) from their mixture has been carried out at different molarity.

The molarity of niobium(V) and tantalum(V) mixture has been adjusted to 8M and tantalum(V) was extracted and separated with dichloromethane solution of PC4AHA. The molarity of remained aqueous phase containing niobium(V) was adjusted to 10M for the extraction of niobium(V) using n-octanol solution of PC4AHA. The organic layer after each extraction was separated and subjected to ICP-MS for the determination of niobium(V) and tantalum(V) The result obtained here show that niobium(V) and tantalum(IV) can be separated without any adverse effect from their mixture. The data is given in Table 10.

Analysis of the standard samples

To check the validity and reliability of the method the niobium(V) and tantalum(V) were separated and determined in standard samples. The results obtained here are in good agreement with the certified values (Table 11).

Transport of niobium and tantalum

PC4AHA was successfully used as a carrier for the selective and efficient transport of tantalum(V) and niobium(V) across a bulk liquid membrane of dichloromethane. The assembly used for the study and experimental condition is described in the initial part of this chapter. Niobium and tantalum concentration in the aqueous phase was determined by ICP-MS. The niobium and tantalum ions are absorbed into the membrane due to complex formation with PC4AHA at the interface between the membrane and receiving solution where niobium and tantalum ions are released to aqueous phase due to the stripping action of 0.1 N HCl. The free carrier diffuses back to the interface at the feed side to form another complex with available fresh ions. The effect of molarity variation of the feed solution on the permeation of niobium and tantalum is also studied. At low molarity the niobium and tantalum complexation with PC4AHA does not take place. The effect of molarity of the receiving solution on the permeation of niobium and tantalum was also studied and data showing that niobium and tantalum strips out quantitatively at lower molarity (0.1 N HCl). The concentration of PC4AHA in the membrane phase controls the transportation of niobium and tantalum. No movement of niobium and tantalum was observed unless a carrier PC4AHA used. Maximum transportation of niobium and tantalum was observed at 26 minutes with $t_{1/2}$ equal to 13.2 min and 19 minutes with $t_{1/2}$ equal to 9.3 min (Figure 5).

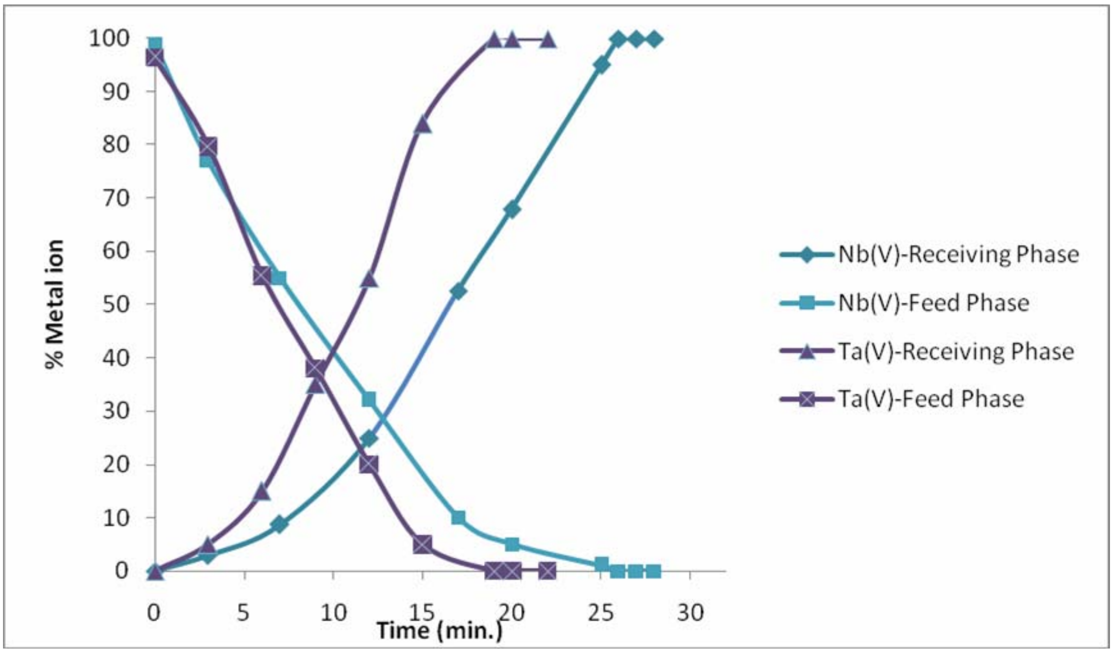


Figure 5 Transportation of niobium(V) and tantalum(V) by PC4AHA

Table 10 Determination of niobium(V) and tantalum(V) from their mixture

Mixture of Nb(V) + Ta(V) *(ng ml^{-1})*	**Niobium(V) found^a**			**Tantalum(V) found^a**		
	(ng ml^{-1})	**Recovery %**	**R**	**(ng ml^{-1})**	**Recovery %**	**R**
10 + 10	9.97 ± 0.02	99.7	0.05	9.99 ± 0.03	99.9	0.08
10 + 5	10.01 ± 0.04	100.1	0.06	5.01 ± 0.05	100.2	0.06
5 + 10	4.99 ± 0.02	99.8	0.08	9.98 ± 0.03	99.8	0.07
10 + 20	10.02 ± 0.05	100.2	0.08	20.02 ± 0.03	100.1	0.08
10 + 30	10.01 ± 0.03	100.1	0.07	29.98 ± 0.05	99.9	0.07

Note: ^{a} The results are average of 10 determinations; R = reproducibility

Table 11 Determination of niobium and tantalum in standard samples

Standard samples		Certified Value (ppm)	Found[a] (ppm)	
			Spectrophotometry	ICP MS
BHVO-1[b]	Nb(V)	19.00	19.02 ± 0.03	19.003 ± 0.005
	Ta(V)	1.23	1.20 ± 0.04	1.213 ± 0.002
GSR-1[c]	Nb(V)	40.00	40.01 ± 0.05	39.998 ± 0.004
	Ta(V)	7.20	7.19 ± 0.03	7.203 ± 0.005
GSR-4[d]	Nb(V)	5.90	5.92 ± 0.05	5.897 ± 0.002
	Ta(V)	0.42	0.42 ± 0.05	0.423 ± 0.003
Sea Water				
Apollo Bunder	Nb(V)	-	0.19 ± 0.03	0.192 ± 0.005
	Ta(V)	-	0.21 ± 0.04	0.212 ± 0.003

Note: [a] The results are average of 10 determinations

Reference geological materials were used:
[b] Basalt, NIST, Gaithersburg, MD, USA
[c,d] Granite, Institute of Rock and Mineral Analysis, Beijing, China

Preconcentration and Recovery

A preconcentration study was carried out with about 5 µg of niobium and tantalum in 1000 mL aqueous phase by extracting 10 times each 100 mL of aqueous phase with same 10 mL of ligand solution. (The niobium and tantalum gets concentrated in 10 mL of ligand solution). For the evaluation of the efficiency of preconcentration, express as recovery, the concentration of niobium and tantalum in organic phase and remaining in aqueous phase was measured by ICP-MS against calibrated standard solution in n-octanol and dichloromethane. The recovery % R, was calculated from

$$R\% = \frac{[As_{std} - As]}{A_{std}} \times 100$$

where As_{std} is the absorbance value for sample containing known amount of standard niobium and tantalum added to sample solution prior to the extraction. A_{std} is the absorbance value for the standard in organic phase with the same analyte concentration as the standard addition and As is the absorption value for the sample. The results are given in Table 10.

CONCLUSION

The present method describes a new extractant PC4AHA is used for the sequential separation and determination of niobium(V) and tantalum(V) in trace amounts from different samples. The application of new extractant is development which tends to aid and promote supramolecular host-guest complexation and will undoubtedly further stimulate the development of more efficient and selective extraction systems.

References

1. F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th Edition, John Wiley & Sons, **1988**.

2. Y. Kakita, H. Gotò, Anal. Chem., **1962**, 34(6), 618.

3. N. N. Greenwood, A. Earnshaw, "Chemistry of the Elements", Pergamon Press, New York, **1989**.

4. N. Vachirapatama, P. Doble, Z. Yu, M. Macka, P. R. Haddad, Anal. Chim. Acta, **2001**, 434, 301.

5. S. M. Eggins, J. D. Woodhead, L. P. J. Kinsley, G. E. Mortimer, P. Sylvester, M. T. McCulloch, J. M. Hergt, M. R. Handler, Chem. Geol., **1997**, 134, 311.

6. A. Sabarudin, M. Oshimaa, T. Takayanagi, L. Hakima, K. Oshita, Y. H. Gaoc, S. Motomizua, Anal. Chim. Acta, **2007**, 581, 214.

7. M. L. Firdaus, K. Norisuye, T. Sato, S. Urushihara, Y. Nakagawa, S. Umetani, Y. Sohrin, Anal. Chim. Acta, **2007**, 583, 296.

8. S. Weyer, C. Munker, M. Rehkamper, K. Mezger, Chem. Geol., **2002**, 187, 295.

9. X.J. Yang, C. Pin, Anal. Chim. Acta, **2002**, 458, 375.

10. P. Roychowdhury, N. K. Roy, A. K. Das, At. Spectrosc., **1995**, 16, 104.

11. K. Satyanarayana, M. A. Nayeem, At. Spectrosc., **1993**, 14, 180.

12. N. Vachirapatama, M. Macka, B. Paull, C. Munker, P. R. Haddad, J. Chromatogr. A, **1999**, 850, 257.

13. N. Vachirapatama, P. Doble, Z. Yu, P. R. Haddad, Chromatographia, **1999**, 50, 601.

14. N. Vachirapatama, P. Doble, P. R. Haddad, Anal. Chim. Acta, **2000**, 409, 35.

15. N. Vachirapatama, P. Doble, P. R. Haddad. J. Chromatogr. A, **2000**, 885, 369.

16. M. Zeinera, M. Ovarib, G. Zarayb, I. Steffan, J. Trace Elem. Med Biol., **2006**, 20, 240.

17. C. Hang, B. Hu, Z. Jiang, N. Zhang, Talanta, **2007**, 71, 1239.

18. G. Steinhauser, J. H. Sterba, K. Poljanc, M. Bichler, K. Buchtela, J. Trace Elem. Med Biol., **2006**, 20, 143.

19. C. J. Scadding, R. J. Watling, A. G. Thomas, Talanta, **2005**, 67, 414.

20. N. Vachirapatama, P. Doble, Z. Yu, M. Mackaa, P. R. Haddada, Anal. Chim. Acta, **2001**, 434, 301.

21. E. Liu, Y. Liu, J. Cheng, Anal. Chim. Acta, **2001**, 443, 101.

22. B. Liu, L. Liu, H. Chen, J. Cheng, Fresenius J. Anal. Chem., **2001**, 369, 195.

23. L. Dongling, H. Xiaoyan, W. Haizhou, Anal. Chim. Acta, **2001**, 449, 237.

24. O. M. El Hussaini, N. M. Rice, Hydrometallurgy, **2004**, 72, 259.

25. H. Matsumiya, S. Yasuno, N. Iki, S. Miyano, J. Chromatogr. A, **2005**, 1090, 197.

26. H. Wang, H. Zhang, J. Cheng, P. Qiu, Microchem. J., **1997**, 55, 332.

27. D. T. Burns, N. Tungkananuruk, S. Janewongpaisan, Anal. Chim. Acta, **2000**, 422, 199.

28. Y. K. Agrawal, Talanta, **2002**, 58, 875.

29. V. Korovin, Y. Shestak, React. Funct. Polym., **1999**, 40, 107.

30. M. E. Campderros, J. Marchese, Hydrometallurgy, **2001**, 61, 89.

31. V. G. Mayorov, A. I. Nikolaev, Hydrometallurgy, **1996**, 41, 71.

32. M. E. Campderros, J. Marchese, J. Membr. Sci., **2000**, 164, 205.

33. S. Inoue, O. Mishima, Q. Zhang, H. Minami, M. Uto, Anal. Lett., **2001**, 34(14), 2465.

34. K. Patel, S. K. Menon, Y. K. Agrawal, Microchem. J., **1996**, 53, 158.

35. V. G. Maiorov, A. I. Nikolaev, V. K. Kopkov, Russ. J. Appl. Chem.,

2001, 74(3), 363.

36. V. G. Maiorov, A. I. Nikolaev, V. K. Kopkov, Russ. J. Appl. Chem., **2002**, 75(9), 1389.

37. V. G. Mayorov, A. I. Nikolaev, Hydrometallurgy, **2002**, 66, 77.

38. H. Wang, H. Zhang, J. Cheng, J. Anal. Chem., **1995**, 351, 683.

39. A. G. Coedo, T. D. Ihpez, F. Alguacil, Anal. Chim. Acta, **1995**, 315, 331.

40 C. Bucher, C. H. Devillers, J.C. Moutet, J. Pécaut, G. Royal, E. Saint-Aman, F. Thomas, J. Chem. Soc. Dalton Trans., **2005**, 22, 3620.

41. S. Banthia, A, Samanta, Org. Biomol. Chem., **2005**, 3, 1428.

42. Q.-Y. Chena, C.-F. Chen, Tetrahedron Lett., **2005,** 46, 165–168.

43. J. Dessingou, R. Joseph, C. P. Rao, Tetrahedron Lett., **2005**, 46, 7967.

44. A. F. Danil de Namor, M. T. Goitia, A. R. Casal, J. Villanueva-Salas, Phys. Chem. Chem. Phys., **2001**, 3, 5242.

45. M. Mahouachi, Y. KIM, S. HO LEE, R. Abid, J. Harrowfield, J. Vicens, Supramol. Chem., **2005**, 17, 323.

46. J. Y. Lee, S. K. Kim, J. H. Jung, J. S. Kim, J. Org. Chem., **2005**, 70, 1463.

47. S. Bozkurt, A. Karakucuk, A. Sirit, M. Yilmaz, Tetrahedron, **2005**, 61, 10443.

48. T. Tilki, I. Şener, F. Karc, A. Gülce, H. Deligöz, Tetrahedron, **2005**, 61, 9624.

49. Z. Liu, L. Jiang, Z. Lianga, Y. Gao, Tetrahedron Lett., **2005**, 46, 885.

50. L. S. Kuznetsova, G. A. Pribylova, A. R. Mustafina, I. G. Tananaev, B. F. Myasoedov, A. I. Konovalov, Radiochemistry, **2004**, 46, 277.

51. S. J. Dalgarno, M. J. Hardie, J. L. Atwood, J. E. Warrenc, C. L. Raston, New J. Chem., **2005**, 29, 649.

52. J. G. Bünzli, F. Besançon, Phys. Chem. Chem. Phys., **2005**, 7, 2191.

53. Y. Israëliz, C. Detellier, Phys. Chem. Chem. Phys., **2004**, 6, 1253.

Chapter IV

Calixarene Hydroxamic Acid for Extraction, Separation, Recovery, Preconcentration, Speciation and Transport of Titanium, Zirconium and Hafnium by Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS)

Abstract

A solvent extraction and separation of titanium, zirconium and hafnium with coumarin-calix[4]arene hydroxamic acid (CC4AHA) is described. Quantitative extraction of titanium, zirconium and hafnium is possible in dichloromethane solution of CC4AHA at 6.0, 8.0 and 0.6 molarity. The binding ratio of titanium, zirconium and hafnium with CC4AHA is 1:1. The trace determination was achieved by directly aspirating the extract for ICP-MS measurements. A liquid membrane transport study of titanium, zirconium and hafnium was carried out from source to the receiving phase under controlled conditions. The synthesized chelating extractant was tested for simultaneous separation of titanium, zirconium and hafnium mixtures. The validation of the procedure was performed by the analysis of certified standard reference materials.

Introduction

Determination of trace amounts of titanium is of great interest because of its increasing industrial applications and extensive uses in catalysts, paint, pigments and corrosion inhibitors /1/. It is valuable alloying agents and coexists in a number of industrially important alloys and steels /1/. Which are used principally in missile, aircraft parts and filament material in electrical applications where lightweight, strength and ability to withstand extremes of temperature are important /2/. Various analytical techniques used for the determination of titanium in different types of matrices include neutron activation analysis /3,4/ inductively coupled plasma atomic emission spectrophotometry /5,6/, X-ray fluorescence /7,8/ and spectrophotometry /9–14/, etc. Spectrophotometry occupies special position due to their simplicity. A number of chromogenic extractants, such as *O*,*O'*-bis(2-ethylhexyl)dithiophosphoric acid, isothipendyl hydrochloride, pipazethate hydrochloride, 3,4-dihydroxybenzoic acid, 2-(2'-furyl)-3-hydroxy chromone, *N*-hydroxy-*N*,*N'*-diphenylbenzamidine have been reported for the determination of titanium at trace levels /15–19/.

Zirconium most commonly occurs with hafnium. It is used in the nuclear industry as a shielding material, in metal alloys, as catalyst in organic reactions in manufacture of water repellent textiles, in dyes pigment and ceramics /46/. The chemistry of zirconium and hafnium are more nearly identical as they have almost identical atomic and ionic radii /21/. Thermal neutron absorption cross section of hafnium is nearly 600 times that of zirconium and because of its ability to absorb neutrons it is used to make control rods for nuclear reactors /22/. Hafnium also has excellent mechanical properties and exceptional corrosion–resistance properties /31/. Hafnium is used as a heavy metal, in nickel-based super alloys, nozzles for plasma arc metal cutting, and high-temperature ceramics /36/. Hafnium compounds are toxic although initial evidence would appear to suggest that the danger is limited but the metal dust presents a fire and explosion hazard /37/. Overexposure to hafnium and its compounds could cause mild irritation of the eyes, skin, and mucous membranes /37/. Due to vital importance of zirconium and hafnium, a number of analytical techniques has been reported in literature /23-39/. Several extractants such as quinalizarine /28,54/, N,N-bis(a-methyl-salicylidene)-dipropylenetriamine /31/, calconcarboxylic acid /38/, 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) /40/, cyanex 302 /41/, cyanex 925 /42/, dibutylsulfoxide /43/, LIX 84-IC (2-hydroxy-5-nonylacetophenoneoxime) /44,51/, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) /45,60/, cyanex 272 /46/, di-2-ethylhexylphosphoric acid (D2EHPA) /47/, Tri-n-octylamine (TNOA) and trioctylmethyl ammonium chloride (Aliquat 336) /48/, 2-ethyl hexyl phosphonic acid mono-2-methyl hexyl ester (PC-88A) /49/, versatic Acid 10 /50/, p-tert-butylthiacalix[4]arene /52/, thiosubstituted organophosphorus acids cyanex 301 and 302 /53/, poly(acrylphenylamidrazone-phenyl-hydrazide-acylphenylhydrazine) /55/, N,N,N',N'-tetraoctyl-3-oxa-pentane-1,5-diamide (TODGA) /56/ , thenoyltrifluoro-acetone /57/, 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) /58/, thoron /59/, poly(acryldinitrophenylamidrazone dinitroacrylphenylhydrazine) /61/ and xylenol orange modified resin /62/ have been reported in literature.

The extractant 7,8-dihydroxy-4-methylcoumarin /20/- though reports higher sensitivity, but the conditions of colour reaction, such as pH and surfactant concentration must be strictly controlled in order to obtain reliable results. Most of the reported methods suffer from a number of limitations, such as tedious and time consuming extraction /10–12/, preconcentration using an ion-exchanger resin /14,15,24,62/, preparation of electrode /31,59/, preparation of column /55,56,60,61/, reduction to lower oxidation state, followed by colour development and extraction /16/. It is necessary to develop a new method which is simple, rapid and highly sensitive.

