IJCPS Vol. 7, No. 2 , Mar-Apr 2018 ISSN:2319-6602
www.ijcps.org International Journal of Chemical and Physical Sciences

4-Methyl-N-n-Octylaniline as a New Liquid Anion Exchanger for the Liquid-Liquid Extraction of Gallium (III): Application to Electronic Waste LED

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doi: 10.30731/ijcps.7.2.2018.52-61

Abstract

Amongst the various high molecular weight amines, 4-Methyl-N-n-octylaniline is introduced as new analytical reagent for the liquid-liquid extraction of gallium (III). The extractive separation of gallium (III) is found to be quantitative in the range from 5.0M to 10.0M hydrochloric acid using 2% 4-Methyl-N-n-octylaniline in xylene as diluent. The effect of acidity and reagent concentration has been discussed. The same parameter has been used to decide probable metal : amine ratio in extracted species by use of log-log plot. The extracted species found was $[RR'NH_2^+GaCl_4^-]$*. The effect of various foreign ions on the extraction of gallium (III) with recommended reagent has been reported by proposed method. The method found to be free from interference of large number of cations and anions. The method has been successfully applied for extractive separation of gallium (III) from binary mixtures, ternary mixtures as well as sequential separation of Ga, In and Tl. The proposed method was applied for recovery of rare gallium from electronic scrap like LED.*

Keywords: 4-Methyl-N-n-octylaniline, extractive separation

Introduction

Gallium is one of the less abundant element in the earth's crust generally less than 19 ppm. It does not exist in elemental form in nature. Fortunately, gallium occurs in very small concentration (≈50 ppm) in ore of other metals and coal. Worldwide, primary gallium is obtained as a side product of metallurgical processing of bauxite ore for aluminium and sphalerite ore for zinc. Gallium is also recycled from scrap generated in the manufacture of GaAs and GaN based devices. Flue dust, a residue from the burning coal is used as feedstock to recover Gallium in Europe and Great Britain[1,2,3]. Gallium is solid at normal room temperature but it becomes liquid when heated slightly. Similar to mercury, cesium and rubidium gallium is liquid over wide range of temperature and has found use in manometer and thermometer for high temperature measurements. At high temperature gallium dissolves most metals. Gallium alloys include some low melting species mainly eutectic gallium-indium and eutectic gallium-tin alloys[4]. Certain other alloys e.g. the compounds V_3Ga, Nb_3Ga, and Zr_3Ga are of more interest because of their superconducting properties below 14.3° , 14.5° and 10.5° respectively. Alloys of gallium with silver and tin are used in dental fillings. Chemical properties of gallium are similar to aluminium. It forms hydrogen, halogen, chalcogen and numerous organometallic compounds[5]. Due to semiconductor properties of Gallium arsenide and Gallium phosphide they are used in rectifiers and transistors. Since GaAs and GaN are able to change electricity into light they are employed in making of light emitting diodes (LED's), laser diodes, photo detectors and solar cells. These components are important for high performance computers and smartphones[6]. In the world of digitalization the demand of gallium is magnified[7]. Currently there is no large scale production of gallium in India and it is impossible to satisfy this great demand just by its separation as byproduct of processing bauxite and zinc ores. There is great need of recovery of gallium from E-waste also.

