SOLVENT EXTRACTION AND SEPARATION OF ALUMINIUM(III) FROM REAL SAMPLES USING SUPRAMOLECULE

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Abstract. The present work investigates the rapid and precise extractive method for the determination of aluminium(III) with hexaacetato calix(6)arene. Toluene, xylene and cyclohexane were found to be the best diluents for quantitative extraction of aluminium(III). In this study, aluminium(III) was extracted at pH 5.0 by equilibrating ten min with 10 mL of 1×10^{-4} M acetyl derivative of calix(6)arene in toluene. Aluminium(III) was stripped quantitatively with 1 N hydrochloric acid and determined photometrically by complexation with eriochrome cynine-R at 535 nm. The method affords the binary separation of aluminium(III) from associate elements. The stoichiometry of the extracted species was determined on the basis of slope analysis method. The temperature dependence of the extraction equilibrium was examined by the temperature variation method and the thermodynamic functions ΔH, ΔG and ΔS were also evaluated for the extraction process. The metal loading capacity was also evaluated. The proposed method was applicable to the analysis of real samples. The results obtained were reproducible and accurate.

Keywords. Acetyl derivative; aluminium(III); calix(6)arene; separation; solvent extraction.

I. Introduction

Aluminium is the third most abundant element after oxygen and silicon in the Earth's crust. The chief ore of aluminium is bauxite [1]. It is light, malleable, ductile and durable hence used in making cars, automobiles, aircraft, photographic equipments, transistors, saucepans, airship frames, kitchen foil, etc. Aluminium is valuable today as it is used in power lines, the building, construction industry and packing foods. Actually it is not as toxic as heavy metals but there is evidence of some toxicity if it is consumed in excessive amount [2]. Higher consumption of it causes a renal failure which results in dialysis, breast cancer, neurotoxicity and Alzheimer's disease[3,4]. Each year 21 million tons of aluminum is made, mostly from bauxite. Hence study of recovery of aluminium is very essential.

There are very few methods reported in the literature for the solvent extraction and separation of aluminium(III) using variety of extractants. Recently organophosphorous extractants have received considerable attention for extraction and separation of aluminium(III). The distribution of Al(III) between aqueous thiocyanate solutions and formic acid solutions with di(2-ethylhexyl)phosphoric acid in organic solvents was investigated under different conditions [5,6]. It was confirmed that the extraction process was governed by the SN^2 mechanism. Solvent extraction of aluminium was carried out in the presence of cobalt, nickel and magnesium from sulphate solutions by cyanex 272, but the numbers of stages were required for both extraction and stripping processes for the recovery of aluminium[7,8]. A rapid method was developed for the solvent extraction separation of iron(III) and aluminium(III) from other elements with cyanex 302 in chloroform as the diluents where, extraction of aluminium(III) was depend on the concentration of reagent [9]. Aluminium(III) was also extracted from mixed sulphate solution using sodium salt of cyanex 272 and D2EHPA[10]. However efficiency was achieved with 0.3 M extractant in two stages. The separation of aluminium(III) and beryllium(II) were carried out quantitatively with different organophosphorous compounds taking advantage of difference in their stripping agents[11-13].

The extraction of aluminium(III) with decanoic acid in 1-octanol was carried out at 25°C and at aqueous ionic strength of 0.1 M $NaClO_4$. However, the aluminium(III) decanoate was highly polymerized in the solvent [14]. The micro amount of aluminium(III) was extracted using 8-quinolinol complex with nitrobenzene [15]. The aluminium(III) was also extracted in the *p*H range 5.9-6.2 by using n-octylaniline from succinate media [16]. The solvent extraction of aluminum(III), gallium(III) and indium(III) was studied by using mixture of 1-octanol and 1-octanol/octane with 8-quinolinol[17].

