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 macrocyclic 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.
(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 $1 \times 10^{-4}$ 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, spectroscopic properties, molecular structures, and complexation of novel calix[4]arene imido compounds with molybdenenum 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-tetramethylbutyl)calix[6]-arene, 5,26,-27,28-tetakis(acetomethoxy)-5,11,17,23-tetakis(1,1,3,3-tetramethyl-butyl)calix[4]arene, p-(1,1,-3,3-tetramethylbutyl)-phenoxyacetone as a monomeric analog, from highly concentrated HCl or HNO₃ 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 HNO₃ 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/.
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$_2$O$_7^{2-}$/HCr$_2$O$_7^{-}$ 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 \( ^{1}\text{H} \) NMR.

Reaction of \( p \)-tert-butyloctahomotetraoxacalix[8]arene \( (\text{LH}_8) \) 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 $7.6 \times 10^{-7}$ 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 Atheron–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 synergetic 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\textsubscript{2}\textsubscript{5})\textsubscript{4}-calix[4]tetrapyrole 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\textsubscript{2}NAC(O)ACH\textsubscript{2}AP(O)Ph(Oct)) developed for the
TRUX (transuranic elements extraction process), by more than two orders of magnitude in the extraction of actinides (Np, Pu, Am). Calixarenes containing monodentate $\text{Ph}_2\text{P(O)CH}_2$ groups at the lower rim is also a better extractant for actinides than the ungrafted $\text{Oct}_3\text{PO}$ or CMPO ligands do /70/. Calixarenes containing $\text{Ph}_2\text{P(O)CH}_2$ 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/.

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

14
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-quinolinyazo)-4-hydroxybenzoic acid (QAHBA) was synthesized for chemically modified nanometer-sized alumina, and it was characterized with infrared spectrum and \(^1\)H 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 fluidized-
bed 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 determined 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 synthesized 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-nonylacetophenoneoxime /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-nonylacetophenone-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, ¹H NMR and ¹³C 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-CO₂)-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.
REFERENCES

62. Tentagel is a trademark of Rapp polymer.
69. (a) F. Arnaud-Neu, V. Böhmer, J. F. Dozol, C. Grüttnner, R.A. Jakobi,


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


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


137. M. H. Patel, V. B. Patel, P. S. Shrivastav, Tetrahedron, **2008**, 64(9), 2057.


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