Solvent extraction plays prominent role in the recovery of gallium. Extraction of gallium from chloride, hydroxide, sulphate and nitrate media with different organic extractant including ethers, ketones, carboxylic acids, organophosphorous compounds, alkyl amines and quaternary ammonium salts, hydroxy quinoline derivatives have been reviewed[8]. Various derivatives of 8-hydroxyquinoline commonly known as Kelex-100 are the reagents of interest for the extraction of gallium (III). The solvent extraction of gallium from concentrated Bayer process liquor was investigated using 12 vol% Kelex-100, a 7-alkyl substituted-8-hydroxyquinoline as extractant, 12vol% isodecanol as modifier and kerosene as diluent. In order to improve kinetics of extraction the effect of addition of various surfactants such as octylamine, petroleum sulphonate and versatic 10 in the organic phase was studied[9]. However, Ga/Al selectivity and efficiency of the extraction and re-extraction processes was enhanced without using additives and modifiers. This fundamental extraction kinetics with the pure Kerosene/Kelex 100 system and a method of selective re-extraction boosted by possible chloro-complex formation in HCl media[10]. Solid phase extraction of gallium(III) with hydrophobic 8-quinolinol derivatives impregnated resin from aqueous acidic and alkaline solutions have been investigated[11] . The method for the extraction of gallium (III) with LIX26 (alkyl substituted 8-hydroxyquinoline) in n-decanol as modifier and kerosene as diluent was studied along with thermodynamic functions ΔH,ΔS and ΔG[12] A synergistic extraction systems consisting of sec-octylphenoxy acetic acid and primary amine N1923 have been studied for selective extraction between Ga/In and Zn.[13] Organophosphorous reagent also plays important role in the solvent extraction of Ga (III). Some of the examples are D2EHPA (Di-2-ethylphosphoric acid)[16], OPAP[14,15], cyanex-921[17] (i.e. Tri-n-octylphosphine oxide TOPO), cyanex-923[18,19],cyanex -301[20]cyanex-925[21]TBP[22,23],TBP and TOA[24], sodium di- (n-octyl) phosphinate[25]. The extractant cyanex-923 is a mixture of four trialkyl phosphine oxides namely dioctyl-hexyl phosphine oxide, dihexyl-octyl phosphine oxide, trihexylphosphine oxide and troctyl phoshine oxide and cyanex-925 contains five isomers of trioctyl phosphine oxide with branched and normal alkyl chains[21]. The extraction of Ga(III) was found quantitative over wide range of HCl at high concentration while it was poor over the entire concentration range HNO_3 and $H_2SO_4$with cyanex-923[18,21].

Extractability of long chain amines has been studied for solvent extraction of many heavy metals and rare earths. Long chain amines are found as powerful extractant for solvent extraction of Ga(III). Effect of amine structure on gallium extraction from strong acid hydrochloric acid solution has been investigated. The degree of extractability of extractants was arranged in the order Adogen-464 > TABAC > TOA, Hostarex A-327, Adogen-364, Hostarex A-324 > THPA > benzyldimethylalkylammonium chloride > THA > HOEF 2562, Adogen 283[26].The use of high molecular weight amine extractants including Adogen-464[27], Aliquot-336S[28], Tris(2-hydroxy-3,5-dimethylbenzylamine[29],n-octylaniline[30], N-n-octylaniline[31], 2-octylaminopyridine[32] , primary amine N1923[13] have been reported in the literature for liquid-liquid extraction of gallium. Seeing this considerable practical and historic interest in the system containing high molecular weight amines as liquid anion exchanger for extraction of Ga(III) , 4-Methyl-N-n-octylaniline is introduced as new analytical reagent for solvent extraction of Ga(III). The proposed method also has been extended for extraction of Ga(III) from electronic waste.

Materials and method

Apparatus

Optical Density measurements were carried out using Equiptronics EQ-824 dual beam UV-visible spectrophotometer with 1cm quartz cells and pH measurements were carried out with Equiptronics Digital pH Meter Model No.EQ-614A.

Reagents

Gallium (III) solution

Preparation of standard stock solution of 1000 µg/ml of Ga(III) was done by dissolving 0.369g of Gallium (III) nitrate(Otto Chemie) in 5ml of concentrated nitric acid and diluting to 100ml with double distilled water. The solution was standardized by direct titration method[33].

4-Methyl-N-n-octylaniline:

It was prepared in the laboratory by N-alkylation of excess of p-Toluidine with 1-Bromo octane (SDFCL) Instrumental techniques likeH^1NMR, FT-IR and Mass spectra were used to check purity of the recrystallised compound. ($CDCl_3$) H^1NMR :0.9(t,-CH_3, 3H), 1.39(m, -CH_2-, 10H), 1.6(m, -CH_2-, 2H), 2.3(s, -CH_3, 3H), 3.1(t, -NH-CH_2-, 2H), 3.5(s, -NH-, 1H), 6.6(d, Ar-H, 2H), 7.0(d, Ar-H, 2H), IR(cm^{-1}):-3382.6 (N-H stretch), Mass m/e:219($M^{+\cdot}$).

4-Methyl-N-n-octylaniline solution

Solutions % w/v were prepared by using xylene as diluent.

Xylenol orange solution:

1×10^{-3}M solution of Xylenol orange was prepared by dissolving 0.190g Xylenol orange in 250mL double distilled water.