A survey of the literature showed that very less work has been reported with calixarene and in particular with calix hydroxamic acid for the extraction of titanium, zirconium and hafnium. Introduction of hydroxamic acid on calixarene will enhance the affinity of metal ion towards the extractant. By keeping this in view, an alternate extractant for the selective extraction, separation and trace determination of titanium, zirconium and hafnium from acidic solutions has been developed.

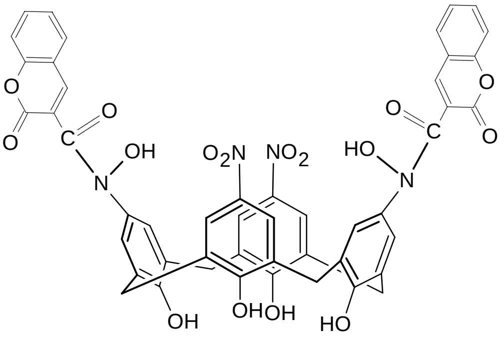
EXPERIMENTAL

Standard Solutions & Reagents

All the chemicals used were of analytical grade obtained from Sigma-Aldrich or Merck. Deionised double distilled water was used, which was further purified by a Millipore Milli-Q water purification system. Titanium(IV) stock solution was prepared by heating 0.06191 g of titanium dioxide with sulphuric acid and ammonium sulphate and finally diluted to 250 ml with double distilled water. Its final concentration (3.14×10^{-3} M) was determined by spectrophotometry /63/. Zirconium(IV) stock solution was prepared by dissolving 0.0339 g zirconyl nitrate hydrate in 8 ml of dilute nitric acid and diluted up to 100 ml with double distilled water. Its final concentration (0.98×10^{-3} M) was determined spectrophotometry /64/. A stock solution of hafnium was prepared by heating 0.022 g of hafnium dioxide in a platinum crucible with 1 ml of 40% hydrofluoric acid and 5 ml of water. The contents were evaporated to dryness, the residue was moistened with sulphuric acid and evaporation was continued until dense white fumes appeared. The residue was dissolved in 100 ml of 0.2 M perchloric acid and its final concentration (1.23×10^{-4} M) was determined spectrophotometrically /65/.

5,17-Dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[coumarin hydrox-amic acid] (Figure 1) was synthesized as described in

Chapter 2. 1.08 × 10^{-3} M (0.1 % w/v) stock solution of CC4AHA was prepared in dichloromethane.



CC4AHA

Figure 1 Coumarin - Calix[4]arene hydroxamic acid (CC4AHA)

Apparatus

Spectra were recorded on a JASCO-980 UV-Vis-NIR spectrophotometer with matching 10 mm quartz cells. A Plasma Scan Model 710 sequential Inductively Coupled Plasma with Plasma Scan multitasking computer and peristaltic pump was used. Thermo Jarrell-Ash Corporation, Franklin, MA, USA, POEMS mass spectrophotometer with a Fassel torch, a concentric glass nebulizer and cryogenic spray chamber was used. The optimized instrumental conditions are summarized in Table 1.

Table 1 Optimized instrumental conditions for ICP-MS

Instrumental parameters	ICP-MS
ICP Plasma	Argon
Forward Power	1.35 KW
Reflected Power	<10 W
Gas flow (L/min)	
Coolant	16
Carrier	0.70
Auxiliary	0.30
Nebuliser Pressure	2 bar
Solution uptake rate	0.8 mL/min
Sampler cone aperture	1 mm
Skimmer cone aperture	0.7 mm
Mass No.	
Ti	48
Zr	90
Hf	178

Extraction Procedure

An aliquot of the titanium(IV) [1.72-75 µg] (molarity range 7.5-8.5), zirconium(IV) [4.5-45 µg] (molarity range 5.5-6.5) and hafnium(IV) [12.9-116.5 µg] (molarity range 0.2-1.0), respectively were transferred into a 60 ml separatory funnel. Desired molarity of aqueous phase was maintained by adding appropriate amount of dilute acid solution. The mixture was there after shaken with 8 ml of 0.1 % (w/v) dichloromethane solution of CC4AHA extractant for 8-10 min. The organic phase was separated, dried over anhydrous sodium sulphate and transferred into a 25 ml volumetric flask. To ensure the complete recovery of the metal ions, the extraction was repeated with 2 ml of CC4AHA extractant solution. The sodium sulphate was washed with 2 ×

2 ml of dichloromethane and the combined extracts and washing were diluted to the mark with dichloromethane. The absorbance of the extract was measured against the extractant blank. The organic extract was also directly inserted to plasma for ICP-MS measurements.

Transport of titanium, zirconium and hafnium

Source phase aqueous 10ml of 8M titanium, 10ml of 6M zirconium solution and 10 ml of 0.6 M hafnium solution and 20 ml of dichloromethane membrane phase with 1.08 x 10^{-3} M CC4AHA as carrier were taken in specially fabricated glass membrane assembly and stirred with teflon coated magnetic and mechanical stirrer. The receiving phase was 20 ml of 0.1 N HCl.

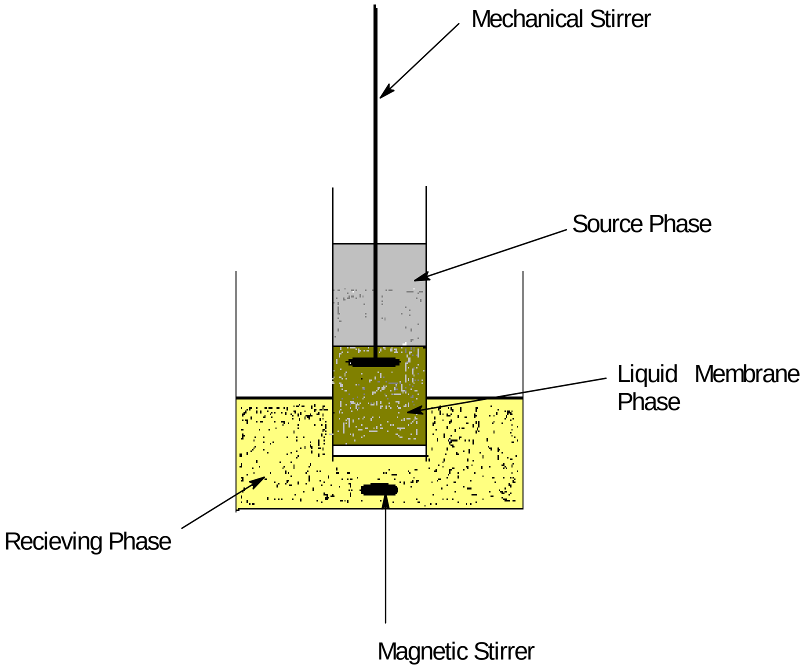


Figure 2 Transport Cell

RESULT AND DISCUSSION

The titanium(IV)-CC4AHA complex is light yellow and has a maximum absorbance at 420.5 nm with molar absorptivity 3.52 × 10^4 L min^{-1} cm^{-1}. Colorless zirconium(IV)-CC4AHA complex has maximum absorbance at 372 nm with molar absorptivity 1.04 × 10^5 L mol^{-1} cm^{-1}. Colorless hafnium(IV)-CC4AHA complex has maximum absorbance at 335 nm with molar absorptivity 1.97 × 10^5 L mol^{-1} cm^{-1}. The extractant blanks do not absorb at these wavelengths. Under the optimum conditions, the calibration curves are linear over the concentration range of 1.72-75 μg ml^{-1} for titanium(IV), 4.5-45 μg ml^{-1} for zirconium(IV) and 12.9-116.5 μg ml^{-1} for hafnium(IV). Ten determinations of each 15 μg ml^{-1} of titanium(IV), zirconium(IV) and hafnium(IV) solutions gave a relative standard deviation of 0.89%, 2.06% and 1.53%, respectively. For the trace determination, the extracts were directly inserted into plasma for ICP-MS measurements which enhances the sensitivity to several times having the detection limits of 1.5, 1.0 and 1.0 ng ml^{-1} for titanium, zirconium and hafnium, respectively.

Influence of molarity and Time

Titanium(IV), zirconium(IV) and hafnium(IV) were extracted with CC4AHA at different molarity (Table 2-4). It was observed that maximum extraction (% E) was found for titanium(IV) between 7.5-8.5 molar, zirconium(IV) at 5.5-6.5 molar and for hafnium(IV) at 0.2-1.0 molar (Table 2-4). It was found that 5-7 min. of shaking time is sufficient for the quantitative extraction of titanium(IV), zirconium(IV) and hafnium(IV). The extracted complexes were stable for 15-20 h at 25°C.

Table 2 Influence of molarity on the extraction of titanium(IV)-CC4AHA complex

Titanium(IV) : 3.45 μg ml^{-1} CC4AHA : 10 ml (1.08×10^{-3} M)

Solvent : Dichloromethane λ_{max} : 420.5 nm

Molarity	**Extraction (%)**	**ε* (L mol^{-1} cm^{-1})**
4.0	15.63	5.50×10^3
5.5	49.16	1.73×10^4
6.5	71.28	2.51×10^4
7.5	99.99	3.52×10^4
8.0	99.99	3.52×10^4
8.5	99.99	3.52×10^4
9.0	80.72	2.80×10^4
10.0	63.43	2.23×10^4

Table 3 Influence of molarity on the extraction of zirconium(IV)-CC4AHA complex

Zirconium(IV) : 9.0 μg ml^{-1} CC4AHA : 10 ml(1.08×10^{-3} M)

Solvent : Dichloromethane λ_{max} : 372 nm

Molarity	**Extraction (%)**	**ε* (L mol^{-1} cm^{-1})**
2.0	21.61	2.24×10^4
3.0	59.38	6.17×10^4
4.5	84.15	8.75×10^4
5.5	99.99	1.04×10^5
6.0	99.99	1.04×10^5
6.5	99.99	1.04×10^5
7.0	73.22	7.8×10^4
8.0	60.84	6.27×10^4

ε* = molar absorptivity

Table 4 Influence of molarity on the extraction of hafnium(IV)-CC4AHA complex

Hafnium(IV)	:	25.9 µg ml^{-1}	CC4AHA	:	10 ml (1.08×10^{-3} M)
Solvent	:	Dichloromethane	λ_{max}	:	335 nm

Molarity	**Extraction (%)**	**ε* (L mol^{-1} cm^{-1})**
0.01	24.22	0.43×10^5
0.1	69.43	1.26×10^5
0.2	99.99	1.96×10^5
0.6	99.99	1.97×10^5
1.0	99.99	1.97×10^5
1.5	81.28	1.45×10^5
2.0	47.51	0.85×10^5

ε* = molar absorptivity

Influence of reagent concentration

The influence of the CC4AHA concentration was studied by extracting a fixed amount of titanium(IV), zirconium(IV) or hafnium(IV) with varying concentration of CC4AHA (Table 5-7). It was found that a 10 ml of 1.08 × 10^{-3} M CC4AHA was adequate for the complete extraction of titanium(IV), zirconium(IV) and hafnium(IV). The lower concentration of CC4AHA gives incomplete extraction while a large excess of the extractant can be used without any difficulty.

Table 5 Influence of reagent concentration on titanium(IV)-CC4AHA complex

Titanium(IV)	:	3.45 µg ml^{-1}	Solvent	:	Dichloromethane
Molarity	:	8 M	λ_{max}	:	420.5 nm

CC4AHA (10^{-4} M)	**-log [CC4AHA]**	**Titanium Conc. (M)**		**log D_{Ti}**
		$[Ti]_{org} \times 10^{-5}$	**$[Ti]_{aq} \times 10^{-5}$**	
0.86	4.06	6.52	0.68	0.97
1.73	3.76	6.85	0.35	1.28
2.60	3.58	6.97	0.24	1.46
3.47	3.45	7.02	0.18	1.58
4.34	3.36	7.20	0.14	1.69

Table 6 Influence of reagent concentration on zirconium(IV)-CC4AHA complex

Zirconium(IV) : 9.0 μg ml^{-1} Solvent : Dichloromethane

Molarity : 6 M λ_{max} : 372 nm

CC4AHA (10^{-4} M)	**-log [CC4AHA]**	**Zirconium Conc. (M)**		**log D_{Zr}**
		$[Zr]_{org} \times 10^{-5}$	**$[Zr]_{aq} \times 10^{-6}$**	
0.86	4.06	9.37	4.96	1.27
1.73	3.76	9.59	2.76	1.54
2.60	3.58	9.70	1.66	1.76
3.47	3.45	9.74	1.26	1.88
4.34	3.36	9.76	1.06	1.96

Table 7 Influence of reagent concentration on hafnium(IV)-CC4AHA complex

Hafnium(IV) : 25.9 µg ml^{-1} Solvent : Dichloromethane

Molarity : 0.6 M λ_{max} : 335 nm

CC4AHA (10^{-4} M)	**-log [CC4AHA]**	**Hafnium Conc. (M)**		**log D_{Hf}**
		$[Hf]_{org} \times 10^{-4}$	**$[Hf]_{aq} \times 10^{-6}$**	
0.86	4.06	1.13	9.85	1.06
1.73	3.76	1.17	5.26	1.35
2.60	3.58	1.20	3.29	1.56
3.47	3.45	1.21	2.46	1.69
4.34	3.36	1.22	2.05	1.77

Influence of solvent

The extraction was carried out with different solvents viz. chloroform, carbon tetrachloride, dichloromethane, benzene, toluene, iso-amyl alcohol and dichloromethane. Amongst the solvent used, dichloromethane is found to be the most adequate solvent for the quantitative analysis of titanium(IV), zirconium(IV) and hafnium(IV) (Table 8-10).

Table 8 Influence of solvent on the extraction of titanium(IV) with CC4AHA

Titanium(IV) : 3.45 μg ml^{-1} Molarity : 8.0 M

Solvent	**Extraction (%)**	**ε* (L mol^{-1} cm^{-1})**
Benzene	NE	NE
Toluene	NE	NE
Iso-amyl alcohol	52.7	1.86×10^4
n-Octanol	54.3	1.91×10^4
Chloroform	78.2	2.76×10^4
Dichloromethane	99.9	3.52×10^4

Note: ε* = molar absorptivity; NE = No Extraction

Table 9 Influence of Solvent on the extraction of zirconium(IV) with CC4AHA

Zirconium(IV) : 9.0 µg ml^{-1} Molarity : 6.0 M

Solvent	**Extraction (%)**	**ε* (L mol^{-1} cm^{-1})**
Benzene	NE	NE
Toluene	NE	NE
Iso-amyl alcohol	46.77	4.86×10^4
n-Octanol	52.91	5.50×10^4
Chloroform	83.76	8.71×10^4
Dichloromethane	99.9	3.52×10^4

Note: ε* = molar absorptivity

NE = No Extraction

Table 10 Influence of Solvent on the extraction of hafnium(IV) with CC4AHA

Hafnium(IV) : 25.9 μg ml^{-1} Molarity : 0.6 M

Solvent	Extraction (%)	ε* (L mol^{-1} cm^{-1})
Benzene	NE	NE
Toluene	NE	NE
Iso-amyl alcohol	64.83	1.25 x 10^{5}
n-Octanol	57.22	1.12 x 10^{5}
Chloroform	73.28	1.43 x 10^{5}
Dichloromethane	99.99	1.96 x 10^{5}

Note: ε* = molar absorptivity; NE = No Extraction

Stoichiometry of the complex

The stoichiometry of the complex was established by two methods. One the slope ratio method was employed viz. by plotting a graph of logarithm of metal distribution ratio (log D_M) against the negative logarithm of the concentration of extractant (-log C), which shows the formation of 1:1 Metal : CC4AHA complex for titanium(IV), zirconium(IV) and hafnium(IV) with a slope 1.00 (Figure 3-5). It confirms that one molecule of extractant is required for one mole of titanium(IV), zirconium(IV) and hafnium(IV).

The extraction of titanium(IV), zirconium(IV) and hafnium(IV) with CC4AHA can be represented as,

$$TiOCl_{2[aq]} + 2\ HA_{[org]} \Leftrightarrow [(TiOA_2)Cl]_{[org]} + 2\ HCl_{[aq]} \quad \text{.....(1)}$$

$$ZrOCl_{2[aq]} + 2\ HA_{[org]} \Leftrightarrow [(ZrOA_2)Cl]_{[org]} + 2\ HCl_{[aq]} \quad \text{.....(2)}$$

$$Hf(SO_4)_{2[aq]} + 2\ HA_{[org]} \Leftrightarrow [(HfA_2)SO_4]_{[org]} + H_2SO_{4[aq]} \quad \text{.....(3)}$$

Where, 2 HA stand for one CC4AHA molecule.

The extraction constant K_{ex} can be given

$$K_{ex} = \frac{[MA_2]Cl_{[org]} \times [H^+]^2_{[aq]}}{[M]^{3+}_{[aq]} \times [HA]^2_{[org]}} \quad \text{.....(4)}$$

D_M is metal distribution ratio between organic and aqueous phases given as,

$$D_M = \frac{[MA_2]Cl_{[org]}}{[M]^{3+}_{[aq]}} \quad \text{.....(5)}$$

Where, the subscripts [aq] and [org] are aqueous and organic phases, respectively.

The distribution constant of the CC4AHA can determined by shaking mechanically for 10 min. a series of solution of CC4AHA with the same volume of aqueous phase of optimum molarity. After phase separation, the absorbance of the organic phase can be measured at the λ_{max}.