Calixarenes are macrocyclic compounds composed of phenolic units connected by methylene bridges to form a hydrophobic cavity that is capable of forming inclusion complexes with a variety of molecules. A new era was dawned with discovery of array of supramolecular compounds by Gutsche who

had described the methods for the synthesis of these ligands. Calixarenes possess a well-defined cavity with simultaneous polar (lower-rim) and nonpolar (upper-rim) properties. Also, they can be derivatized in terms of cavity size and functional group to yield analyte selective compounds capable of forming inclusion complexes. The cavity size of calixarenes is quite variable as a result of their conformational flexibility. Robert, et al. tested calix(4)arenes for the selective removal of aluminium(III) from a pickling bath solutions [18]. However no significant extraction was found for all the tested ligands. By substituting acetyl group to the lower rim of calix(6)arene its capacity of complexation can be increased. Thus it becomes specific receptors for metal ions [19]. The acetyl derivative of calix(6)arene have been used for extraction of transition metals [20-22] and P-block metals [23,24]. However, there is no systematic study carried out with calixarene and its derivative for aluminium(III). Therefore, in this paper an endeavor is made to explore the possibility of utilizing acetyl derivative of calix(6)arene for solvent extraction and separation of aluminium(III) under microgram concentration.

II. Experimental:

2.1 Instrumentation

A systronics UV-Visible spectrophotometer (Model No-108) with matched 10 mm quartz cuvettes and a digital pH meter (Systronics Model No-361) with combined glass and calomel electrodes were used.

2.2 Preparation of solutions

A stock solution of aluminium(III) was prepared by dissolving 0.0494 g of $AlCl_3$ unhydrous in 2 mL concentrated HCl and diluted to 100 mL with double distilled water. It contained 100 μg/mL of aluminium(III). A diluted solution containing 10 μg/ml of aluminium(III) was prepared by tenfold dilution. It was standardized volumetrically by back titration with EDTA using solo chrome black T as an indicator. Ascorbic acid (0.1%) was prepared by dissolving 0.1 g of ascorbic acid in 100 ml double distilled water. Buffer reagent of pH 4.5 was prepared by dissolving 27.2 g of sodium acetate and 8 ml of 1 N acetic acid and diluted it to 200 ml with double distilled water. Stock eriochrome cynine-R: It was prepared by dissolving 0.150 g of eriochrome cyanine-R in 50 ml double distilled water and its pH was adjusted to 2.9 with 1 N acetic acid and diluted to 100 ml with double distilled water. The working dye was prepared by diluting 10 ml of stock to 100 ml with double distilled water. The acetyl derivative of calix(6)arene was synthesized in our laboratory [25].

2.3 Solvent extraction procedure for determination of aluminium(III)

An aliquot of solution containing 20 μg/mL of aluminium(III) was taken and its pH was adjusted to 5.0 with dilute HCl or NaOH. The total volume of the solution was made up to 10 mL with double distilled water and it was transferred to 60 mL separatory funnel. Then 10 mL of 0.0001 M acetyl derivative of calix(6)arene in toluene was added to it and shaken vigorously for ten min to achieve the equilibrium. The two phases were allowed to settle and separate. Aluminium(III) was stripped with 10 mL of 1 N HCl from the organic phase, aqueous phase was separated, evaporated to moist dryness in order to remove excess of hydrochloric acid and determined spectrophotometrically at 535 nm as its complex with eriochrome cynine-R [26]. The concentration of aluminium(III) was computed from the calibration curve.

III. Results and Discussion

3.1 Extraction as a function of pH

Aluminium(III) was extracted at pH varying from 2.0 - 10.0 with 1×10^{-4} M of acetyl derivative of calix(6)arene in toluene. The extraction of ion-pair complex of aluminium was found to be quantitative in the range 4.5-5.5. Hence extraction was carried out at pH 5.0 for routine work. Above and below pH 5.0, the extraction was incomplete. Since poor complexation takes place under these conditions (Fig. 1).

3.2 Effect of period of equilibration

The extraction of aluminium(III) was carried out with varying periods of shaking ranging from 1 to 20 min by equilibrating aqueous solution containing 20 ppm of aluminium(III) with 0.0001 M hexaacetato calix(6)arene in toluene at aqueous pH 5.0. It was observed that eight min equilibrium time was adequate for quantitative extraction of aluminium(III). However prolonged shaking up to 20 min had no adverse effect on the percentage of extraction. In general procedure 10 min equilibrium time was recommended in order to ensure the complete extraction.