All other chemicals used were of analytical grade. More dilute solutions were prepared by accurate dilution. Doubly distilled water was used throughout. Waste LEDs were collected from electronic repair shops at Ulhasnagar electronic market, Mumbai, Maharashtra.

Extraction Procedure

Measured quantity of hydrochloric acid was added to suitable volume of solution containing 50µg of Ga(III) to make the concentration 0.5M to 10M in a volume of 10mL.Decant the solution to 125mL separating funnel containing 1-2% of 4-Methyl-N-octylaniline in xylene and shake for two minutes. Allow the two phases to separate. Strip Ga(III) from organic phase by gentle wrist shaking with (2×10mL) of water. Then evaporate the stripped solution to remove organic impurities and to reduce the volume. The pH of stripped solution was adjusted to 1.5 to 2.0 with dilute nitric acid. Then add 4mL of 1×10^{-3}xylenol orange and dilute to 25mL. Measure the Optical Density at 540nm using reagent blank[34,36]. Amount extracted calculated by using calibration curve.

Results and Discussion

Effect of acidity and reagent concentration

Quantitative extraction of Ga(III) was tried by varying concentration of HCl from 0.5M to 10M and the concentration of 4-Methyl-N-n-octylaniline from 1-2% keeping aqueous to organic volume ratio 2.5:1. It was observed that percentage extraction increases with increase in acid concentration as well as increase in reagent concentration (Fig.1). The quantitative extraction of 50µg gallium was observed with 2% reagent and concentration of HCl medium ranging from 5-10M. This is due to the stable ion pair formation in the observed range. To check other parameters, further extraction experiments were carried out at 7M HCl concentration and 2% reagent concentration although excess of reagent concentration had no unfavorable effect on quantitative extraction.

Nature of extracted complex and extraction mechanism

To ascertain the nature of extracted species logD-logC plot was used. Distribution ratio was calculated by using the equation D = %E / (100 - %E) × Vaq/Vorg. Log-log plot of the distribution ratio versus 4-Methyl-N-n-octylaniline concentration at 3.0M and 3.5M concentration of HCl gave slopes 0.84 and 1.1 respectively indicating that metal to amine ratio in extracted species is 1:1 (Fig.2). Hence the probable extraction complex at 3.0M as well as 3.5M HCl concentration is $[RR'NH_2^+ GaCl_4^-]$. To explain formation of this ion pair, the probable mechanism was given as follows:

$[RR'NH]_{org} + HCl_{aq} == [RR'NH_2^+Cl^-]_{org}$

$GaCl_{3aq} + Cl^-_{aq} == GaCl^-_{4\,aq}$

$[RR'NH_2^+Cl^-]_{org} + GaCl^-_{4\,aq} == [RR'NH_2^+ GaCl_4^-]_{org} + Cl^-_{aq}$

$R= C_6H_4\text{-}CH_3 \qquad R'= C_8H_{17}$

The mechanism can be explained as follows:

4-Methyl-N-n-octylaniline in organic phase gets protonated by shaking with HCl medium and forms $[RR'NH_2^+Cl^-]_{org}$ neutral species. Ga(III) in HCl medium exists as $GaCl^-_{4\,aq}$complex anion. During extraction this complex anion is exchanged with Cl^- anion of $[RR'NH_2^+Cl^-]$ species. Thus $GaCl_4^-$ is transferred from aqueous phase to organic phase.

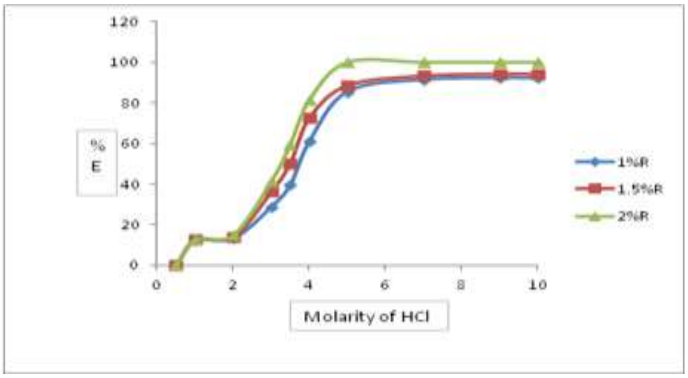

Fig.1: Percentage extraction of Ga(III) with1%, 1.5% and 2% 4-Methyl-N-n-octylaniline in xylene as a function of HCl concentration