Figure 3 Influence of extractant concentration on the stoichiometry of titanium(IV)-CC4AHA complex

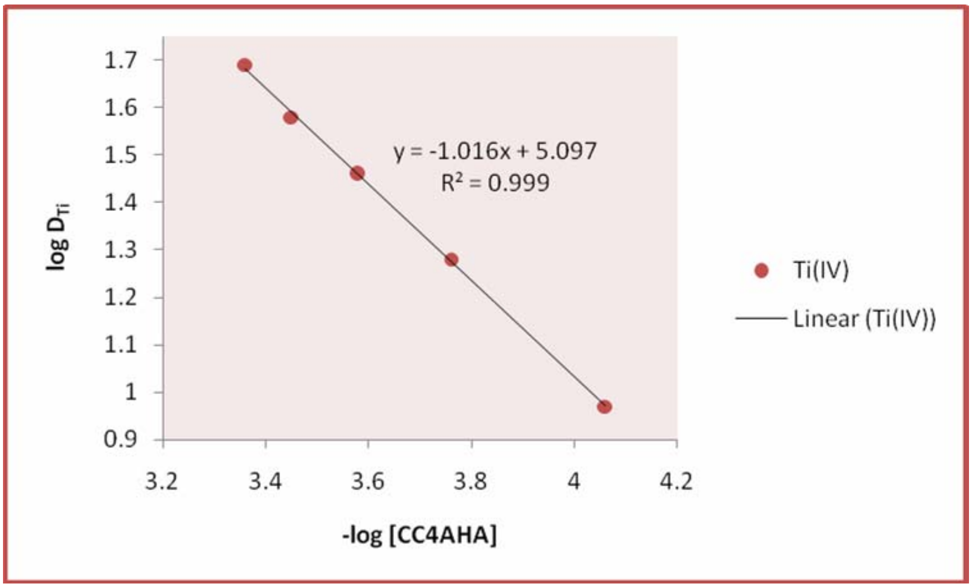


Figure 4 Influence of extractant concentration on the stoichiometry of zirconium(IV)-CC4AHA complex

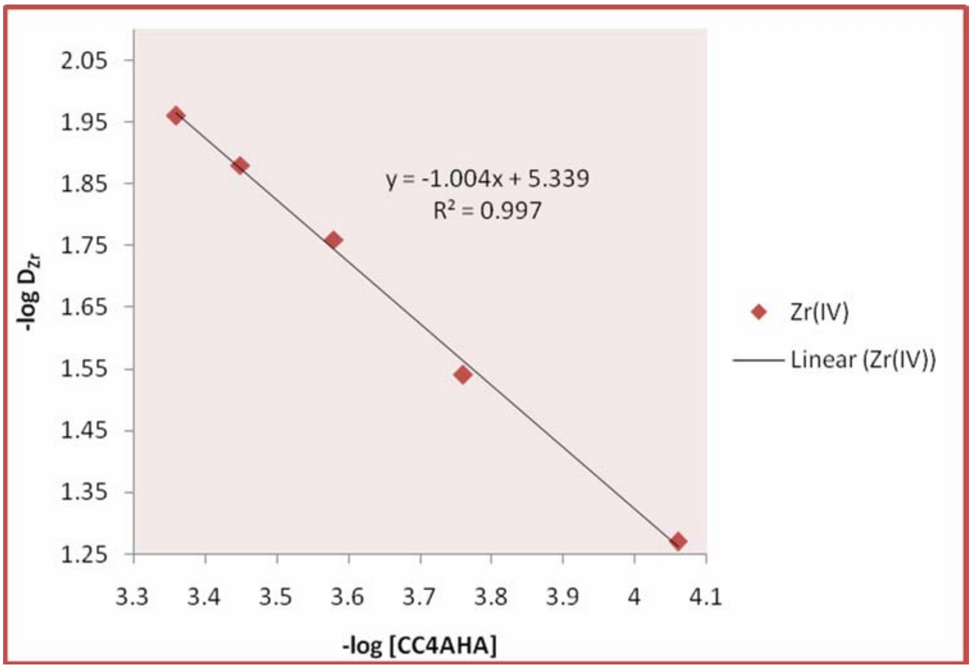
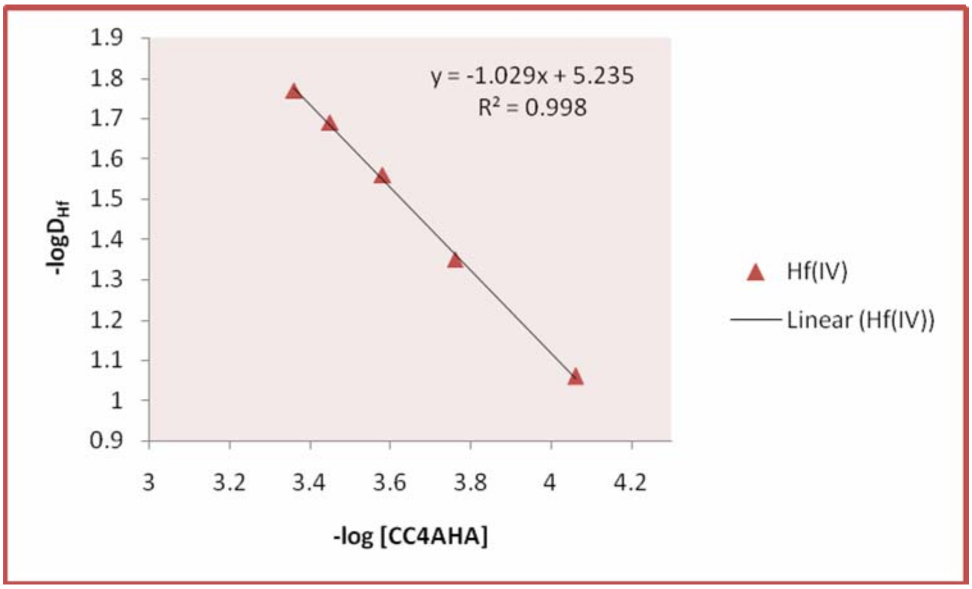


Figure 5 Influence of extractant concentration on the stoichiometry of hafnium(IV)-CC4AHA complex



Influence of diverse ions

In order to examine the utility of the present method, the influence of various ions in the separation and determination of titanium, zirconium and hafnium was studied. Interference studies were performed by measuring the absorbance of the extracted organic phase and also by ICP-MS of both the extract as well as aqueous phase. The tolerance limit was set as the amount of foreign ion causing a change of absorbance of 0.019% on absorbance or 1.80% error in the recovery of titanium, zirconium and hafnium.

Titanium, zirconium and hafnium were extracted in presence of large number of competitive ions at the optimum molarity and none of them affected the absorbance of titanium, zirconium and hafnium. The moderate amount of metal ions associated with titanium, zirconium and hafnium were tolerated (Table 11-13).

Table 11 Influence of diverse ions on titanium(IV)-CC4AHA complex

Titanium(IV) : 15 µg ml^{-1} CC4AHA : 10 ml (1.08×10^{-3} M)

Solvent : Dichloromethane λ_{max} : 420.5 nm

Diverse ion	Amount added (mg)	Titanium Found (µg ml^{-1})	
		Spectrophotometry	ICP-MS
Ti^{4+}	--	--	--
As^{3+}	40	15.02 ± 0.03	15.002 ± 0.004
Be^{2+}	40	15.03 ± 0.04	15.005 ± 0.003
Mg^{2+}	50	15.01 ± 0.05	15.004 ± 0.005
Ca^{2+}	50	14.99 ± 0.02	15.002 ± 0.004
Sn^{2+}	45	14.98 ± 0.01	14.997 ± 0.004
Cd^{2+}	40	15.04 ± 0.04	15.004 ± 0.005
Cu^{2+}	40	14.99 ± 0.03	15.003 ± 0.004
Cr^{3+}	40	15.04 ± 0.05	15.001 ± 0.003
Hg^{2+}	40	15.02 ± 0.03	15.002 ± 0.003
Ni^{2+}	50	15.02 ± 0.03	15.003 ± 0.002
Fe^{2+}	50	14.96 ± 0.04	14.998 ± 0.005
Fe^{3+}	45	15.03 ± 0.04	14.998 ± 0.004

Mn^{2+}	45	15.01 ± 0.02	15.004 ± 0.004
Zn^{2+}	45	14.98 ± 0.03	14.997 ± 0.004
Al^{3+}	40	15.04 ± 0.02	15.001 ± 0.003
V^{5+}	40	15.01 ± 0.04	15.003 ± 0.005
Nb^{5+}	40	15.03 ± 0.04	15.003 ± 0.002
Ta^{5+}	40	14.97 ± 0.05	14.998 ± 0.003
Mo^{6+}	40	14.99 ± 0.04	15.004 ± 0.003
Zr^{4+}	40	15.03 ± 0.03	15.001 ± 0.005

Table 12 Influence of diverse ions on zirconium(IV)-CC4AHA complex

Zirconium(IV) : 15.0 µg ml^{-1} Solvent : Dichloromethane

Molarity : 6 M λ_{max} : 372 nm

Diverse ion	**Amount added (mg)**	**Zirconium Found (µg ml^{-1})**	
		Spectrophotometry	**ICP-MS**
Zr	-	-	-
Ag^+	35	15.03 ± 0.02	15.003 ± 0.003
As^{3+}	40	15.01 ± 0.04	15.001 ± 0.003
Be^{2+}	30	15.04 ± 0.03	14.998 ± 0.004
Mg^{2+}	40	14.99 ± 0.01	14.997 ± 0.002
Ca^{2+}	45	15.03 ± 0.02	15.001 ± 0.003
Sn^{2+}	40	14.96 ± 0.03	15.002 ± 0.005
Cd^{2+}	40	14.99 ± 0.02	14.999 ± 0.005
Co^{2+}	35	14.99 ± 0.04	15.004 ± 0.004
Cu^{2+}	35	15.03 ± 0.05	15.002 ± 0.003
Cr^{3+}	35	15.02 ± 0.03	15.001 ± 0.004
Hg^{2+}	40	15.01 ± 0.05	15.003 ± 0.003
Ni^{2+}	40	15.04 ± 0.03	14.996 ± 0.002
Fe^{2+}	50	15.02 ± 0.04	15.003 ± 0.003
Fe^{3+}	40	14.98 ± 0.02	14.997 ± 0.005

Mn^{2+}	50	15.03 ± 0.03	15.002 ± 0.002
Zn^{2+}	50	14.96 ± 0.04	15.005 ± 0.004
Al^{3+}	50	15.04 ± 0.03	15.002 ± 0.003
Ti^{4+}	40	15.02 ± 0.04	15.003 ± 0.003
V^{5+}	40	15.01 ± 0.05	14.997 ± 0.002
Mo^{6+}	40	14.98 ± 0.05	14.998 ± 0.003
Nb^{5+}	40	14.98 ± 0.02	15.003 ± 0.003
Ta^{5+}	40	15.04 ± 0.04	15.001 ± 0.004
Hf^{4+}	50	15.01 ± 0.02	15.003 ± 0.003

Table 13 Influence of diverse ions on hafnium(IV)-CC4AHA complex

Hafnium(IV) : 15 μg ml^{-1}

Solvent : Dichloromethane

Molarity : 0.6 M

λ_{max} : 335 nm

Diverse ion	Amount added (mg)	Hafnium found (μg ml^{-1})	
		Spectrophotometry	**ICP-MS**
Hf^{4+}	-	-	-
Ag^{+}	20	15.03 ± 0.04	15.002 ± 0.003
Pb^{+2}	20	14.98 ± 0.02	15.004 ± 0.004

Co^{+2}	22	14.96 ± 0.04	15.003 ± 0.003
Ni^{+2}	22	14.98 ± 0.02	15.001 ± 0.005
Mn^{+2}	16	15.03 ± 0.04	15.002 ± 0.003
Cd^{+2}	16	15.05 ± 0.02	14.999 ± 0.005
Zn^{+2}	16	15.02 ± 0.02	15.003 ± 0.004
Fe^{+3}	20	15.03 ± 0.04	14.997 ± 0.005
Li^{+}	20	14.96 ± 0.03	14.998 ± 0.005
K^{+}	20	114.98 ± 0.04	15.002 ± 0.004
Hg^{+2}	25	15.03± 0.05	15.004 ± 0.004
Cu^{+2}	16	15.02 ± 0.05	15.003 ± 0.002
Cr^{+3}	25	15.03 ± 0.03	14.997 ± 0.003
Mg^{+2}	20	14.97 ± 0.05	15.002 ± 0.004
Ca^{+2}	20	15.02 ± 0.04	15.003 ± 0.003

Transport of titanium, zirconium and hafnium

CC4AHA was successfully used as a carrier for the selective and efficient transport of titanium(IV), zirconium(IV) and hafnium(IV) across a bulk liquid membrane of dichloromethane. The assembly used for the study and experimental condition is described in the initial part of this chapter. Titanium(IV), zirconium(IV) and hafnium(IV) concentration in the aqueous phase was determined by ICP-MS.

The titanium(IV), zirconium(IV) and hafnium(IV) ions are absorbed into the membrane due to complex formation with CC4AHA at the interface between the membrane and receiving solution where titanium(IV), zirconium(IV) and hafnium(IV) ions are released to aqueous phase due to the stripping action of 0.1 N HCl. The free carrier diffuses back to the interface at the feed side to form another complex with available fresh ions.

The effect of molarity variation of the feed solution on the permeation of titanium, zirconium and hafnium is also studied. At low molarity the titanium, zirconium and hafnium complexation with CC4AHA does not take place. The effect of molarity of the receiving solution on the permeation of titanium, zirconium and hafnium was also studied and data showing that titanium, zirconium and hafnium strips out quantitatively at lower molarity (0.1 N HCl).

The concentration of CC4AHA in the membrane phase controls the transportation of titanium, zirconium and hafnium. No movement of titanium, zirconium and hafnium was observed unless a carrier CC4AHA used. Maximum transportation of titanium, zirconium and hafnium was observed at 18 minutes with $t_{1/2}$ equal to 9.4 min and 14 minutes with $t_{1/2}$ equal to 7.2 min and 26 min with $t_{1/2}$ equal to 13.3 respectively (Figure 6).

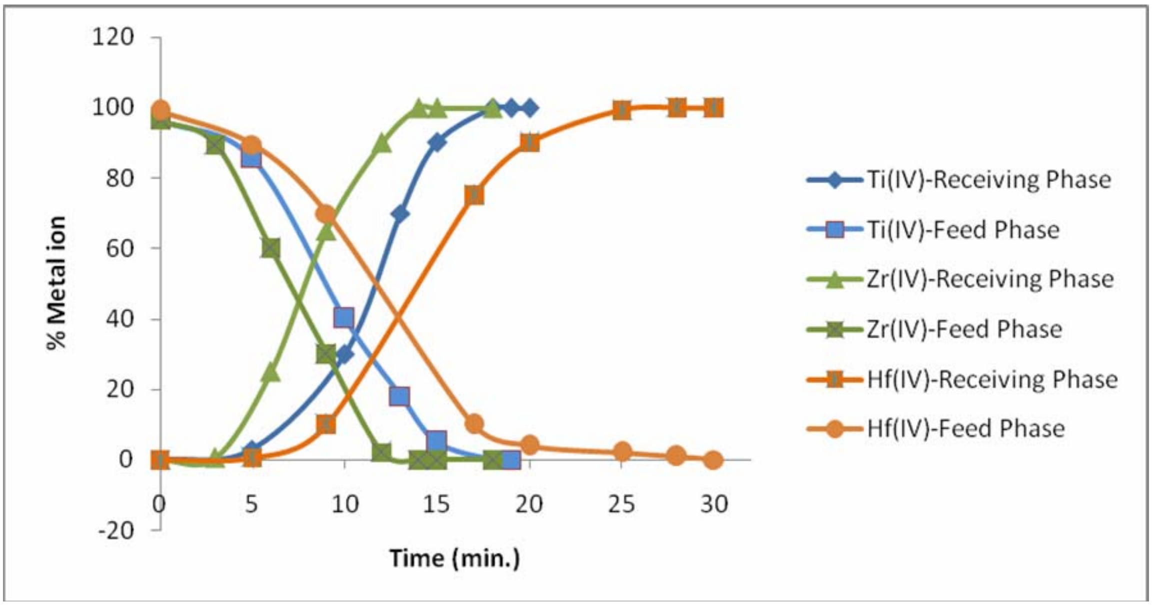


Figure 6 Transportation of titanium, zirconium and hafnium by CC4AHA

Preconcentration and Recovery

The concentration of titanium(IV), zirconium(IV) and hafnium(IV) in natural water samples is too low for its direct determination. Therefore, a preconcentration or enrichment step is necessary to bring the sample to the detectable limits of the existing instrumental method. The method was studied for the preconcentration of titanium(IV), zirconium(IV) and hafnium(IV).

A preconcentration study was carried out with about 5 µg of metal solution in 1000 mL aqueous phase by extracting 10 times each 100 mL of aqueous phase with same 10 mL of ligand solution. (The metal gets concentrated in 10 mL of ligand solution). For the evaluation of the efficiency of preconcentration, express as recovery, the concentration of tantalum in organic phase and remaining in aqueous phase was measured by ICP-MS against calibrated standard solution in dichloromethane. The recovery % R, was calculated from

$$R\% = \frac{[As_{std} - As]}{A_{std}} \times 100$$

where As_{std} is the absorbance value for sample containing known amount of standard tantalum added to sample solution prior to the extraction. A_{std} is the absorbance value for the standard in organic phase with the same analyte concentration as the standard addition and As is the absorption value for the sample.

Analysis of samples

To check the validity of the proposed method for titanium, zirconium and hafnium extraction, the metal ions are determined in standard geological, steel samples and environmental samples. The certified reference materials analysed to determine the accuracy of the proposed procedure (Table 14-15).

Table 14 Determination of titanium in standard samples€

Standard sample	Certified Titanium (%)	Titanium Found (%)
		ICP-MS
Ilmenite-1[a]	0.605	0.601 ± 0.04
Ilmenite-2[b]	1.188	1.182 ± 0.02
Steel-1[c]	0.442	0.446 ± 0.05
Steel-2[d]	0.870	0.872 ± 0.02
SY-3[e]	0.130	0.136 ± 0.03
CRM 782-1[e]	0.0025	0.0022 ± 0.003

€ : The values are average of 10 determinations

[a] Composition of samples (%): TiO_2, 60.6; Fe_2O_3, 24.2; FeO, 9.3; Al_2O_3, 0.96; MnO, 0.39; Cr_2O_3, 0.12; MgO, 0.89; P_2O_5, 0.21; V_2O_5, 0.15; ZrO_2,0.90; SiO_2, 0.41; Rare earths, traces 2.0.

[b] Composition of samples (%):TiO_2, 54.2; Fe_2O_3, 14.2; FeO, 26.6; Al_2O_3, 1.25; MnO, 0.4; Cr_2O_3, 0.07; MgO, 1.03; P_2O_5, 0.12; V_2O_5, 0.16; ZrO_2,0.80; SiO_2, 0.68; Rare earths, traces 0.34.

[c] Composition of samples (%): Ni, 41.9; Fe, 36; Cr, 12.46; Ti-2.95, Mo-5.83; Si, 0.28; Al, 0.24; Co, 0.21; Mn, 0.08; Cu, 0.032; C, 0.03.

[d] Composition of samples (%): C, 0.08; Zr, 0.05; Ti, 2.9; Al, 2.9; Mo, 4.8; Cr, 18; Co, 18.5; B, 0.006.

[e] Geo-standard reference materials.

Table 15 Concentration (μg/g) of zirconium and hafnium in samples€

Sample	Analyte			
	Zirconium		Hafnium	
	Certified Value	Present method	Certified Value	Present method
STM-1[a]	1210.0	1205.2 ± 0.04	28.0	27.56 ± 0.02
AC-E[b]	780.0	777 .4 ± 0.03	27.9	26.95 ± 0.05
Beach Sand[c]				
Sample 1	-	9023 ± 52.41	-	263 ± 3.74
Sample 2	-	9051 ± 67.93	-	301 ± 8.62
Sample 3	-	3567 ± 38.27	-	93.72 ± 42.59

€ : The values are average of 10 determinations

[a] Material: Nephelene syenite; US Geological Survey, Denver, USA

[b] Material: Granite; IWG-GIT

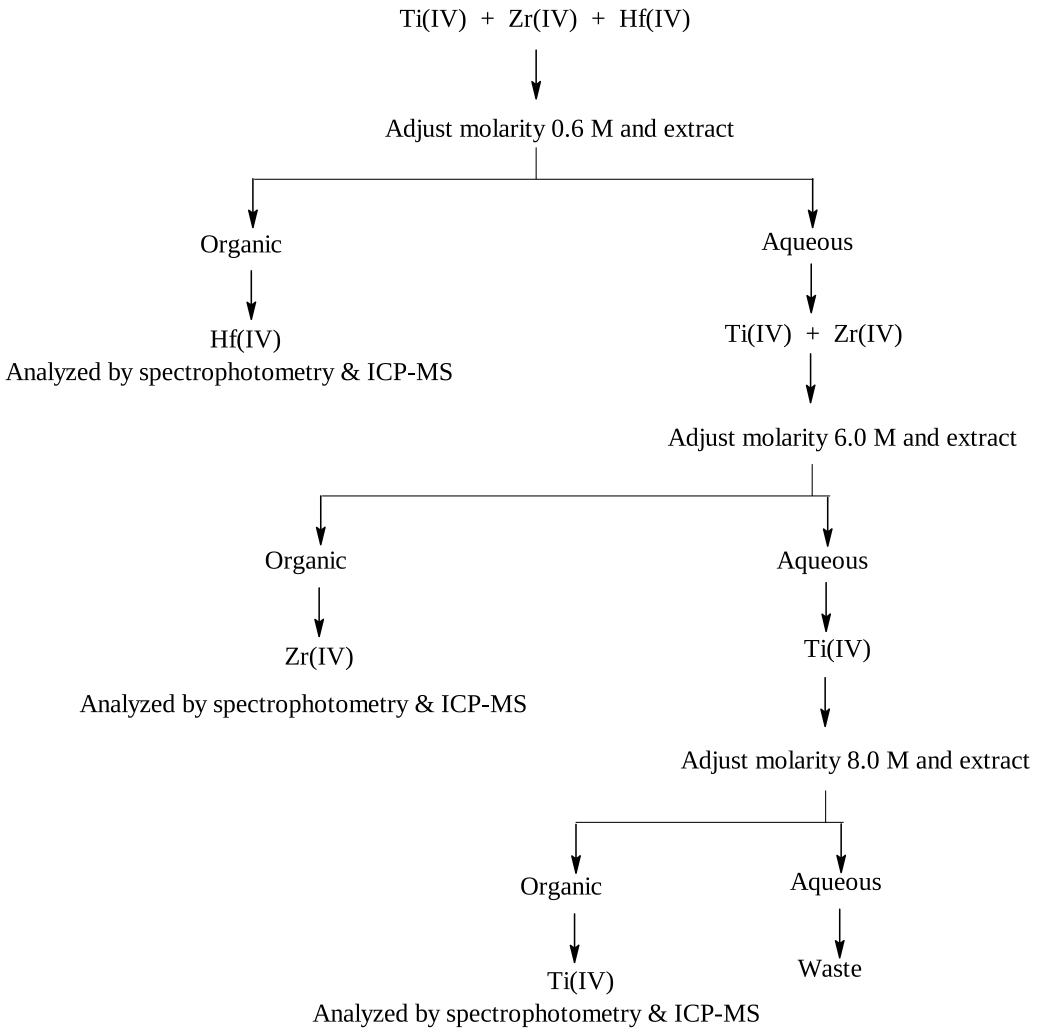
[c] Sand was collected from Tamilnadu Coast

Separation of titanium(IV), zirconium(IV) and hafnium(IV)

In order to check the accuracy and applicability of the proposed method, titanium(IV), zirconium(IV) and hafnium(IV) have been separated from their mixture. The separation of titanium(IV), zirconium(IV) and hafnium(IV) from their mixture has been carried out at different molarity.