3.3 Effect of extracting solvents

It is well known that diluents are played an important role in the solvent extraction of metals. During extraction of aluminium(III) several polar and non polar solvents with varying dielectric constants were tested as the diluents. The extraction of aluminium(III) using cyclohexane, toluene, xylene were found

to be quantitative because the ion pair complex has high value (343.83) of distribution ratio in them. For dichloromethane and 1, 2 dichloroethane the distribution ratio was 24.0. Kerosene 18.46, carbon tetrachloride 20.88 and chloroform 19.58 were found to be poor solvents. It may be noted that nature of solvent and its dielectric constant affect the extraction of aluminium(III). Toluene was preferred as it was relatively less toxic, easy to handle, gives better phase separation and easily available at low cost.

3.4 Effect of reagent concentration

Aluminium(III) was extracted at pH 5.0 in toluene with different concentrations of acetyl derivative of calix(6)arene. The concentration was varied from 1×10^{-6} M to 2×10^{-4} M. The extraction of aluminium(III) from 1×10^{-6} M to 0.5×10^{-5} M was in the range of 32-60%. From 1×10^{-5} M to 0.6×10^{-4} M it was in the range of 70-90%. For 0.7×10^{-4} M it was found to be nearly equal to 92.73%. For 0.8×10^{-4} M and 0.9×10^{-4} M it was 96.36% and 97.09% respectively. It was found that from 1×10^{-4} and above the extraction was quantitative. Hence commonly 1×10^{-4} M of extractant was used for the routine work. It was observed that the application of high reagent concentration was not advisable, as there was no marked increase in the extraction of aluminium(III).

3.5 Nature of extracted species

The composition of extracted species was ascertained by plotting log D against log of the reagent concentration at a fixed pH 5.0 (Fig. 2) shows a slope 2.97. Therefore, the probable composition of extracted species is 1:3 i.e. $[Al(Reagent)_3]$.
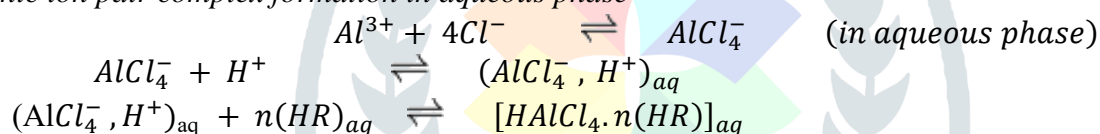
3.6 Mechanism of complexation

Acetyl derivative of calixarene is a neutral extractant often extracting uncharged metal complexes in aqueous solution under certain condition and also extract charged metal ions and complexes. At the lower pH, aluminium(III) forms a stable $AlCl_4^-$ ions in the aqueous solution. It also forms a stable complex with acetyl derivative of calixarene in the organic phase and undergoes a solution reaction at lower pH. The mechanism of extraction can be summarized as

1. Distribution of acetyl derivative of calix(6)arene

$(HR)_{aq} \rightleftharpoons (HR)_{org}$ where HR= hexaacetato calix(6)arene

2. Formation of uncharged complex

Anionic ion pair complex formation in aqueous phase

$$Al^{3+} + 4Cl^- \rightleftharpoons AlCl_4^- \quad (in\ aqueous\ phase)$$

$$AlCl_4^- + H^+ \rightleftharpoons (AlCl_4^-, H^+)_{aq}$$

$$(AlCl_4^-, H^+)_{aq} + n(HR)_{aq} \rightleftharpoons [HAlCl_4.n(HR)]_{aq}$$

3. Transformation of ion pair complex to organic Phase

$$[HAlCl_4.n(HR)]_{aq} \rightleftharpoons [HAlCl_4.n(HR)]_{org}$$

3.7 Stoichiometry of the extracted species

The overall extraction of aluminium(III) from dilute hydrochloric acid solution (pH-5.0) by acetyl derivative of calixarene in toluene is represented by solution reaction, expressed by Eq. (1) and the extraction equilibrium constant, K'_{ex}, can be described by Eq. (2).