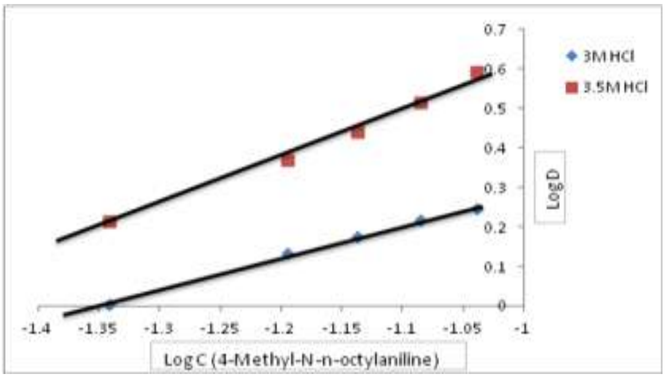

Fig. 2: Log-Log plot of Distribution ratio versus 4-Methyl-N-n-octylaniline concentration at 3.0M and 3.5M concentration of HCl

Effect of various diluents

Gallium(III) was extracted with 4mL of 2% (W/V) 4-Methyl-N-n-octylaniline in various diluents like benzene, xylene, toluene, amyl acetate, carbon tetrachloride, chloroform, hexane, nitrobenzene, amyl alcohol. It was seen that benzene, xylene, toluene, amyl acetate gave quantitative extraction i.e. 100%, 100%, 98.9% and 100% respectively while carbon tetrachloride, chloroform, hexane, nitrobenzene, amyl alcohol gave comparatively less extraction i.e. 90%, 56.04%, 87.2%, 26.3%, 7.7% respectively. Xylene is recommended as diluent throughout extraction experiments as it is comparatively less carcinogenic than benzene and toluene and gives clear cut phase separation.

Effect of time of equilibrium

To study effect of equilibration time extraction of 50µg of Ga(III) in 7M HCl with 2% 4-Methyl-N-n-octylaniline in xylene in 2.5:1 aq:org volume ratio were carried out by varying shaking time ranging from 30 seconds to 10 minutes. The study showed that 1 minute shaking time was needed for complete extraction of Ga(III). To ensure quantitative extraction 2 minute shaking time is recommended in general procedure. However, the prolonged shaking up to 10 minute had no adverse effect on the quantitative extraction.

Effect of phase volume ratio

Extraction of 50µg Ga(III) in 7M HCl with 2% 4-Methyl-N-n-octylaniline in xylene was carried out by varying aqueous:organic phase volume ratio ranging from 1:1 to 10:1 was carried out. The study showed that extraction of Ga(III) was remaining quantitative although aq:org phase volume ratio was changed up to 5:1, while it decreased beyond it. This indicated stability of ion pair was not affected under wide variations of aq:org phase volume ratio. However in large ratio of aq:org phase distribution ratio of extraction species is small.Aq:org phase volume ratio of 2.5:1 is recommended in throughout extraction procedure.

Effect of foreign ions

To study effect of foreign ions on extraction of 50µg Ga(III) large excess of cation and anion, were added to the aqueous phase in the form of their salts or compounds. Initially quantitative extraction was tried with 10 mg of cation and 100 mg of anion added as foreign ion. If interference is intensive then amount of foreign ion was decreased. Error of 2% in recovery of analyte was accepted and accordingly tolerance limit was set. Study showed that a large number of cations and anions offer no interference (Table 1). For the extraction of 50µg Ga(III) 10 mg of Co(II), Ni(II), Cu(II), Zn(II), Ba(II), Mg(II) ; 5 mg each of Cd(II), Cr(II), Mn(II), Ca(II), Pb(II), Hg(II), Sn(II), As(III), Bi(III), Ce(IV), Tl(III) were tolerated. The interference due to Sb(III) and Ge(IV) was removed by masking with acetate. 1 mg of Fe(II) was tolerated but Fe(III) showed serious interference. Interference due to each of 1 mg Zr(II) and Al(III) was removed by masking with tartarate and citrate respectively. Among the anions 100 mg each of acetate, succinate, ascorbate, citrate, tartarate, thiourea ; 50 mg each of F^-, Br^-, HPO_4^{-2}, oxalate; 10 mg each of $S_2O_3^{-2}$, SCN^- were tolerated. EDTA shows serious interference.