The molarity of titanium(IV), zirconium(IV) and hafnium(IV)mixture has been adjusted to 0.6M and hafnium(IV) was extracted and separated with dichloromethane solution of CC4AHA. The molarity of remained aqueous phase containing titanium(IV) and zirconium(IV) was adjusted to 6.0 for the extraction of zirconium(IV) using dichloromethane solution of CC4AHA. For the separation of titanium(IV), the molarity of the remained aqueous phase containing titanium(IV) was adjusted to 8.0 and extracted with using dichloromethane solution of CC4AHA. The organic layer after each extraction was separated and subjected to ICP-MS for the determination of hafnium(IV), zirconium(IV) and titanium(IV). The scheme for the sequential separation of hafnium(IV), zirconium(IV) and titanium(IV) is shown in Figure 9.

Figure 9 Sequential separations of hafnium, zirconium and titanium



CONCLUSION

The present method describes a new extractant CC4AHA is used for the sequential separation and determination of titanium(IV), zirconium(IV) and hafnium(IV) in trace amounts from standard and environmental samples. The extraction procedure is very simple, rapid, sensitive and possible at laboratory scale. Separation of metal ions is achieved by the judicious choice of molarity.

REFERENCES

1. R. E. Krebs, The History and Use of Our Earth's Chemical Elements: A Reference Guide (2nd edition), **2006**.
2. "Titanium", Encyclopaedia Britannica Concise, **2007**.
3. M. Blauw, Nucl. Instrum. Meth. Phys. Res. A, **2003**, 505, 20.
4. M. Diksic, T.F. Cole, Anal. Chim. Acta, **1977**, 93, 261.
5. Y. K. Agrawal, S. Sudhakar, Talanta, **2002**, 57, 97.
6. H. C. dos Santos, M.G.A. Korn, S.L.C. Ferreira, Anal. Chim. Acta, **2001**, 426, 79.
7. W. O. Siyanbola, A.Y. Fasasi, I.I. Funtua, O.M. Afolabi, T.A. Adesiyan, A. R. Adetunji, Nucl. Instrum. Meth. Phys. Res. B, **2004**, 215, 240.
8. N. Sen, N.K. Roy, A.K. Das, Talanta, **1989**, 36, 697.
9. M. K. T. Bassan, K.V. Iyer, M. Sudersanan, Indian J. Technol., **2003**, 10, 291.
10. Y. Yigzaw, B.S. Chandravanshi, Mikrochim. Acta, **1996**, 124, 81.
11. B. Keshavan, K.P. Krishnaprasad, J. Indian Chem. Soc., **1991**, 68, 117.
12. S. Inoue, S. Hoshi, M. Matsubara, Talanta, **1987**, 34, 889.
13. S. P. Bag, A. K. Chakrabarti, J. P. Goswami, J. Indian Chem. Soc., **1981**, 58, 901.
14. M. Soylak, U. Sahin, L. Elci, Anal. Chim. Acta, **1996**, 322, 111.
15. Y. Sasaki, S. Tagashira, Y. Murakami, M. Ichikawa, Anal. Sci., **1998**, 14, 603.

16. B. Melwanki, J. Seetharamappa, S.P. Masti, Anal. Sci., **2001**, 17, 1121.

17. S.L.C. Ferreira, A.C. SpinolaCosta, M.G.M. Andrade, B.F. Santos, N.O. Leite, Anal. Lett., **1993**, 26, 1001.

18. R. Dass, J. R. Mehta, Mikrochim. Acta, **1994**, 113, 37.

19 C. P. Savariar, K. Vijayan, Talanta, **1989**, 36, 1047.

20. M. Tarek, M. Zaki, A.K. Abdel-Kader, M. M. Abdalla, Talanta, **1990**, 37, 1091.

21. F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th Edition, John Wiley & Sons, **1988**.

22. N. N. Green wood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, **1984**.

23. L. Delons, S. Lagarde, L. Poriel, M. Lemaire, A. Favre-Reguillon, S. Pellet-Rostaing, **2006**, Patent WO 2006040458.

24. L. Poriel, S. Pellet-Rostaing, V. Lamotte, M. Lemaire, A. Favre-Reguillon, Sep. Sci. Technol., **2006,** 41(12), 2711.

25. H. C. Loh, S. M. Ng, M. Ahmad, M. N. Taib, Anal. Lett., **2005**, 38, 1305.

26. M. B. Gholivand, A. Babakhanian, M. Joshaghani, Anal. Chim. Acta, **2007**, 584, 302.

27. M. Taghizadeh, R. Ghasemzadeh, S. N Ashrafizadeh, K. Saberyan, M. Ghanadi Maragheh, Hydrometallurgy, **2008**, 90, 115.

28. S. Shariati, Y. Yamini, J. Colloid Interface Sci., **2006**, 298, 419.

29. K. Akhtar, M. Waheed Akhtar, A. M. Khalid, J. Hazard. Mater., **2008**, 156, 108.
30. S. Shariati, Y. Yamini, M. Khalili Zanjani, J. Hazard. Mater., **2008**, 156, 583.
31. B. Rezaei, S. Meghdadi, R. Fazel Zarandi, J. Hazard. Mater., **2008**, 157, 18.
32. M. Taghizadeh, R. Ghasemzadeh, S. N. Ashrafizadeh, K. Saberyan, M. G. Maragheh, Miner. Eng., **2007**, 20, 1401.
33. S. M. Boswell, H. Elderfield, Mar. Chem., **1998**, 25, 197.
34. L. Delons, S. Lagarde, L. Poriel, M. Lemaire, A. Favre-Reguillon, S. Pellet-Rostaing, Sep. Sci. Technol., **2006**, 41, 1927.
35. L. Poriel, F. Chirty, M. Lemaire, A. Favre-Reguillon, S. Pellet-Rostaing, Sep. Sci. Technol., **2006**, 41, 2883.
36. J. B. Hedrick, U.S. Geological Survey Minerals Yearbook, **2000**, 87.1–87.10.
37. Lenntech, http://www.lenntech.com/Periodic-chart-elements/-Hf-en.htm.
38. H. Levytska, O. Orshuliak, Talanta, **2007**, 71, 1441.
39. J. M. Begovich, W. G. Sisson, Hydrometallurgy, **1983**, 10(1), 11.
40. B. R. Reddy, J. R. Kumar, A. V. Reddy, Miner. Eng., **2004**, 17, 553.
41. B. R. Reddy, J. R. Kumar, K. P. Raja, A. V. Reddy, Miner. Eng., **2004**, 17, 939.
42. A. Da Silva, E. El-ammouri, P. A. Distin, Can. Metall., **2000**, 39, 37.
43. M. H. Khan, A. Ali, Radiochim. Acta, **2002**, 90, 297.

44. B. R. Reddy, J. R. Kumar, Sep. Purif. Technol., **2005**, 42, 169.

45. S. Oszwaldowski, R. Lipka, M. Jarosz, Anal. Chim. Acta, **1998**, 361, 177.

46. B. R. Reddy, J. R. Kumar, A. V. Reddy, Anal. Sci., **2004**, 20, 501.

47. R. K. Biswas, M. A. Hayat, Hydrometallurgy, **2002**, 63(2), 149.

48. X. J. Yang, A. G. Fane, C. Pin, Chem. Eng. J., **2002**, 88, 37.

49. B. R. Reddy, J. R. Kumar, A. V. Reddy, D. N. Priya, Hydrometallurgy, **2004**, 72, 303.

50. H. Y. Lee, S. G. Kim, J. K. Oh, Hydrometallurgy, **2004**, 73, 91.

51. B. R. Reddy, J. R. Kumar, A. V. Reddy, Hydrometallurgy, **2004**, 74, 173.

52. D. Yuan, W. Zhu, M. Xu, Q. Guo, J. Coord. Chem., **2004**, 57(14), 1243.

53. B. R. Reddy, J. R. Kumar, A. V. Reddy, J. Chem. Technol. Biotechnol., **2004**, 79, 1301.

54. H. Karami, M. F. Mousavi, Y. Yamini, M. Shamsipur, Microchim. Acta, **2006**, 154, 221.

55. X. Chang, Q. Su, X. Wei, B. Wang, Microchim. Acta, **2001**, 137, 209.

56. A. Zhang, Y. Wei, H. Hoshi, M. Kumagai, Sep. Sci. Technol., **2005**, 40, 811.

57. N. E. El-Hefny, Y. A. El-Nadi, J. A. Daoud, Solvent Extr. Ion Exch., **2006**, 24, 703.

58. K. J. Reddy, J. R. Kumar, A. V. Reddy, Solvent Extr. Ion Exch., **2006**, 24, 419.

59. H. A. Arida, Talanta, **2008**, 76, 40.

60. S. Oszwaldowski, J. Jakubowska, Talanta, **2003**, 60, 643.

61. X. Chang, Q. Su, D. Liang, X. Wei, B. Wang, Talanta, **2002**, 57, 253.

62. P. Peralta-Zamora, L. Cornejo-Ponce, M. S. Bueno, J. W. Martins, Talanta, **1997**, 44, 811.

63. R. Purohit, S. Devi, Analyst, **1992**, 117, 1175.

64. H. J. G. Challis, Analyst, **1969**, 94, 94.

65. Z. Marczenko, Spectrophotometric Determination of Elements, John Wiley & Sons, New York, **1976**, 555.

Chapter V

Selective Supercritical Fluid Extraction of Titanium(IV) using Calixarene Hydroxamic Acid and Simultaneous On-line Determination by Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS)

Abstract

Titanium(IV) is extracted with coumarin-calix[4]arene hydroxamic acid (CC4AHA), in dichloromethane by supercritical carbon dioxide (SC-CO_2)-dichloromethane (modifier) medium. An aliquot of aqueous titanium solution of is extracted accurately. Influence of six experimental factors: pressure, temperature, extraction times, molarity of aqueous solution, solvent and interference of ions were studied and optimized. Quantitative analysis of the extracts was performed online by inductively coupled plasma mass spectrometry (ICP-MS). The results showed that Ti(IV) could be quantitatively extracted from the matrix at 50°C temperature, 17 MPa pressure, at 8.0 molarity, 6 min of extraction time. To check the validity of the proposed method for titanium extraction, the metal ions are determined in standard geological samples.

INTRODUCTION

In the past two decades, increasing attention has been directed on the supercritical fluid extraction (SFE) as an interesting alternative to conventional extraction methods /1–3/. The high diffusivity and temperature–pressure dependence of solvent strength are among the attractive properties which make supercritical fluids excellent candidates for the extraction and recovery of organic compounds from solid materials /4–6/. The most widely used supercritical fluid is carbon dioxide because it is an excellent solvent for SFE due to its moderate critical constants (Temp. = 31°C and Pc = 7.4 MPa), inertness, tunable solvating strength, nontoxic, non-flammable and relatively inexpensive and possesses high solvent power for a wide range of nonpolar and intermediately polar organic compounds. Solutes can often be separated from the supercritical fluid by simply venting the benign CO_2 into the atmosphere, leaving pure solutes behind. Moreover, supercritical CO_2 can easily penetrate and diffuse into small pores of solid matrices and effectively remove organic and inorganic species. In recent years, the supercritical fluids modified by addition of extractant have been used in the development of analytical methods for the extraction of metal ions from various solid and liquid matrices /7-16/. The most critical aspect of such chelation-SFE of metal ions is the high stability and fast kinetics of the metal complexes, high solubilities of the chelating agents and their metal complexes in SC- CO_2.

Various analytical techniques used for the determination of titanium in different types of matrices include neutron activation analysis /17,18/ inductively coupled plasma atomic emission spectrophotometry /19,20/, X-ray fluorescence /21,22/ and spectrophotometry /23-28/. A number of extractants have been reported for the determination of titanium at trace levels /29-33/.

The literature survey revealed that so far no data are available on the SC-CO_2 extraction of titanium using hydroxamic acids and calixarene in particular. With this in view, an economical, simple and environmentally safe procedure has been developed, which can be used for the supercritical fluid extraction of titanium from aqueous samples.

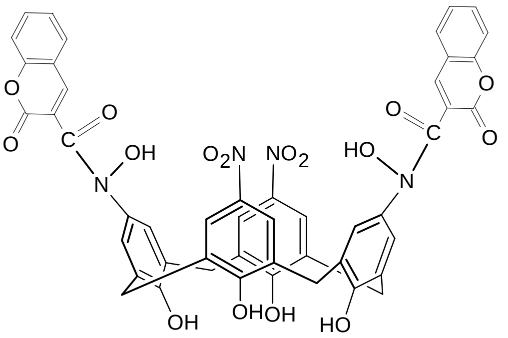
EXPERIMENTAL

Standard Solutions & Reagents

All the chemicals used were of analytical grade obtained from Sigma-Aldrich or Merck. Deionised double distilled water was used, which was further purified by a Milipore Milli-Q water purification system. The solvent carbon dioxide gas 99.9% purity was purchased from the Bombay Carbon

Dioxide Co., Mumbai and used as such. Titanium(IV) stock solution was used as such as mentioned in chapter 4.

5,17-Dinitro-25,26,27,28-tetrahydroxy-11,23-calix[4]arene-*bis*-[coumarin hydroxamic acid] (Figure 1) was synthesized as described in Chapter 2. 1.08 × 10^{-3} M (0.1 % w/v) stock solution of CC4AHA was prepared in dichloromethane.



CC4AHA

Figure 1 Coumarin - calix[4]arene hydroxamic acid (CC4AHA)

Apparatus

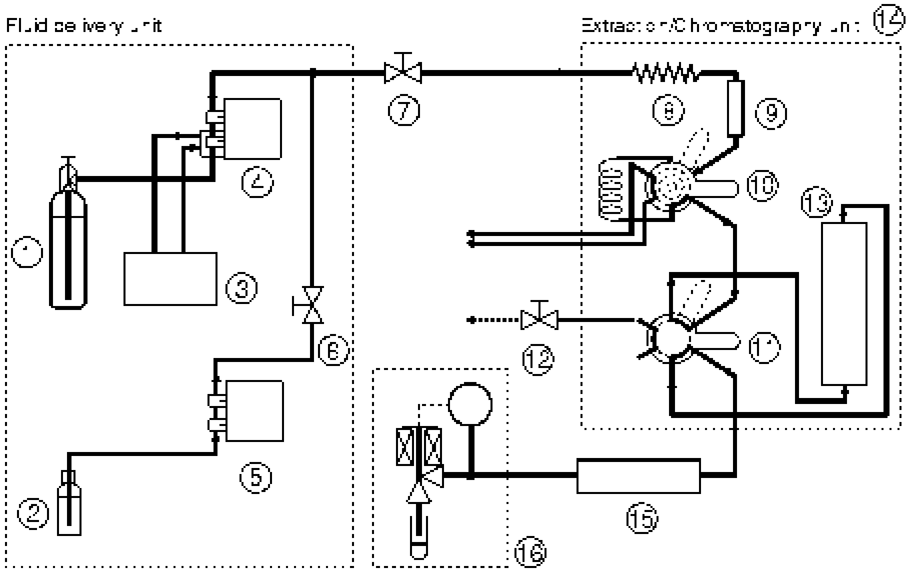
Supercritical extractions are performed using a JASCO Supercritical Fluid Extractor / Chromatograph, 900-series configured for dynamic mixing with a two-pump system (Figure 2). It has the facility of on line organic co-solvent addition to supercritical fluid gas. The flow rate of the pump can be operated from 0.01 to 10.0 ml min^{-1}. First, the CO_2 gas cooled at 25.3°C before compression takes place using CH-201 series cooling circulator.

Methanol was used as cooling solvent JASCO-880-81 back pressure regulator used is capable of giving pressure in the range of 7.18–44.88 MPa. JASCO-965 series air circulating oven was used for controlling and maintaining the temperature of the extraction vessel. Special stainless steel vessel with 80 ml to 15ml capacities were fabricated to a maximum operating pressure of 7000 psi design temperature of 93°C and also fitted with Rheodyne valve. The extract was collected in an especially fabricated glass vessel attached with valve and peristaltic pump to direct measurement.

A Plasma Scan Model 710 sequential Inductively Coupled Plasma with Plasma Scan multitasking computer and peristaltic pump was used. Thermo Jarrell-Ash Corporation, Franklin, MA, USA, POEMS mass spectrophotometer with a Fassel torch, a concentric glass nebulizer and cryogenic spray chamber was used. The optimized instrumental conditions are summarized in Table 1.

Table 1 Optimized instrumental conditions for ICP-MS

Instrumental parameters	ICP-MS
ICP Plasma	Argon
Forward Power	1.35 KW
Reflected Power	<10 W
Gas flow (L/min)	
Coolant	16
Carrier	0.70
Auxiliary	0.30
Nebuliser Pressure	2 bar
Solution uptake rate	0.8 mL/min
Sampler cone aperture	1 mm
Skimmer cone aperture	0.7 mm
Mass No.	
Ti	48



1- Liquid CO_2 Cylinder; 2- Modifier; 3- Cooling circulator; 4- CO_2 pump; 5- Modifier pump; 6- Stop valve; 7- Stop valve; 8- Pre-heatig coil; 9- Mixer; 10- Injector; 11- Line switching valve; 12- Stop valve (optional); 13- Extraction vessel or column; 14- Oven; 15- Detector; 16- Back pressure regulator

Figure 2 Schematic diagram of Supercritical fluid extraction system

Supercritical Carbon Dioxide (SC-CO_2) extraction (SFE)

The extraction studies were performed in a dynamic mode at the optimum flow rate of the gas and the co-solvent. The SC-CO_2 gas, at a known pressure and temperature, was mixed with 1.08×10^{-3} M solution of CC4AHA in dichloromethane and allowed to flow over the extraction vessel. An 8 M acidic solution containing titanium with a volume of 2 µL was placed in the liquid extraction vessel along with the ceramic fibre glass needles and 1.08×10^{-3} M dichloromethane solution of CC4AHA as co-solvent fluid phase.