$$AlCl_{4(aq)}^- + n[HR]_{(org)} + H_{(aq)}^+ = [HAlCl_4.n(HR)]_{(org)} \tag{1}$$
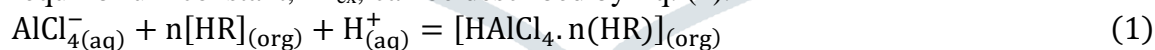
Where, HR = acetyl derivative of calixarene.

$$K'_{ex} = \frac{[HAlCl_4.n(HR)]_{(org)}}{[AlCl_4^-]_{(aq)}[HR]_{(org)}^n[H^+]_{(aq)}} \tag{2}$$

But

$$D = \frac{[HAlCl_4.n(HR)]_{(org)}}{[AlCl_4^-]_{(aq)}} \quad\quad Therefore,\ K'_{ex} = \frac{D}{\left([HR]_{(org)}^n[H^+]_{(aq)}\right)}$$

Or $\log K'_{ex} = \log D - \log[HR]^n + pH$ (3)

The stoichiometry of extracted species was determined by analyzing the experimental data. The conventional slope analysis method was used for the determination of stoichiometry. It was observed that distribution coefficient (D) was independent on aluminium(III) concentration, which is a clear indication that the extracted species is mononuclear in the whole range of the experimental study. The graph log D versus log [Molar concentration of acetyl derivative of calix(6)arene in toluene], (Fig. 2). It gives a linear graph with slope 2.97 i.e. 3.0 indicating that three ligands react with one mole of aluminium(III) ion while the graph of log *D* verses pH (Fig. 3) shows a linear plot with slope 1.11 is nearly equal to integer one which clearly shows that one ligand is being associated with one mole of metal ion in the extracted species to form

an ion–pair complex $[Al(HR)_3]_{org}$ in the organic phase. Overall the extraction reaction can be represented as,

$$AlCl_{4(aq)}^- + 3[HR]_{(org)} + H_{(aq)}^+ = [HAlCl_4 \cdot 3(HR)]_{(org)} \tag{4}$$
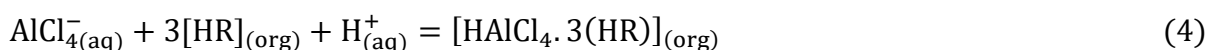
3.8 Effect of temperature on the extraction of aluminium(III)

The effect of temperature in the range between 298 K and 328 K on the extraction of aluminium(III), at pH 5.0 by hexaacetato calix(6)arene into toluene was studied. It was found that the distribution coefficient decreases with rise in temperature. According to Van't Hoff, the K'_{ex} relates with temperature as shown below,

$$\frac{d(lnK'_{ex})}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^0}{R} \tag{5}$$

Where, R = 8.314 J K^{-1} mol^{-1}

The change in enthalpy (ΔH^0) is evaluated from the plot of lnK'$_{ex}$ against 1000/T by using Eq. (5). The graph is linear with slope 22.92 and the enthalpy change of the extraction reaction was evaluated as ΔH^0 = -190.532 kJ mol^{-1} which means reaction is exothermic (Fig. 4).

The standard free energy (ΔG^0) and entropy change (ΔS^0) at room temperature (T) 298 K were calculated using Eq. (6) and (7) respectively.

$$\Delta G° = -2.303 \times RT \log K'_{ex} \tag{6}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{7}$$

The thermodynamic parameters obtained for the solvent extraction of aluminium(III) are ΔG^0 = -111.508 kJ mol^{-1}, ΔH^0 = -190.532 kJ mol^{-1}, and ΔS^0 = -265.18 J K^{-1} mol^{-1} (Table 1). The high negative value of standard Gibb's free energy indicates the transport of cation from the aqueous phase to organic phase and it also favors the formation of ion–pair complex. The negative value of enthalpy indicates the reaction is exothermic and percentage extraction decreases with increase in temperature. Also, the negative value of entropy shows that the percentage of extraction is favor with decrease in temperature.