Table 1: Effect of foreign ion

Ion added	**Added as**	**Tolerance mg**	**Ion added**	**Added as**	**Tolerance mg**
Acetate	Sodium acetate	100	Zn(II)	$ZnCl_2$	5
Succinate	Succinic acid	100	Cd(II)	$Cd(NO_3)_2.4H_2O$	5
Ascorbate	Ascorbic acid	100	Cr(III)	$CrCl_3.6H_2O$	5
Citrate	Citric acid	100	Mn(II)	$MnCl_2.4H_2O$	5
Tartarate	Sodium potassium tartarate	100	Ca(II)	$CaCl_2$	5
Thiourea	Thiourea	100	Hg(II)	$HgCl_2$	5
Oxalate	Oxalic acid	50	Pb(II)	$(CH_3COO)_2Pb.3H_2O$	5
Br^-	Potassium bromide	50	Sn(II)	$SnCl_2.2H_2O$	5
HPO_4^{-2}	K_2HPO_4	50	As(III)	$NaAsO_2$	5
F^-	NaF	10	Ce(IV)	$(NH_4)4Ce(SO_4)4.2H_2O$	5
$S_2O_3^{-2}$	$Na_2S_2O_3$	10	Ge(IV)a	GeO_2	5
SCN^-	KSCN	10	Sb(III)a	$SbCl_3$	5
EDTA	EDTA	Interfere	In(III)	$InCl_3$	5
Co(II)	$CoCl_2.6H_2O$	10	Zr(II)b	$Zr(NO)_2.XH_2O$	1
Ni(II)	$NiCl_2.\ 6H_2O$	10	Al(III)c	$Al(NO_3)_3.9H_20$	1
Cu(II)	$CuCl_2.\ 2H_2O$	10	Fe(II)d	$FeSO_4.7H_2O$	1
Ba(II)	$BaCl_2.\ 2H_2O$	10	Fe(III)	$NH_4Fe(SO_4)_2.12H_2O$	Interfere
Mg(II)	$MgCl_2.\ 2H_2O$	10	Tl(III)	$Tl(NO_3)_3.3H_2O$	1

a-masking with 50mg acetate b-masking with 50mg tartarate
c-masking with 50mg citrate d-masking with 20mg ascorbate

Separation of Ga(III) from synthetic mixtures

Separation and determination of Gallium (III) in synthetic binary mixtures

Liquid liquid extraction of 50µg Ga(III) in 7M HCl using 4-Methyl-N-n-octylaniline in xylene is found to be useful to separate and determine Ga(III) in various synthetic mixtures, which exists in association with variety of alloys. It was found that Ni(II), Cu(II), Mg(II), Pb(II) remained unextracted under recommended extraction conditions of Ga(III) from 7M HCl solution by 2% 4-Methyl-N-n-octylaniline in xylene. The loaded organic phase was stripped with water (2×10mL) and Ga(III) was determined spectrophotometrically. The raffinate containing added metal ion was estimated by the standard procedures such as complexometric titration and spectrophotometry.(Table 2).

Table 2: Separation of binary mixtures containing Ga (III)

Metal ions	Amount taken	Recovery %	Procedure for estimation
Ga(III) Ni(II)	50µg 5000µg	100 100	EDTA complexometry[35]
Ga(III) Cu(II)	50µg 1000µg	100 99.5	EDTA complexometry[35]
Ga(III) Mg(II)	50µg 2000µg	100 100	EDTA complexometry[35]
Ga(III) Pb(II)	50µg 2000µg	100 99.5	BPR spectrophotometry[36]
Ga(III) Sb(II)	50µg 2000µg	100 99.7	Potassium Iodide spectrophotometry[36]
Ga(III) Bi(III)	50µg 2000µg	100 100	EDTA complexometry[35]

Gallium in ternary mixtures

The optimized method was applied to the extraction and determination of Ga(III) from 7M HCl containing 50µg Ga(III) along with known amount of other elements. Suitable masking agents were added to achieve selective extraction of Ga(III) in presence of certain interfering ions. The amount of Ga(III) extracted was in good agreement with the amount added. (Table 3)