RESULTS AND DISCUSSION

Influence of various parameters, including temperature, pressure, time and pH of solution, are investigated to maximize the extraction efficiency of titanium (IV) ions from samples by SC-CO_2 extraction. SFE conditions are optimized using the step-by-step design.

Extraction efficiency

The extraction efficiency (%E), which is described as

$$\%E = \left\{1 - \frac{[M]_f}{[M]_i}\right\} \times 100$$

where $[M]_i$ is the initial concentration of titanium in the sample solution before extraction and $[M]_f$ is the final concentration of titanium remaining in the sample after extraction.

Influence of extraction temperature

The solubility of the complex increases with increase in temperature. However, the solvating power of supercritical carbon dioxide decreases with increase of temperature. So influence of temperature on extraction depends upon the solubility of the matrix in the supercritical carbon dioxide at different temperature.

The influence of temperature on the extraction of titanium from the aqueous phase was investigated at different temperatures (40°C, 50°C, 60°C, 70°C and 80°C). The pressure and extraction time were kept constant at 20 MPa and 15 minutes respectively. As the extraction temperature increased from 40°C to 55°C, the extraction is also increases. Maximum extraction is observed in between 48°C-54°C (Figure 3). After this temperature, extraction efficiency decreases with increase in the temperature to 80°C. As a result, 50°C is chosen as the optimum extraction temperature for the following SC-CO_2 extractions.

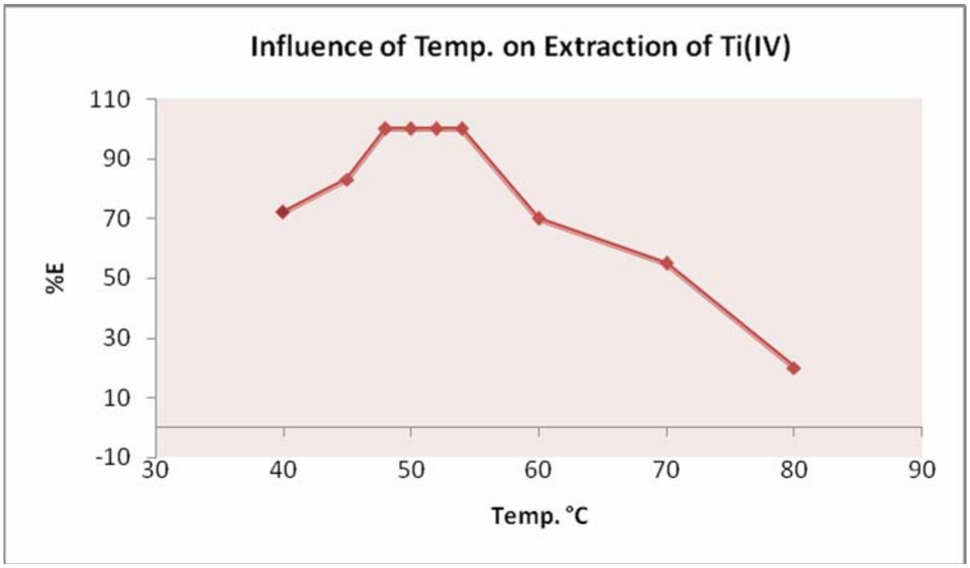


Figure 3 Influence of temperature on extraction of Ti(IV)

Influence of extraction pressure

The influence of pressure on the extraction of titanium from the aqueous phase was investigated at different extractions pressures (8 to 20 MPa). The temperature and extraction time were kept constant at 50°C and 15 minutes respectively. Maximum extraction (99.99%) was achieved within 16-18 MPa. Increasing the pressure of the system did not alter this extraction efficiency, and it remained constant under all pressures investigated. As a result, 17 MPa is chosen as the optimum extraction pressure for the following SC-CO_2 extractions (Figure 4).

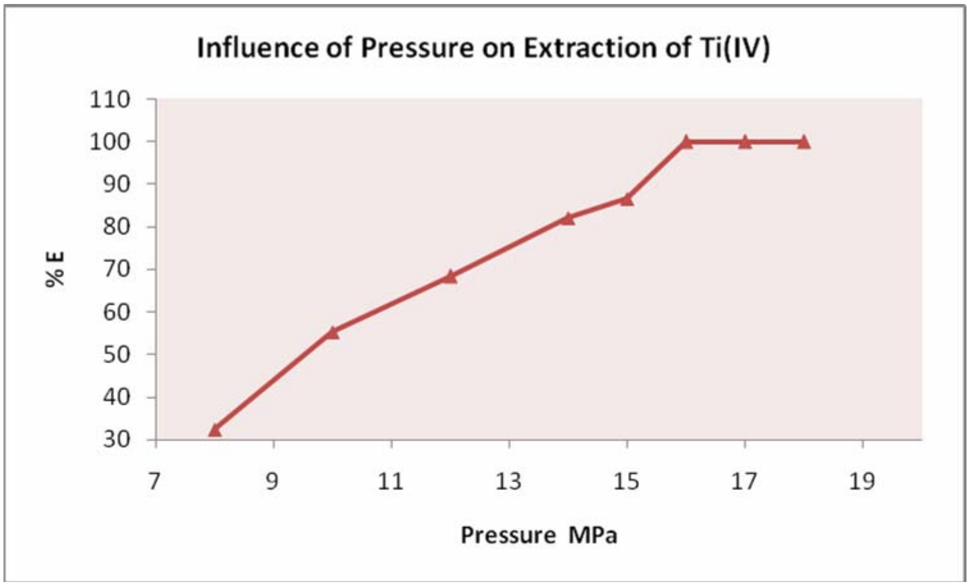


Figure 4 Influence of pressure on extraction of Ti(IV)

Influence of extraction time

Maximum extraction (99.99%) was achieved within 5 min of time. The temperature and pressure were kept constant at 50°C and 17 MPa respectively. After a certain time the extraction efficiency does not increase with increase in the time (Figure 5).

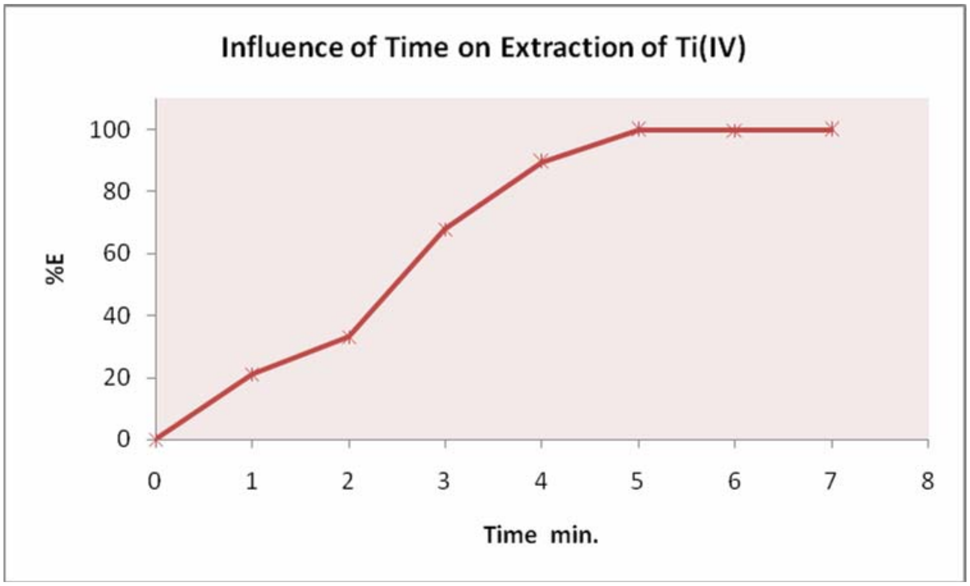


Figure 5 Influence of temperature on extraction of Ti(IV)

Influence of molarity on extraction

The optimum molarity for maximum extraction was determined by carrying out the extraction of titanium with CC4AHA at different molarity. The extraction of titanium increases with the increase of molarity until it level off at the molarity 8.0. Thus the optimum molarity for an efficient extraction lies within the range of 7.5–8.5 molarity for titanium. The low extractability at lower molarity values may be attributed to the proton extraction to organic phase rather than the metal ion itself. The temperature, pressure and extraction time were kept constant at 50°C, 17 MPa and 7 minutes respectively (Figure 6).

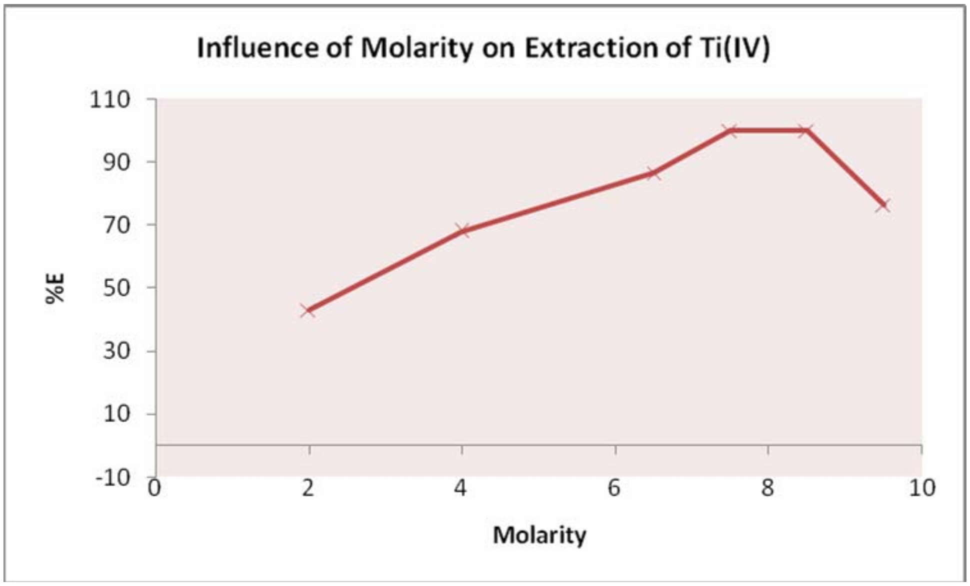
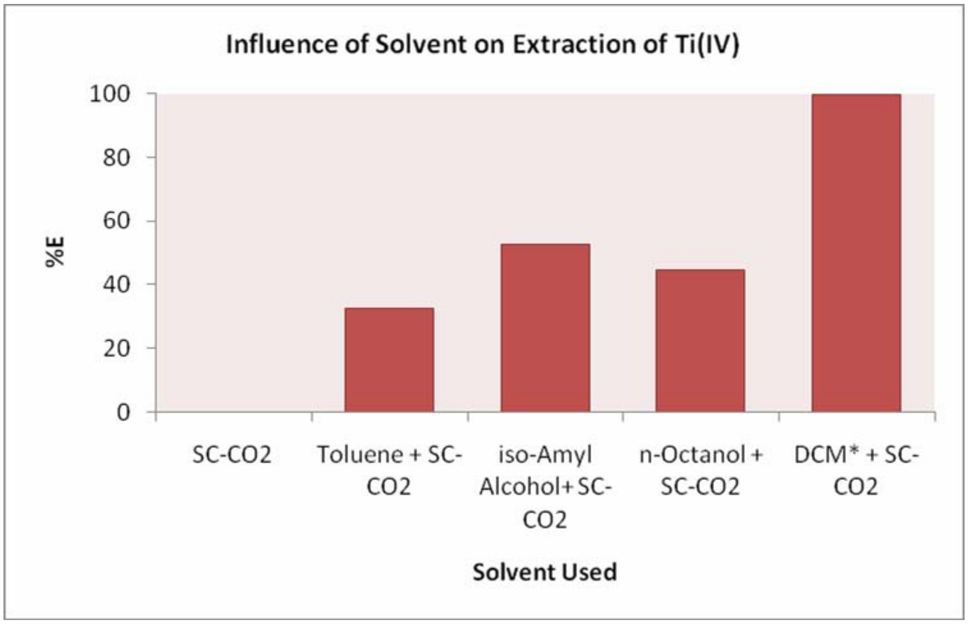


Figure 6 Influence of molarity on extraction of Ti(IV)

Influence of the solvent on extraction

The extraction experiments were carried out with pure and modified SC-CO_2. Extraction efficiencies were examined with pure and modified SC-CO_2 with various solvents viz, n-octanol, toluene, iso-amyl alcohol and dichloromethane etc. It has been observed that dichloromethane modified SC-CO_2 was found to be the most appropriate solvents for quantitative extraction of titanium (Figure 7).



*DCM=Dichloromethane

Figure 7 Influence of solvent on extraction of Ti(IV)

Interference Studies

The extraction performance of the presented extractant will be influenced under foreign metal ions. A series of standard solutions are spiked with potential interfering metal ions to study the potential interference. Interference studies were made by using the solution containing 20 ng ml^{-1} titanium and various concentrations of the foreign ions. The intensity of the extracted (organic) phase was measured by ICP-MS. Results shows that, titanium can be extracted easily in the presence of large number of interfering ions (Table 2).

Table 2 Influence of Interfering Ions on extraction of titanium(IV)-CC4AHA

Diverse ion	Amount added (mg)	Titanium Found (ng ml^{-1})
		ICP-MS
Ti^{4+}	--	--
As^{3+}	40	19.995 ± 0.005
Be^{2+}	40	20.004 ± 0.003
Mg^{2+}	50	19.993 ± 0.004
Ca^{2+}	50	19.997 ± 0.007
Sn^{2+}	45	19.996 ± 0.005
Cd^{2+}	40	20.005 ± 0.003
Cu^{2+}	40	19.998 ± 0.004
Cr^{3+}	40	19.994 ± 0.002
Hg^{2+}	40	19.995 ± 0.005
Ni^{2+}	50	20.003 ± 0.006
Fe^{2+}	50	20.005 ± 0.005
Fe^{3+}	45	20.003 ± 0.004
Mn^{2+}	45	19.995 ± 0.004
Zn^{2+}	45	19.998 ± 0.005
Al^{3+}	40	20.003 ± 0.003

V^{5+}	40	20.004 ± 0.007
Nb^{5+}	40	19.996 ± 0.004
Ta^{5+}	40	19.993 ± 0.005
Mo^{6+}	40	20.002 ± 0.003
Zr^{4+}	40	19.998 ± 0.006

Analysis of samples

To check the validity of the proposed method for titanium extraction, the metal ions are determined in standard geological samples. The results obtained in good agreement with the certified values (Table 3). The 5 µg mL^{-1} of the titanium was recovered as shown in the flow diagram (Figure 8). The titanium was also recovered from the geological samples. The aqueous matrix containing titanium was filtered and passed to the mixing coil chamber. The molarity was raised to 8.0 and valve V_1 was opened to pass the liquid to the separator. The reagent CC4AHA in dichloromethane was added via valve V_2. The organic phase was then transferred to reagent chamber by valve V_3 for preconcentration and or circulation. The waste matrix drains out from valve V_4. The organic layer was passed to extraction chamber by a dual valve V_3 and with 0.1 N HCl to stripped the purest titanium. The organic layer was also inserted into plasma for ICP-MS measurement. The reagent was pumped by valve V_5 to reagent chamber for recirculation.

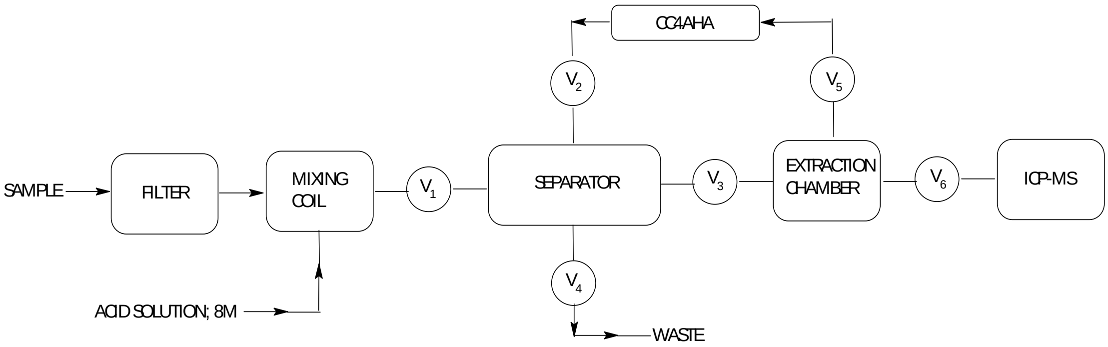


Figure 8. Preconcentration and Separation of Titanium

Table 3 Determination of titanium in standard samples[€]

Standard sample	Certified Titanium (%)	Titanium Found (%)
		SC-CO_2-ICP-MS
Ilmenite-1[a]	0.605	0.605 ± 0.002
Ilmenite-2[b]	1.188	1.185 ± 0.001
Steel-1[c]	0.442	0.443 ± 0.003
Steel-2[d]	0.870	0.869 ± 0.003
SY-3[e]	0.130	0.133 ± 0.001
CRM 782-1[e]	0.0025	0.0024 ± 0.002

€ : The values are average of 10 determinations

[a] Composition of samples (%): TiO_2, 60.6; Fe_2O_3, 24.2; FeO, 9.3; Al_2O_3, 0.96; MnO, 0.39; Cr_2O_3, 0.12; MgO, 0.89; P_2O_5, 0.21; V_2O_5, 0.15; ZrO_2,0.90; SiO_2, 0.41; Rare earths, traces 2.0.

[b] Composition of samples (%):TiO_2, 54.2; Fe_2O_3, 14.2; FeO, 26.6; Al_2O_3, 1.25; MnO, 0.4; Cr_2O_3, 0.07; MgO, 1.03; P_2O_5, 0.12; V_2O_5, 0.16; ZrO_2,0.80; SiO_2, 0.68; Rare earths, traces 0.34.

[c] Composition of samples (%): Ni, 41.9; Fe, 36; Cr, 12.46; Ti-2.95, Mo-5.83; Si, 0.28; Al, 0.24; Co, 0.21; Mn, 0.08; Cu, 0.032; C, 0.03.

[d] Composition of samples (%): C, 0.08; Zr, 0.05; Ti, 2.9; Al, 2.9; Mo, 4.8; Cr, 18; Co, 18.5; B, 0.006.

[e] Geo-standard reference materials.

CONCLUSION

The titanium metal was successfully extracted from several samples using supercritical carbon dioxide modified with a chelating agent. Modified SC-CO_2 extraction technique provides a better approach and potential industrial applications for the removal of titanium from environmental matrices in the field of decontamination of titanium metal containing wastes.