3.9 Effect of stripping agents for aluminium(III)

After extraction of aluminium(III) at pH 5.0, it was stripped by using several mineral acids in varying concentrations of 0.01 N to 4 N. For HNO$_3$ from 0.01 N to 1 N stripping was incomplete and from 2 N to 4 N, extraction was found to be quantitative. For 0.01 N to 0.05 N of HCl the extraction was less than 90 % and for 0.5 N it was 98.86%. However stripping was quantitative from 1 N to 4 N for HCl. Using acetic acid as a stripping agent, aluminium(III) was not completely stripped below 0.5 N but for 1 N to 4 N it was found to be a good stripping agent. For perchloric acid it was found that with increasing the concentration above 1 N, the percentage extraction was decreased and for 0.5 N and below it was found to be quantitative. When aluminium(III) was stripped using H$_2$SO$_4$ as a stripping agent then for 0.01 N to 0.05 N H$_2$SO$_4$ the extraction was less than 80% and for 0.1 N it was 93.14%. For 0.5 N to 4 N of H$_2$SO$_4$ the extraction was found to be quantitative. It was observed that halides of aluminium(III) was stable towards heat than its nitrates during evaporation because of melting point difference, therefore 1 N HCl was used as a stripping agent (Table 2).

3.10 Loading capacity of hexaacetato calix(6)arene

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of same concentration. When aluminium(III) was extracted repeatedly with 10 mL of 1 x 10^{-4} M of acetyl derivative of calix(6)arene. It was found that 10 mL of 1 x 10^{-4} M of acetyl derivative of calix(6)arene extracted aluminium(III) up to 150 ppm. On further increase in concentration of aluminium(III) the percentage of extraction was found to be decreased.

3.11 IR spectroscopic analysis

In order to support the formation of ion pair complex, the IR spectra of the organic phase was studied. The result of IR spectra shows the stretching frequency for >C=O of acetyl group of pure hexaacetato calix(6)arene(HR) as 1764.6 cm^{-1} and with aluminium as [Al(HR)$_3$] it decreases to 1761.01 cm^{-1}. This decrease in >C=O stretching frequency indicates involvement of carbonyl oxygen in the complex formation. It is assumed that no true covalent bond formation exists, but an ion dipole electrostatic attraction between the metal ion and oxygen is possible [27].

Also the two bands for C-O stretching frequencies at 1179.1 cm^{-1} and 1219.8 cm^{-1} in acetyl derivative of calix(6)arene were shifted to lower stretching frequencies at 1176.58 cm^{-1} and 1217.08 cm^{-1} respectively in its complex with aluminium. The medium bands which are not present in the spectrum of free ligand appeared at 731.02, 555.50 and 455.20 cm^{-1} is attributed to υ_{M-O} vibrations. The appearance of

υ_{M-O} vibrations supports the involvement of oxygen atom in complexation with metal ion under investigation. All above results clearly indicates the formation of ion pair complex.

3.12   Applications

3.12a. Foreign ions effect

The suitability of the above developed method was examined by applying it to the separation and determination of aluminium(III) in a verity of binary mixtures which are commonly associated with it. The effect of large number of foreign ions on the extraction of 10 ppm of aluminium(III) with proposed reagent was investigated following the recommended procedure. Initially the foreign ions were added to aluminium(III) solution in large excess say 500 ppm. When interference was intensive the test were repeated with successively smaller amount of foreign ions. It was observed that most of the alkali metals were tolerated by 1:20 ratio. The maximum transition metals and anions were tolerated in very high ratio. It is observed that method is free from interferences from a large number of cations and anions. The tolerance limit was set at the amount of the foreign ion that could be present to give an error less than $\pm$ 1% in the recovery of aluminium(III) (Table 3).

3.12b. Analysis of real samples

In order to test the accuracy and applicability of the proposed method it was used to extract and separate aluminium(III) from real samples. The results obtained by this present method are in good agreement with the certified value. The stock solution of samples was prepared as follows.

Pharmaceutical samples

One tablet of each gelucil (Pfizer Ltd., Vapi 396195, Gujarat), gass off (R.S. Bhargawa Farmacy 1008/1 Baran, Panni Mili Industrial Estate, Bulandshar UP, India) and digen (Abbott India Ltd., L18, Vema Industrial Area, Verna Salcette, Goa 403722) was dissolved in minimum quantity of aqua regia solution. It was kept overnight at room temperature, evaporated to moist dryness, taken in to minimum quantity of water, filtered and diluted to 100 mL.