Table 3: Separation of Gallium (III) from synthetic ternary mixtures

Composition of ternary mixture	Gallium found	
	µg*	% recovery
Ga(III) 50µg ; In(III) 500 µg ; Hg(II) 1000 µg	49.7	99.5
Ga(III) 50µg ; Cd(II) 1000 µg ; Ba(II) 1000 µg	50	100
Ga(III) 50µg ; Ge(IV)[a] 1000 µg ; Sn(II) 1000 µg	49.5	99.1
Ga(III) 50µg ; Zr(II)[b] 500 µg ;Tl(III) 100 µg	49.7	99.5

a-masking with 50mg acetate b-masking with 50mg tartarate

*Average of five determinations

Sequential separation of Group XIII elements (Ga, In, Tl)

It was based on difference in extraction behavior of Ga, In and Tl under different concentrations of hydrochloric acids. Ternary mixtures containing gallium (III), indium (III) and thallium (III) were prepared. To an aliquot of solution containing a mixture of gallium (50µg/80µg/100µg), indium (100µg/200µg/500µg) and thallium (500µg/1000µg/1000µg) add sufficient hydrochloric acid to make its concentration 0.6M in the volume of 10mL. Thallium (III) was first extracted from aqueous solution by shaking for 2 min with 10mL of 2% 4-Methyl-N-n-octylaniline in xylene. Under these conditions only thallium is selectively extracted in the organic phase and both gallium and indium remain in aqueous phase. Thallium in the organic phase was stripped with acetate buffer (2×12.5) mL and determined complexometrically. Evaporate aqueous phase to reduce the volume and add sufficient concentrated hydrochloric acid to adjust acidity 7M in the volume of 25mL and then Gallium (III) was extracted and determined by the proposed method. Indium(III) remaining in aqueous phase determined spectrophotometrically. Percentage recovery observed for each metal was 99.9%.

Gallium in synthetic Galinstan

Gallium is an important constituent of Galinstan alloy (Eutectic liquid mixture alloy) used in medical thermometer in place of mercury. Its recovery from various synthetic mixtures containing Ga, In, Sn in ion form similar to composition of Galinstan was obtained by recommended procedure in 7M HCl using 2% reagent in xylene. (Table 4)

Table 4: Separation and determination of Gallium in Galinstan

Galinstan	Composition of the mixture	Ga found	
		µg*	% recovery
Sample 1	Ga (68 µg) ; In (22 µg) ; Sn (10 µg)	67.8	99.7
Sample 2	Ga (80 µg) ; In (12 µg) ; Sn (8 µg)	79.9	99.8
Sample 3	Ga (70 µg) ; In (20 µg) ; Sn (10 µg)	69.9	99.8

*Average of five determinations

Gallium in Electronic waste containing LED

Gallium is rare and it is important constituent of LED (light emitting diodes). Waste LED’s lead to serious disposal problem. The proposed method was successfully applied for recovery of Ga(III) in LED thin film. Leach liquor from Gallium coated portion of LED waste was prepared by keeping the waste in contact with 2M HCl for 24 hour[18]. The solution was filtered and made upto 100mL keeping the overall acidity to 7M of HCl. An aliquot of this solution was analyzed for Ga(III) content by recommended procedure. The amount of Gallium in the leach liquor found by proposed method and by ICP AES method was in good agreement.(Table 5)

Table 5: Recovery of Ga (III) from electronic waste LED

Waste LED matrix	Ga(III) found by ICP AES method ppm	Ga(III) found by Proposed method* ppm	Recovery %
Sample1	6.155	6.1	99.1
Sample2	6.486	6.4	98.6

*Average of five determinations

Conclusions

The method is simple, rapid and does not require long extraction period. The method offers quantitative extraction of Ga(III) with very low reagent concentration and with a wide volume ratio of aqueous to organic phase which avoids excessive use of chemicals. Thus it is ecofriendly. The proposed method was carried out with xylene as diluent which is comparatively less carcinogenic than benzene which was used in earlier methods. Due to high concentration of hydrochloric acid the extraction process was free from number of interfering cations and anions. Since extraction was possible at microgram level, it was successfully applied to recover trace amount of gallium present in LED waste.

Acknowledgement

Authors are very grateful to IIT Bombay for providing instrumental facility like IR, PMR, Mass, ICP AES at low cost and to Dr. R.J. Patil for his valuable guidance.

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