REFERENCES

1. K. D. Bartle, A. A. Clifford, S. A. Jafar, G. F. Shilstone, Phys. Chem. Ref. Data, **1991**, 20, 713.
2. M. McHugh, V. Krukonis, Supercritical Fluid Extraction, 2nd Ed., Butterworth-Heinemann, Stoneham, MA, **1994**.
3. R. Dohrn, G. Burner, Fluid Phase Equilibria, **1995**, 52, 345.
4. A. Daneshfar, M. Barzegar, M. Ashraf-Khorasani, J. M. Levy, J. High Resol. Chromatogr., **1995**, 18, 446.
5. D. L. Tomasko, S. J. Macnaughton, N. R. Foster, C. A. Eckert, Sep. Sci. Technol., **1995**, 30, 1901.
6. M. D. David, J. N. Seiber, Anal. Chem., **1996**, 68, 3038.
7. N. G. Smart, T. Carleson, T. Kast, A. A. Clifford, M. D. Burford, C. M. Wai, Talanta, **1997**, 44, 137.
8. C. Y. Tai, G. You, S. Chen, J. Supercrit. Fluids, **2000**, 18, 201.
9. J. S. Wand, K. Chiu, Anal. Sci., **2007**, 23, 1337.
10. S. Iwao, S. Abd El-Fatah, K. Furukawa, T. Seki, M. Sasaki, M. Goto, J. Supercrit. Fluids, **2007**, 42, 200.
11. J. S. Wang, C. M. Wai, J. Supercrit. Fluids, **2007**, 40, 176.
12. Y. K. Agrawal, Fullerenes, Nanotubes, Carbon Nanostruct., **2006**, 14, 621.
13. T. Wang, K. A. Debelak, J. A. Roth, J. Supercrit. Fluids, **2008**, 47, 25.
14. C. Kersch, G. J. Witkamp, G. F. Woerlee, Solvent Extr. Ion Exch., **2005**, 23, 189.
15. S. Wang, Y. Lin, C. M. Wai, Sep. Sci. Technol. , **2003**, 38(10), 2279.

16. J. Liu, W. Wang, Z. Wang, G. Li, B. Han, Sep. Sci. Technol. , **2002**, 37(11), 2691.

17. M. Blauw, Nucl. Instrum. Meth. Phys. Res. A, **2003**, 505, 20.

18. M. Diksic, T. F. Cole, Anal. Chim. Acta, **1977**, 93, 261.

19. Y. K. Agrawal, S. Sudhakar, Talanta, **2002**, 57, 97.

20. H. C. dos Santos, M.G.A. Korn, S.L.C. Ferreira, Anal. Chim. Acta, **2001**, 426, 79.

21. W. O. Siyanbola, A.Y. Fasasi, I.I. Funtua, O.M. Afolabi, T.A. Adesiyan, A. R. Adetunji, Nucl. Instrum. Meth. Phys. Res. B, **2004**, 215, 240.

22. N. Sen, N.K. Roy, A.K. Das, Talanta, **1989**, 36, 697.

23. M. K. T. Bassan, K.V. Iyer, M. Sudersanan, Indian J. Technol., **2003**, 10, 291.

24. Y. Yigzaw, B.S. Chandravanshi, Mikrochim. Acta, **1996**, 124, 81.

25. B. Keshavan, K.P. Krishnaprasad, J. Indian Chem. Soc., **1991**, 68, 117.

26. S. Inoue, S. Hoshi, M. Matsubara, Talanta, **1987**, 34, 889.

27. S. P. Bag, A. K. Chakrabarti, J. P. Goswami, J. Indian Chem. Soc., **1981**, 58, 901.

28. M. Soylak, U. Sahin, L. Elci, Anal. Chim. Acta, **1996**, 322, 111.

29. Y. Sasaki, S. Tagashira, Y. Murakami, M. Ichikawa, Anal. Sci., **1998**, 14, 603.

30. B. Melwanki, J. Seetharamappa, S.P. Masti, Anal. Sci., **2001**, 17, 1121.

31. S. L. C. Ferreira, A. C. SpinolaCosta, M. G. M. Andrade, B. F. Santos, N. O. Leite, Anal. Lett., **1993**, 26, 1001.

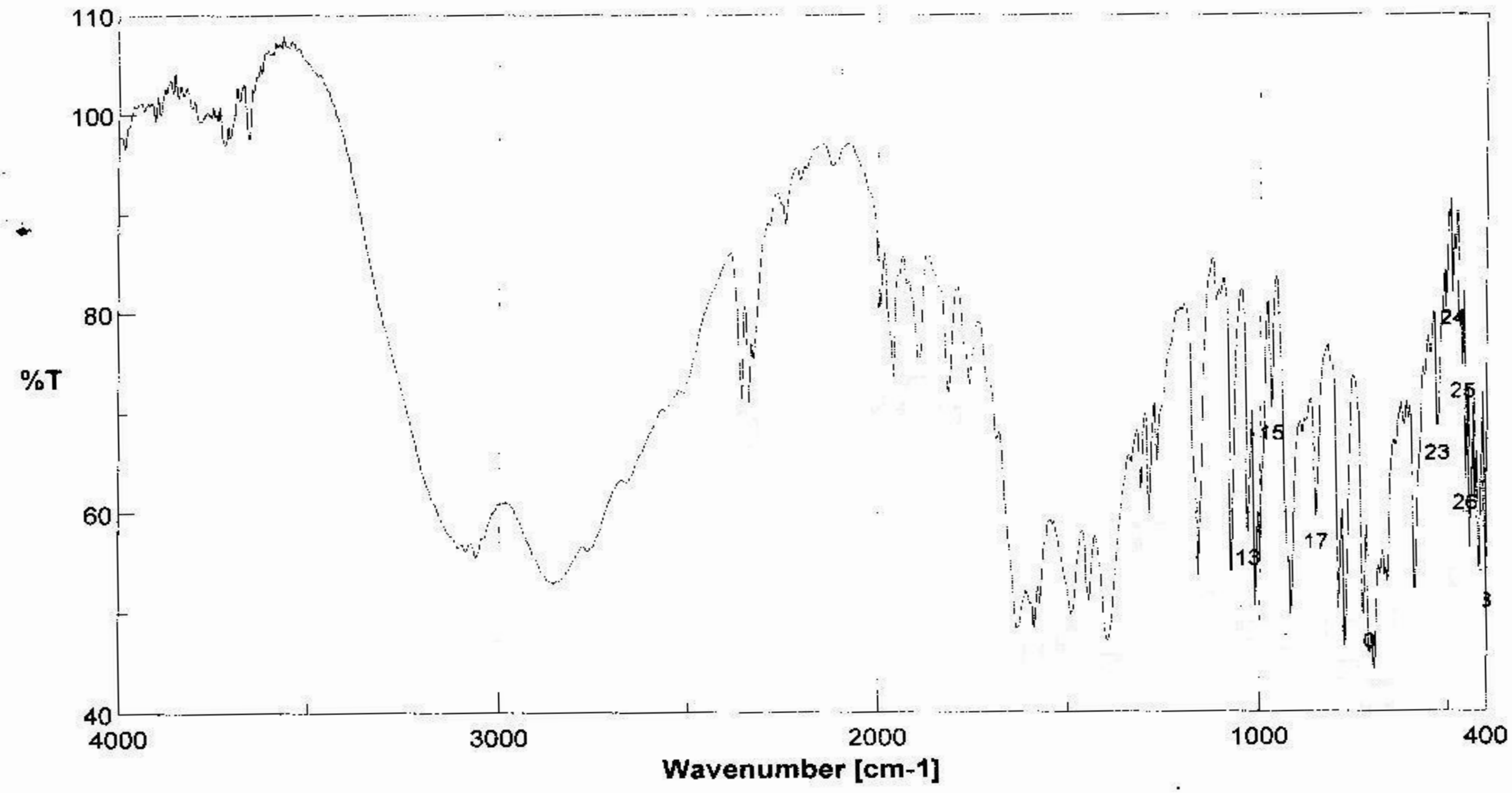
32. R. Dass, J. R. Mehta, Mikrochim. Acta, **1994**, 113, 37.

33. C. P. Savariar, K. Vijayan, Talanta, **1989**, 36, 1047.

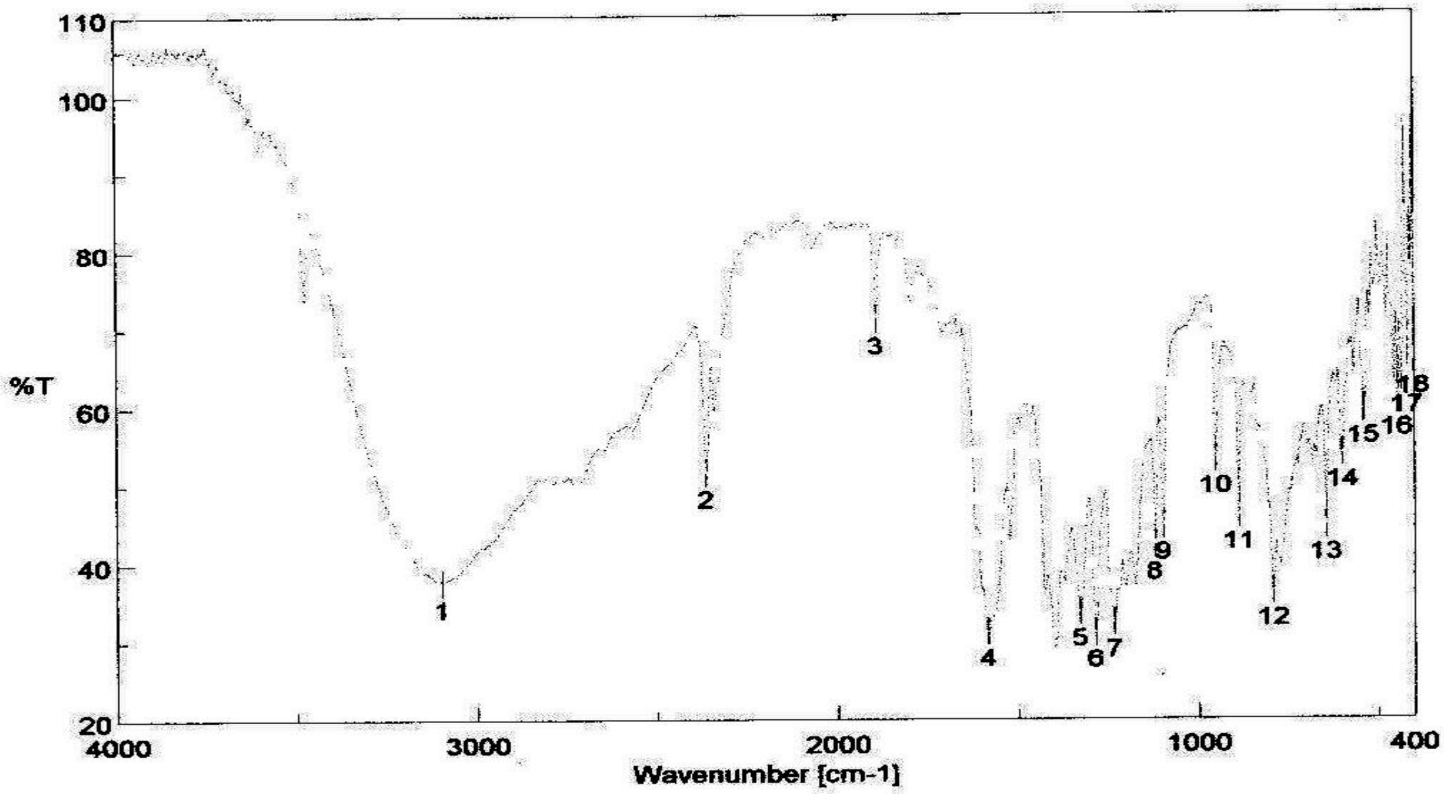
34. K. L. Toews, R. M. Scholl, C. M.Wai, N. G. Smart, Anal. Chem., **1995**, 67, 4040.

APPENDIX I

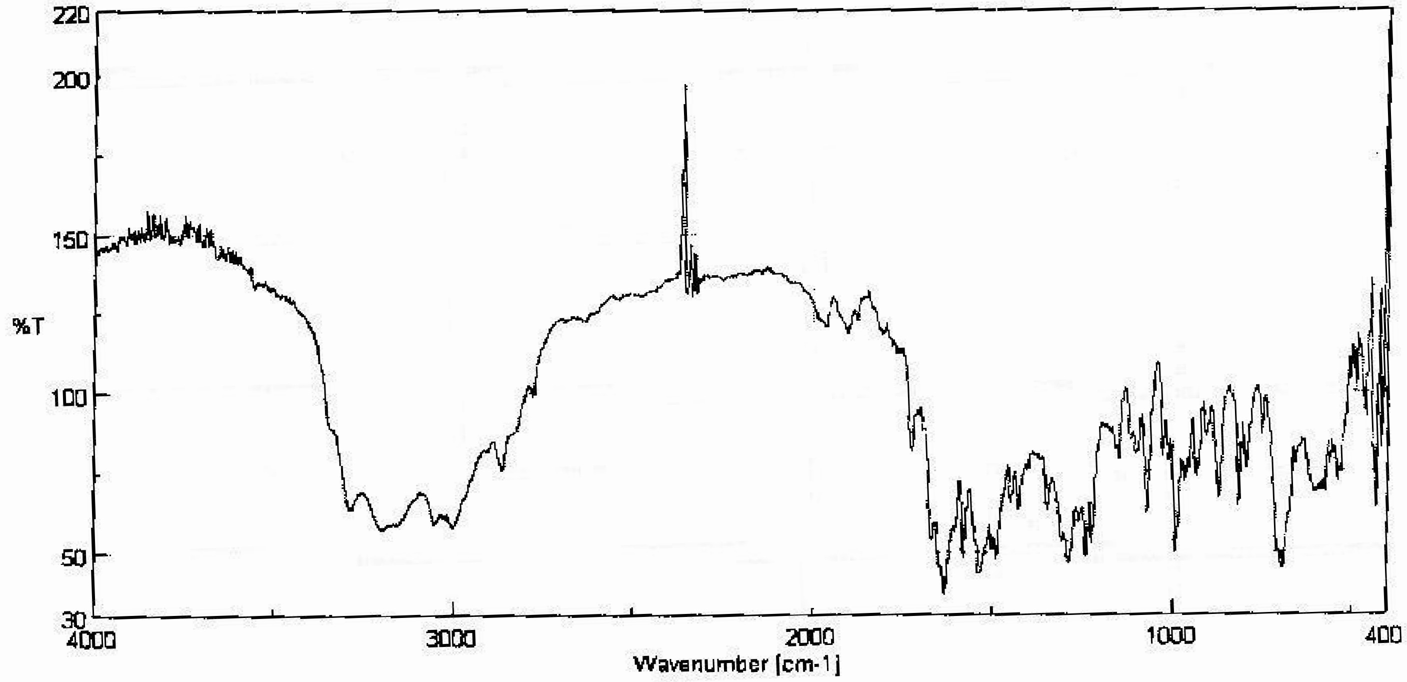
IR spectra of Coumarin Calixarene Hydroxamic Acid [compound 12]



IR spectra of Pyridine Calixarene Hydroxamic Acid [compound 9]

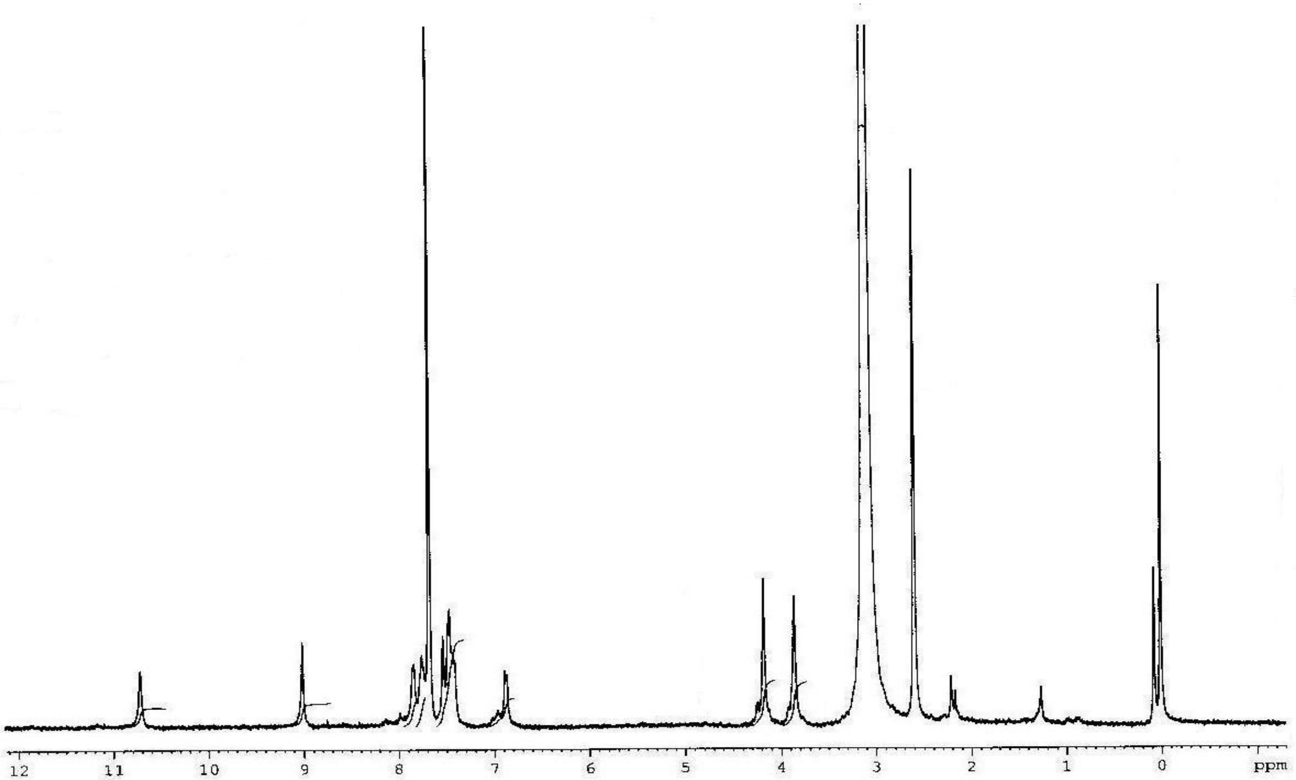


IR spectra of Calix-Crown Hydroxamic Acid [compound 16]