Alloy

Brass alloy (0.15 g) dissolved in minimum quantity of 1:1 HNO_3 and was filter out to remove any metastanic acid. Then 1.5 mL of H_2SO_4 was added and heated to sulphure trioxide fumes. Then it was taken in to 25 mL of double distilled water and was neutralized by 10% NaOH, filtered, acidified with drop of concentrated H_2SO_4 and diluted to 50 mL.

Chalk

For the analysis of the aluminium(III) present in the chalk, 1.0 g of powdered sample of chalk was taken then 1:1 HCl was added drop wise to it the effervesces was ceased. Then it was taken in to 25 mL of double distilled water and neutralized to pH 4.5 with 10% NaOH. Then solution was filtered, acidified with drop of 1:1 HCl and was diluted to 50 mL.

Silicate ore

For the analysis, 0.5 g of silicate ore (Koradi region, Nagpur) was dissolved in to mixture of 5 mL HNO_3, 20 mL HCl and 3 mL of 1:1 H_2SO_4. Then it was evaporated to moist dryness, taken in to the minimum quantity of double distilled water and was filtered by using whatman filter paper. Then the solution was diluted to 25 mL with 2 N HCl.

Potash alum

For the analysis, 0.2 g of sample was dissolved in hot water and sulphates were precipitated by adding a 0.25% of $BaCl_2$ solution. Then solution was filtered and diluted to 50 mL by double distilled water.

Aluminium coin

For the analysis, 1.0 g of aluminium coin (old coin of 20 paisa) powder was dissolved in minimum quantity of aqua regia till it was completely dissolved, then solution was evaporated to moist dryness and made volume upto 50 mL with double distilled water. Finally the solution was acidified with 1 mL of concentrated HCl and then diluted to 100 mL.

Polyethylene

For analysis of amount of aluminium(III) in the polyethylene, 2 g of sample was dissolved in 20 mL of concentrated H_2SO_4 and was heated to fumes until the polymer was completely charred. Then 20 mL of concentrated HNO_3 was drop wise added to oxidize all the carbon. After that 5 mL of $HClO_4$ was added drop wise and solution was heated till the volume becomes 5 mL. Finally, the solution was diluted to 25 mL water and again evaporated to moist dryness and then resultant solution was filtered and diluted to 50 mL with double distilled water.

Now one mL of aliquot of each of above solution was taken and then its pH was maintained to 5.0 and extracted with 10 mL of 1 x 10^{-4} M of acetyl derivative of calix(6)arene and determined spectrophotometrically by complexation with eriochrome cynine-R at 535 nm (Table 4).

IV. Conclusions

The proposed method is simple, rapid, selective and reliable. The use of relatively less toxic solvent like toluene is favorable. A very low reagent concentration 0.0001M is required for the quantitative recovery of aluminium(III). Aluminium(III) can be easily stripped by low concentration of mineral acids. The equilibrium constant and thermodynamic parameters ΔH, ΔS and ΔG in the extraction of aluminium(III) with acetyl derivative of calix(6)arene are evaluated. The extraction mechanism corresponds to an ion pair formation in which a complex stoichiometric formula $[HAlCl_4.3(HR)]_{(org)}$ is formed in the organic phase. The large number of diverse ions are tolerate in high ratio. The method is free from interference from a large number of foreign ions which are often associated with naturally occurring aluminium(III). The time required for the extraction separation is very short. The developed method involves a one-stage extraction step and the extraction process can be complete within 20-30 min. Also the method is applicable to separate and determine very low concentration aluminium(III) in alloy, ore, pharmaceutical samples and verity of real samples.