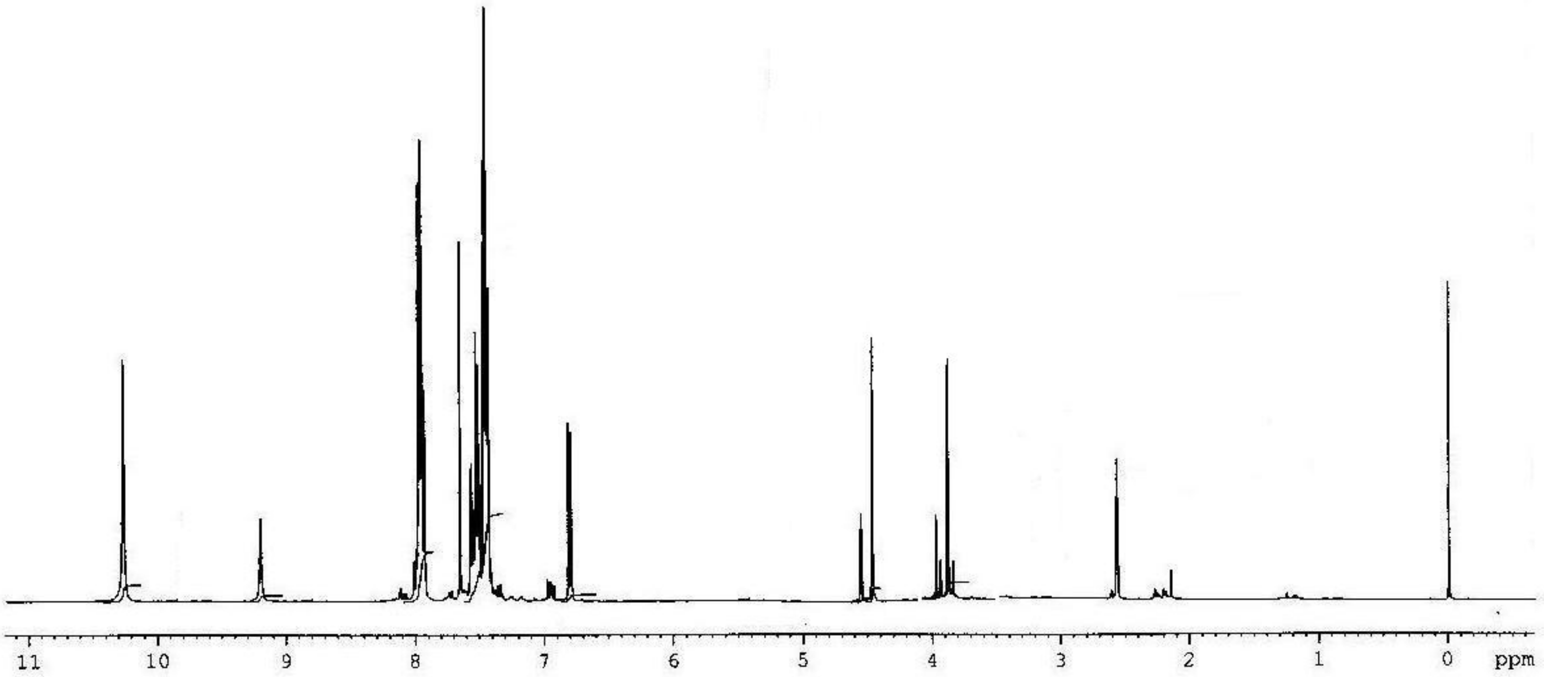


APPENDIX II

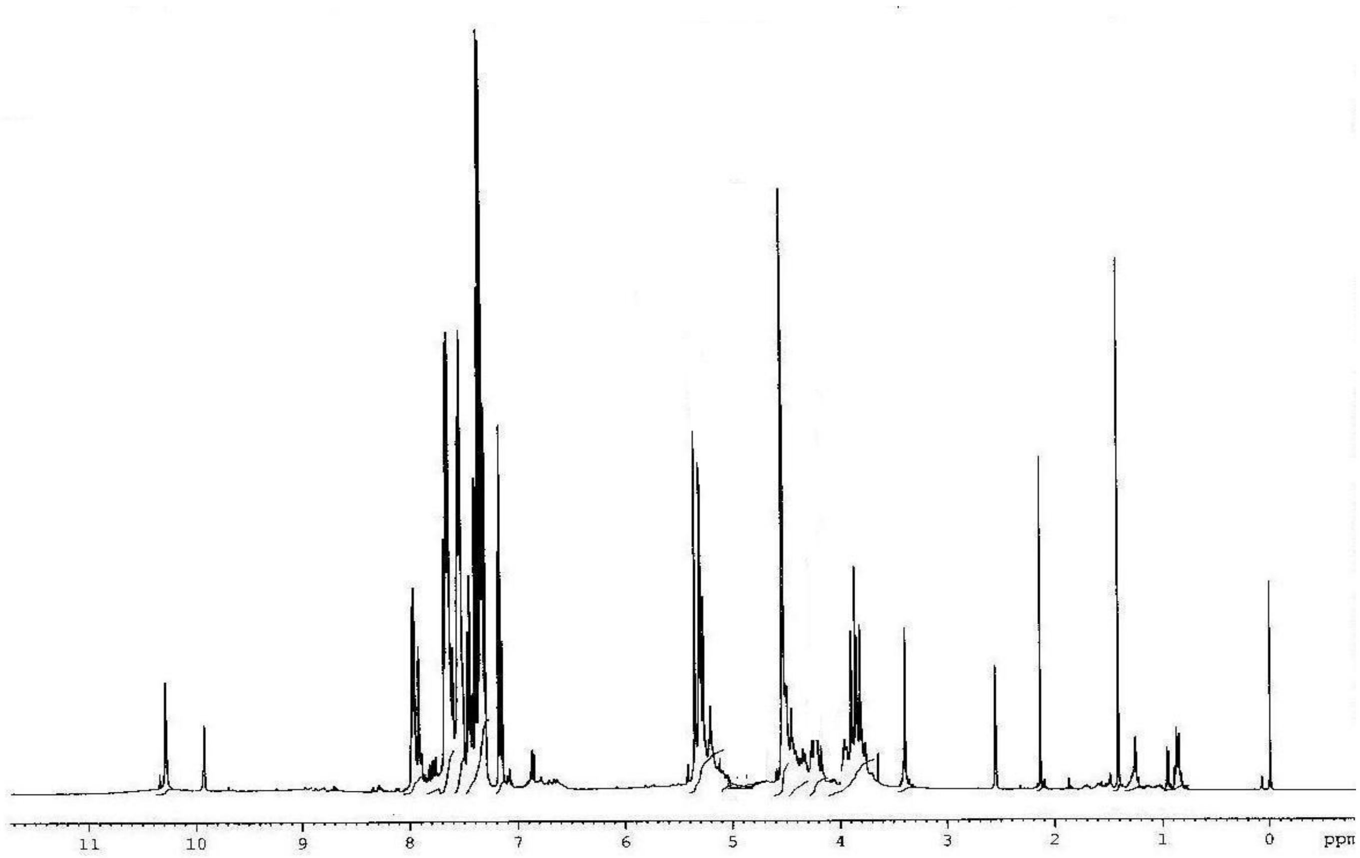
^{1}H NMR spectra of Coumarin Calixarene Hydroxamic Acid [compound 12]



^{1}H NMR spectra of Pyridine Calixarene Hydroxamic Acid [compound 9]

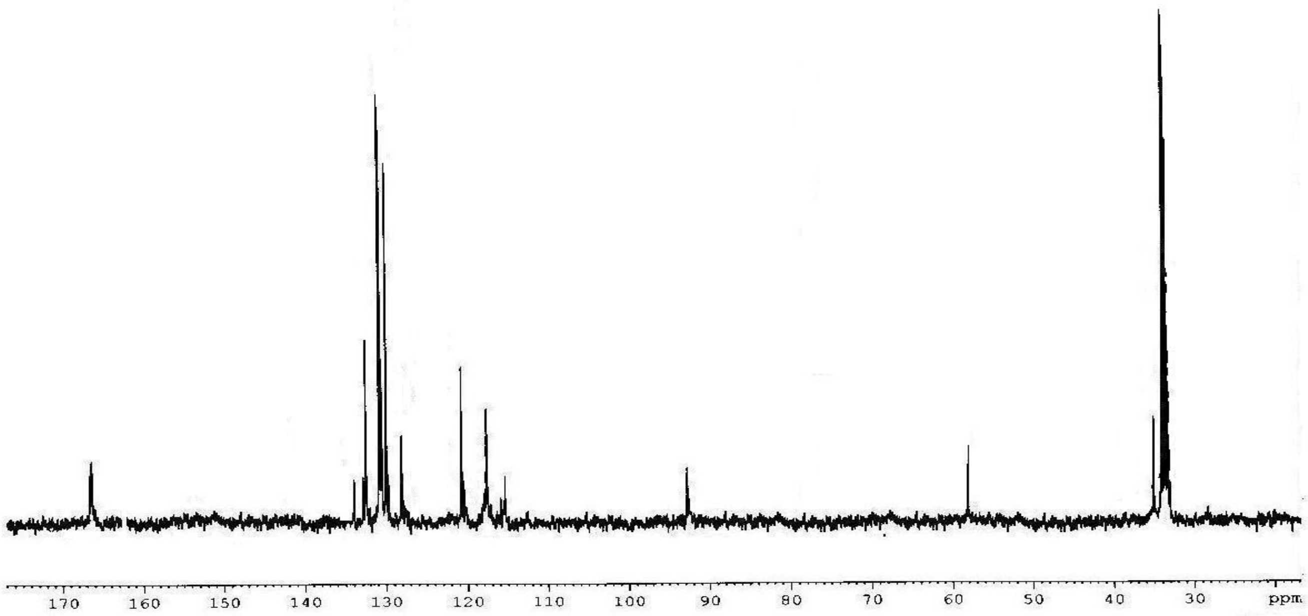


^{1}H NMR spectra of Calix-Crown Hydroxamic Acid [compound 16]

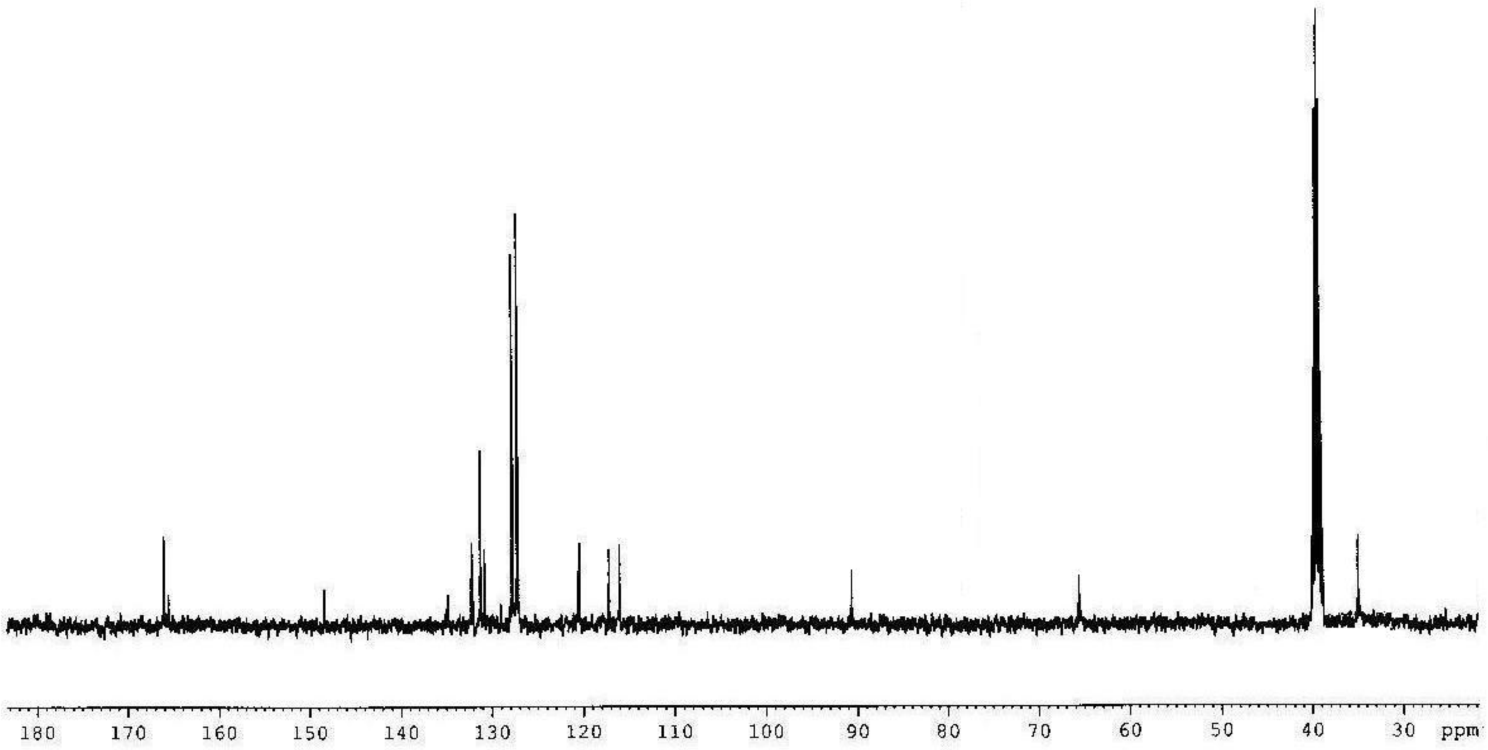


APPENDIX III

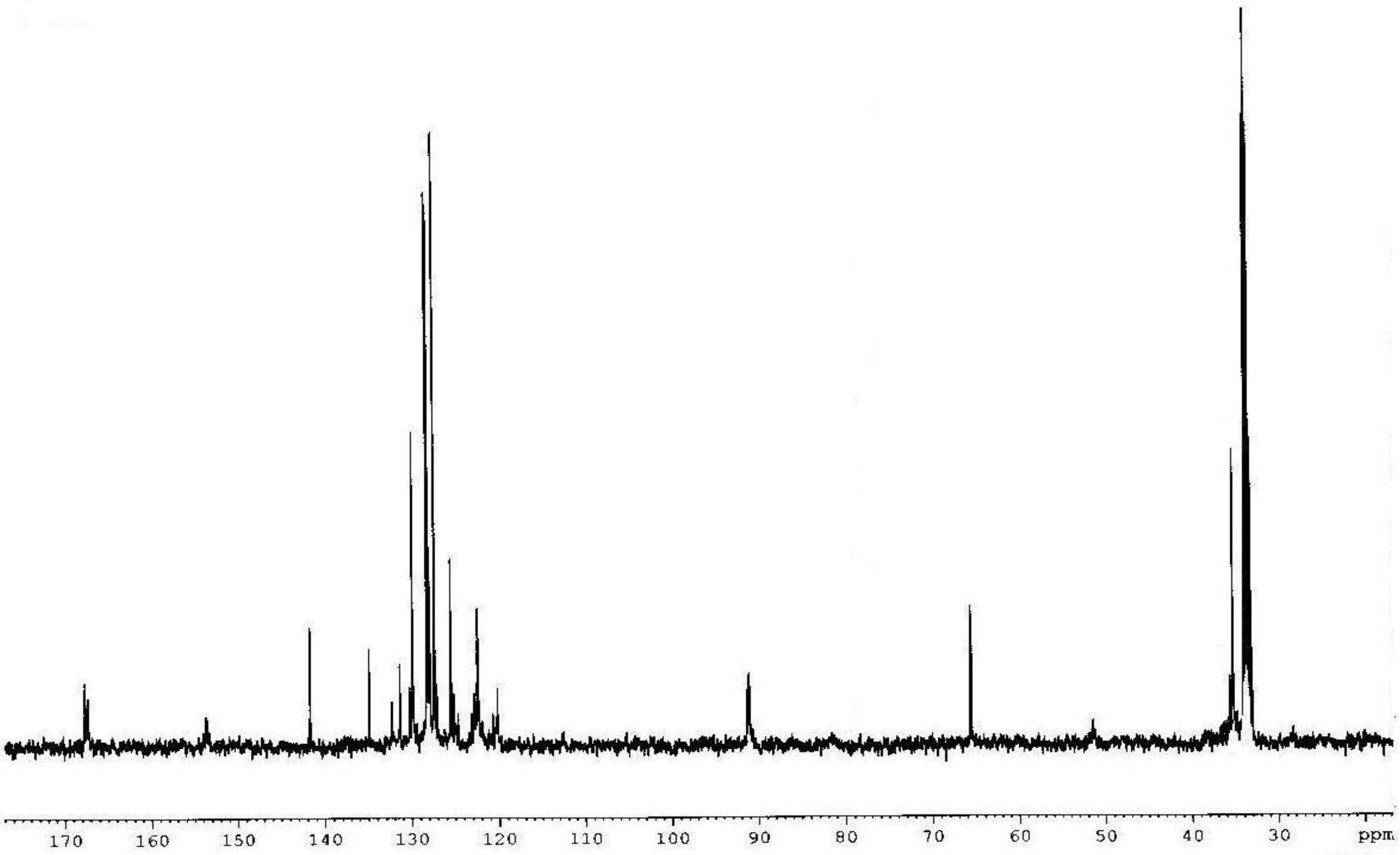
^{13}C NMR spectra of Coumarin Calixarene Hydroxamic Acid [compound 12]

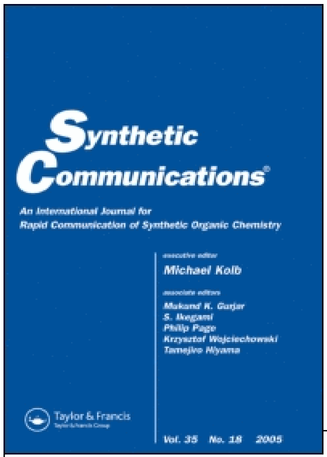


^{13}C NMR spectra of Pyridine Calixarene Hydroxamic Acid [compound 9]



^{13}C NMR spectra of Calix-Crown Hydroxamic Acid [compound 16]





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Environmentally Benign Syntheses of Calixarene Derivatives

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Environmentally Benign Syntheses of Calixarene Derivatives

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Abstract: New hydroxamic acid derivatives of calixarene have been synthesized by conventional and microwave method.

Keywords: Calixarene; hydroxamic acid; microwave

The calixarenes are a class of cyclooligomers formed via a phenol–formaldehyde condensation.[1] Their rigid conformation enables calixarenes to act as host molecules as a result of their preformed cavities. By functionally modifying the upper and/or lower rims, it is possible to synthesize their various derivatives with applications such as enzyme mimetics,[2] ion-sensitive electrodes or sensors,[3] selective membrames,[4] nonlinear optics,[5] high-performance liquid chromatography (HPLC) stationary phase,[6] and anion[7] and cation[8] extractant.

The elimination of volatile organic solvents in organic syntheses is the most important need in green chemistry. Microwave-irradiated organic reactions make syntheses simpler, save energy, and prevent solvent wastes, hazards, and toxicity. Keeping this in mind, in the present investigation the microwave-assisted syntheses of tetranitrocalix[4]arene (TNC4A) **(3)**, hexacarboxycalix[6]arene (HCC6A) **(5)**, pyridinium bearing calix[4]-arenehydroxamic acid (PC4AHA) **(9)**,coumarin-calix[4]arenehydroxamic acid (CC4AHA) **(12)**, and tetracarboxycalix[6]crownhydroxamic acid (TCC6CHA) **(16)** are reported.

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Compounds **3** and **5** (Fig. 1) were synthesized by the acid-catalyzed condensation of formaldehyde with *p*-nitrophenol and *p*-hydroxy benzoic acid respectively.[9,10] Compound **3** was partially reduced with hydrazine hydrate in the presence of Raney Ni (W-2) at 0–10 °C for 1 h to obtain corresponding hydroxylamine **(6)**, which was condensed with isonicotinoyl chloride **(8)** and coumarin-3-carbonyl chloride **(11)** in the presence of an aqueous suspension of sodium bicarbonate at 0–10 °C to yield PC4AHA **(9)** and CC4AHA **(12)** (Fig. 1), respectively. The products were purified by crystallization from chloroform.

Compound **5** was refluxed with 1,4-dibromo butane in the presence of K_2CO_3 using acetonitrile as a solvent at 80 °C for 24 h to yield compound **13**. This was further reacted with diethylene triamine in the presence of K_2CO_3 to obtain compound **14**. Compound **14** was refluxed with thionyl chloride in the presence of dimethylformamide for 4 h and condensed with N-phenylhydroxylamine in the presence of an aqueous suspension of sodium bicarbonate at 0–10 °C to get TCC6CHA **(16)** (Fig. 2).

The microwave-assisted synthetic procedures were developed for calixarene derivatives to give better yield, purity, and time savings. They are also solvent free and prevent waste.

The composition and the structure of synthesized calixarene derivatives have been confirmed by elemental analysis (for C,H,N), FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

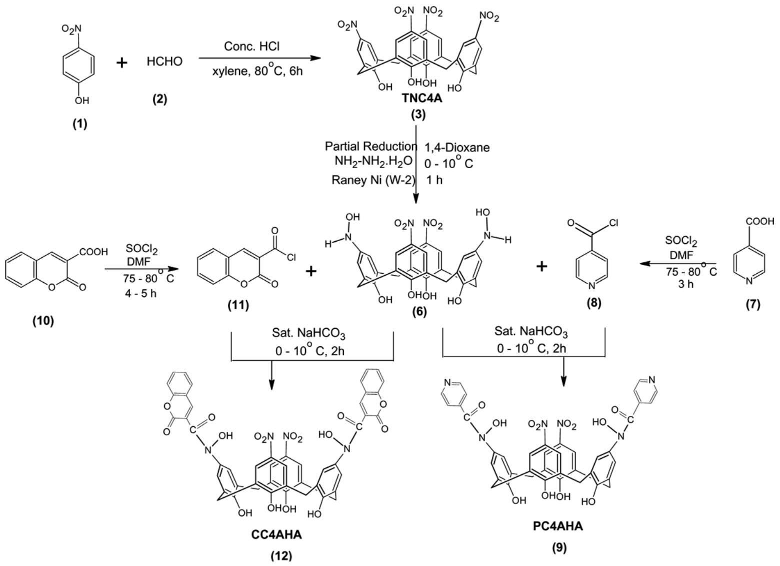

Figure 1. Synthetic route for compounds **9** and **12**.

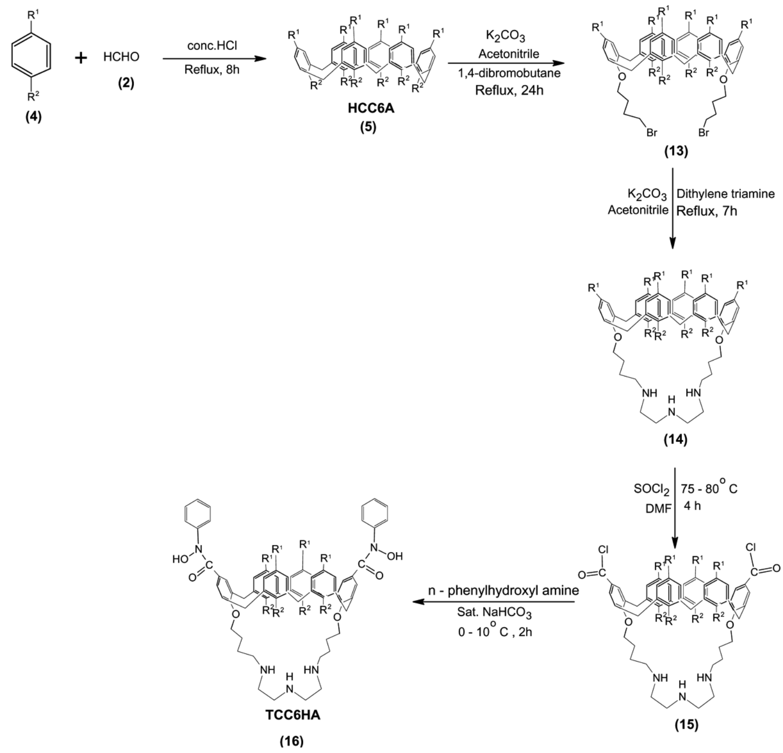

Figure 2. Synthetic route for compounds **16** ($R^1 = COOH$, $R^2 = OH$).

The Fourier transform infrared spectrometer (FT-IR) (KBr) spectrum of compounds **3**, **5**, **9**, **12**, and **16** displayed three sharp bands at 3185, 1635, and 920 cm^{-1}, confirming the υ_{OH}, $\upsilon_{C=O}$, and υ_{N-O} of the hydroxamic acid functional group. The band at 3185 cm^{-1} is due to O–H stretching vibration. It is known that O–H stretching vibration bands occur at around 3600 cm^{-1}; hydrogen bonding shifts these bands to lower frequencies. In hydroxamic acids, the –OH group is placed very close to the polar carbonyl C=O group. The band at 1635 cm^{-1} is assigned to the C=O of the hydroxamic acid group. A sharp band at 920 cm^{-1} is attributed to N–O stretching vibrations. Compounds **3**, **9**, and **12** displayed a sharp band at 1350 cm^{-1} for $-NO_2$ stretching vibrations.

The structures of compounds **3**, **5**, **9**, **12**, and **16** were established by elemental analysis and ^1H NMR and ^{13}C NMR spectra. These compounds display singlets around 7.82, 7.70, 7.60, 7.51, 7.45, and 6.82 for aromatic protons. A pair of doublets appears at δ 4.50 and 3.90 for $ArCH_2Ar$ protons in the ^1H NMR. Prominent signals appeared at δ 9.00, 9.20, and 9.90 for aromatic hydroxyl protons and at δ 10.27, 10.28, and 10.70 for the hydroxamic group. In compounds **3**, **9**, and **12**, a prominent downfield shift in the position of the hydroxyl signal suggested that nitro groups were present at positions *para* to the hydroxyl groups. A singlet appears at δ 10.32 for each carboxyl hydrogen present in compounds **5** and **16**. Notice that this peak is not sharp; it was broadened by hydrogen bonding and exchange. Two singlets appear at 8.01 and 3.40 for NH and CH_2CH_2OAr respectively.

The ^{13}C NMR (dimethyl sulfoxide (DMSO)) spectrum of compounds **3**, **5**, **9**, **12**, and **16** displayed singlets at δ 116–125 and 128–137 for aromatic protons and one singlet near δ 167 and 166 for ketone groups. In addition, compounds **5** and **16** displayed a singlet at 166.86 for the carboxylic acid group and doublets at δ 35.12 and 34.63 for bridged methane groups. Compound **16** displayed one triplet at δ 51.48 for crown moiety.

The results obtained from elemental analysis of compounds **3**, **5**, **9**, **12**, and **16** confirm the presence of hydroxamic acid groups.

In conclusion, we have synthesized novel hydroxamic derivatives of calixarenes by conventional and microwave methods.

EXPERIMENTAL

Melting points are uncorrected and were obtained using a melting-point apparatus (Electroquip). IR spectra were recorded on Jasco FT/IR 6100 spectrometer. ^1H NNR and ^{13}C NMR were recorded on a DRX 300 spectrophotometer operating at 300 MHz in $CDCl_3$ with TMS as an internal standard. Microwave synthesis was carried out using a Kenstar OM 20 DGQ domestic microwave oven.

Synthesis of Compound (3)

Conventional Method

Compound **3** was synthesized by a previously reported method.[9]

Microwave Method

A mixture of *p*-nitrophenol (1 g, 0.0073 M), 37% formaldehyde (0.6 ml, 0.0073 M), and conc. hydrochloric acid (1 ml) was placed into the Kenstar domestic microwave at 20% power output for 180 s to obtain a white solid, which was washed with hot water and with hot alcohol to get compound **3**.

Data

TNC4A: yield 93%, mp 140–142 °C, IR (KBr): υ = 3185, 1635, 1350, 920 cm^{-1}. ^{1}H NMR (DMSO): $\delta = 9.20$ (s, 4H, ArOH), 4.50 (d, 4H, ArCH$_2$Ar), 3.90 (d, 4H, ArCH$_2$Ar), 7.82 (s, 8H, ArH). ^{13}C NMR (DMSO): $\delta = 35.12$ (d, Ar-CH$_2$-Ar), 119.05–132.10 (s, ArC).

Synthesis of Compound (5)

Conventional Method

Compound **5** was synthesized by a previously reported method.[10]

Microwave Method

A mixture of *p*-hydroxybenzoic acid (1 g, 0.0072 M), 37% formaldehyde (4 ml, 0.0015 M), and conc. hydrochloric acid (2.5 ml) was placed into the Kenstar domestic microwave at 40% power output for 120 s to obtain a white solid, which was washed with hot distilled water to remove acidic impurities and recrystallized from acetone–petroleum ether (60–80 °C) to get compound **5**.

Data

HCC6A: yield 95%, mp 110–111 °C, IR (KBr): υ = 3185, 1635, 920 cm^{-1}. ^{1}H NMR (DMSO): $\delta = 9.90$ (s, 6H, ArOH), 4.44 (d, 6H, ArCH$_2$Ar), 3.85 (d, 6H, ArCH$_2$Ar), 7.45 (s, 12H, ArH), 10.32 (s, 6H, COOH). ^{13}C NMR (DMSO): $\delta = 34.63$ (d, Ar-CH$_2$-Ar), 120.20–125.52 (s, ArC), 127.26–134.94 (s, ArC), 166.86 (s, COOH). Anal. calcd. for $C_{48}H_{36}O_{18}$: C, 64.0%; H, 4.03%. Found: C, 63.91%; H, 4.10%.

Synthesis of Compound (6)

Conventional Method

Nitrocalix[4]arene (10 g, 0.015 M), hydrazine hydrate (10 ml, 0.205 M), and Raney-Ni (W-2) (2–2.5 g) in 1,4-dioxane were stirred at 0–10 °C for 1 h to get compound **6**, which was filtered immediately and used in situ for the preparation of hydroxamic acid derivatives.

Microwave Method

Nitrocalix[4]arene (1 g, 0.0015 M), hydrazine hydrate (1 ml, 0.0205 M), and Raney-Ni (W-2) (0.2–0.3 g) were placed into the Kenstar domestic microwave at 0% power output for 120 s to get compound **6**.

Synthesis of Compound (9)

Conventional Method

Thionyl chloride (15 ml) was slowly added to a stirred mixture of isonicotinic acid **7** (10 g, 0.0813 M) and dimethylformamide (1 ml). The mixture was stirred at 75–80 °C for 3 h. The isonicotinoylchloride hydrochloride **8** was precipitated as a white powder by adding 50 ml of dried petroleum ether.

Acid chloride **8** (2.3 g, 0.0016 M) was condensed with compound **6** (3.60 g, 0.0064 M) in the presence of an aqueous suspension of sodium bicarbonate (2 g) at 0–10 °C for 2 h to get compound **9**.

Microwave Method

A mixture of isonicotinic acid **(7)** (1 g, 0.0081 M), dimethylformamide (0.1 ml), and thionyl chloride (1.5 ml) was placed into the Kenstar domestic microwave at 40% power output for 120 s. The isonicotinoylchloride hydrochloride was precipitated as a white powder by adding 50 ml of dried petroleum ether.

The acid chloride **8** (1.5 g, 0.0011 M) was condensed with compound **6** (1 g, 0.0015 M) in the presence of an aqueous suspension of sodium bicarbonate (2 g) in the oven at 0% power output for 120 s to get compound **9**.

Data

PC4AHA: yield 91%, mp 186–188 °C, IR (KBr): $\upsilon = 3185, 1635, 1350, 920\,\text{cm}^{-1}$. ^{1}H NMR (DMSO): $\delta = 10.27$ (s, 2H, NOH), 9.20 (s, 4H, ArOH), 4.50 (d, 4H, $J = 12.9$ Hz, $ArCH_2Ar$), 3.90 (d, 4H, $J = 12.9$ Hz, $ArCH_2Ar$), 7.70 (s, 4H, ArH), 7.82 (s, 4H, ArH), 6.82–7.45 (s, 8H, ArH). ^{13}C NMR (DMSO): $\delta = 35.12$ (d, Ar-CH_2-Ar), 119.05–126.62 (s, ArC), 128.21–137.48 (s, ArC), 167.12 (s, C=O). Anal. calcd. for $C_{40}H_{30}N_6O_{12}$: C, 61.07%; H, 3.84%; N, 10.68%. Found: C, 61.48%; H, 3.55%; N, 10.72%.

Synthesis of Compound (12)

Conventional Method

Thionyl chloride (10 ml) was slowly added to a stirred mixture of coumarin-3-carboxylic acid[11] (3 g, 0.015 M) and dimethylformamide (0.8 ml). The mixture was stirred at 75–80 °C for 4–5 h. The coumarin-3-carbonylchloride was precipitated as a white powder by adding 40 ml of dried petroleum ether. The acid chloride was condensed with freshly prepared compound **6** (3.60 g, 0.0064 M) in the presence of an aqueous suspension of sodium bicarbonate (2 g) at 0–10 °C for 2 h to obtain compound **12**.

Microwave Method

A mixture of coumarin-3-carboxylic acid[11] (1 g, 0.05 M), dimethylformamide (0.3 ml), and thionyl chloride (3.35 ml) was placed into the Kenstar domestic microwave at 40% power output for 120 s. The coumarin-3-carboylchloride was precipitated as a white powder by adding 40 ml of dried petroleum ether.

The acid chloride was condensed with compound **6** (1 g, 0.0015 M) in the presence of an aqueous suspension of sodium bicarbonate (2 g) in the oven at 0% power output for 120 s to get compound **12**.

Data

CC4AHA: yield 93%, mp 239–241 °C, IR (KBr): $\upsilon = 3185, 1635, 1350, 920\,\text{cm}^{-1}$. ^{1}H NMR (DMSO): $\delta = 10.70$ (s, 2H, NOH), 9.00 (s, 4H, ArOH), 4.26 (d, 4H, $J = 12.9$ Hz, ArCH$_2$Ar), 3.82 (d, 4H, $J = 12.9$ Hz, ArCH$_2$Ar), 7.70 (s, 4H, ArH), 7.82 (s, 4H, ArH), 6.82–7.40 (s, 10H, ArH). ^{13}C NMR (DMSO): $\delta = 35.12$ (d, Ar-CH$_2$-Ar), 116.05–120.62 (s, ArC), 127.18–134.80 (s, ArC), 166.07 (s, C=O). Anal. calcd. for $C_{48}H_{32}N_4O_{16}$: C, 62.61%; H, 3.50%; N, 6.08%. Found: C, 62.75%; H, 3.45%; N, 6.01%.

Synthesis of Compound (16)

Conventional Method

Anhydrous K_2CO_3 (0.7 g, 0.005 M) to a suspension of compound **5** (5 g, 0.005 M) and 1,4-dibromopropane (2.7 g, 0.0125 M) in acetonitrile

(100 ml), was added and the reaction mixture was stirred under reflux for 24 h. After the solvent was removed under reduced pressure, the residue was then purified by crystallization form chloroform to get compound **13**.

Anhydrous K_2CO_3 (0.5 g, 0.00358 M) and diethylene triamine (2.0 g, 0.002 M) were added to a solution of compound **13** (2 g, 0.00179 M) in acetonitrile (25 ml). The mixture was refluxed about 7 h. The solvent was removed by rotary evaporator. Then CH_2Cl_2 (10 ml) was added. The organic layer was then washed with distilled water (2 × 5 ml), and organic phase was evaporated under reduced pressure to dryness. Residue was purified by crystallization from chloroform to get compound **14**.

Compound **14** was refluxed with thionyl chloride in the presence of dimethylformamide for 4 h, and excess thionyl chloride was removed under reduced pressure to get compound **15**, which was added to a mixture of N-phenyl hydroxyl amine and sodium bicarbonate in 1,4-dioxane at 0–10 °C within 1 h. Reaction mixture was further stirred for 1 h more, then filtered. Solid was washed with water and purified by crystallization from chloroform to get compound **16**.

Microwave Method

A mixture of compound **5** (1 g, 0.001 M), 1,4-dibromobutane (0.6 g, 0.0025 M), and anhydrous K_2CO_3 (0.15 g, 0.001 M) was placed into the Kenstar domestic microwave at 20% power output for 240 s to get compound **13**.

A mixture of **13** (0.5 g, 0.0005 M), anhydrous K_2CO_3 (0.13 g, 0.00090 M), and diethylene triamine (0.5 g, 0.0005 M) was placed into the Kenstar domestic microwave at 20% power output for 180 s to get compound **14**.

Compound **14** (2 g, 0.0017 M), dimethylformamide (0.3 ml), and thionyl chloride (2.5 ml) was placed into the Kenstar domestic microwave at 40% power output for 120 s to get compound **15**, which was condensed with N-phenyl hydroxyl amine in the presence of sodium bicarbonate (2 g) in the microwave oven at 0% output for 120 s to get compound **16**.

Data

TCC6HA: yield 66%, mp 219–222 °C, IR (KBr): $\upsilon = 3185, 1635, 1350, 920\,\text{cm}^{-1}$. ^{1}H NMR (DMSO): $\delta = 10.28$ (s, 2H, NOH), 9.90 (s, 4H, ArOH), 4.44 (d, 6H, $J = 13.5$ Hz, $ArCH_2Ar$), 3.85 (d, 6H, $J = 13.5$ Hz, $ArCH_2Ar$), 7.45 (s, 8H, ArH), 7.51 (s, 4H, ArH), 7.60 (s, 4H, ArH), 7.17 (s, 6H, ArH), 10.32 (s, 4H, COOH), 8.01 (br s, 3H, NH), 3.40 (s, 4H, CH_2CH_2OAr). ^{13}C NMR (DMSO): $\delta = 34.63$ (d, Ar-CH_2-Ar), 120.20–125.52 (s, ArC), 127.26–134.94 (s, ArC), 166.86 (s, COOH), 167.73 (s, C=O). Anal. calcd. for $C_{72}H_{71}O_5N_{18}$: C, 66.81%; H, 5.53%; N, 5.41%. Found: C, 66.75%; H, 5.60%; N, 5.57%.

REFERENCES

1. Gutsche, C. D. *Calixarenes*. Royal Society of Chemistry: Cambridge, 1989.
2. Molenveld, P.; Engbersen, J. F. J.; Reinhoudt, D. N. Synthesis of a dinuclear Zn^{II}-calix[4]arene enzyme model with additional general base groups–Catalytic activity in phosphate diester transesterification. *Eur. J. Org. Chem.* **1999**, *12*, 3269.
3. Shishkanova, T. V.; Sýkora, D.; Sessler, J. L.; Král, V. Potentiometric response and mechanism of anionic recognition of heterocalixarene-based in selective electrodes. *Anal. Chim. Acta* **2007**, *587*(2), 247.
4. Lisowska-Oleksiak, A.; Lesińska, U.; Nowak, A. P.; Bocheńska, M. Ionophores in polymeric membranes for selective ion recognition; impedance studies. *Electrochim. Acta.* **2006**, *51*(11), 2120.
5. Thallapally, P. K.; Lloyd, G. O.; Atwood, J. L.; Barbour, L. J. Diffusion of water in a nonporous hydrophobic crystal. *Angew. Chem. Int. Ed.* **2005**, *44*(25), 3848.
6. Purse, B. W.; Gissot, A.; Rebek, J. Jr. A deep cavitand provides a structured environment for the menschutkin reaction. *J. Am. Chem. Soc.* **2005**, *127*(32), 11222.
7. Tabakci, M.; Memon, S.; Yilmaz, M. Synthesis and extraction properties of new 'proton-switchable' tri- and tetra-substituted calix[4]arene derivatives bearing pyridinum units. *Tetrahedron* **2007**, *63*(29), 6861.
8. Tu, C.; Surowiec, K.; Bartsch, R. A. Efficient divalent metal cation extractions with di-ionizable calix[4]arene-1,2-crown-4 compounds. *Tetrahedron* **2007**, *63*(19), 4184.
9. Jogani, S. K.; Menon, S. K.; Agrawal, Y. K. Synthesis and characterisation of a calix(4)arene schiff base and its complexation studies with transition metal ions. *Synth. React. Inorg. Met.-Org. Chem.* **2002**, *32*(3), 603.
10. Gidwani, M. S.; Menon, S. K.; Agrawal, Y. K. Chelating polycalixarene for the chromatographic separation of Ga(III), In(III) and TI(III). *React. Funct. Polym.* **2002**, *53*, 143.
11. Wood, L. C.; John, S. Coumarin-3-carboxylic Acids. *J. Org. Chem.* **1965**, *82*, 389.