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Table 1. Thermodynamic functions of extraction of aluminium(III) with hexaacetato calix(6)arene in toluene

Temp / (K)	log D	dlog K'_{ex}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS J mol^{-1}K^{-1}
298	2.536	19.536		-111.508	-265.18
303	2.536	19.536		-113.379	-254.629
308	2.536	19.536		-115.250	-244.421
313	1.938	18.937	-190.532	-113.491	-246.139
318	1.630	18.631		-113.440	-242.428
323	0.997	17.997		-111.305	-245.285
328	0.550	17.550		-110.217	-244.864

Table 2. Effect of stripping agents on percentage extraction of aluminium(III)

%Extraction / Stripping agents	0.01 N	0.05 N	0.1 N	0.5 N	1 N	2 N	3 N	4 N
HNO$_3$	57.14	71.43	76.00	86.86	96.00	99.71	99.71	99.71
HCl	86.29	89.14	97.71	98.86	99.71	99.71	99.71	99.71
CH$_3$COOH	4.57	10.00	22.29	28.88	99.71	99.71	99.71	99.71
HClO$_4$	99.71	99.71	99.71	99.71	95.14	94.29	93.43	92.29
H$_2$SO$_4$	75.71	77.43	93.14	99.71	99.71	99.71	99.71	99.71

Table 3. Effect of foreign ions on the extraction and determination of aluminium(III), Al(III) = 10 ppm; equilibration period = 10 min; extractant = 10 mL of 0.0001 M of acetyl derivative of calix(6)arene in toluene, strippent = 1 N hydrochloric acid, A:O = 1:1

Tolerance limit	Foreign ions
1:20	Li^+, Na^+, K^+, Zn^{2+}, Cl^-
1:15	NO_2^-, I^-
1:10	Ca^{2+}, Ba^{2+}, Mg^{2+}, CO_3^{2-}, NO_3^-, Br^-,
1:5	Mn^{2+}, Ni^{2+}, Cu^{2+}, [b]Mo^{6+}, [a]Ag^+, Pb^{2+}, PO_4^{3-}, SO_3^{2-}, oxalate
1:2	SO_4^{2-}
1:1	[e]V^{5+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Zr^{+4}, Cd^{2+}, Hf^{4+}, [a]Au^{3+}, Hg^{2+}, [b]In^{3+}, [d]Sn^{2+}, [c]Bi^{2+}, F^-, tartarate

[a]Masked with Br^- ion, [b]Masked with oxalate ion, [c]Masked with tartaret ion, [d]masked with I^- ion, [e]Masked with F^- ion

Table 4. Analysis of aluminium(III) in real samples

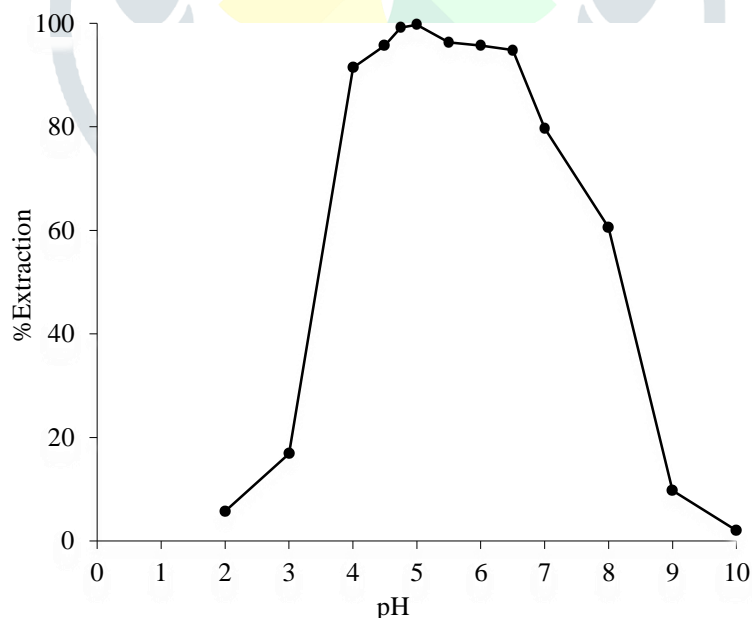| Samples	Amount found by proposed method (µg)	Certified value (µg)	% Recovery	*RSD %
Gelucil	19.13	19.20	99.64	0.47
Gass off	20.13	20.20	99.66	0.19
Digen	17.13	17.20	99.60	0.68
Brass alloy	13.73	13.80	99.50	0.69
Chalk	3.14	3.20	98.13	2.40
Silicate ore	14.72	14.80	99.51	0.66
Potash Alum	20.93	21.00	99.67	0.29
Aluminium Coin	19.73	19.80	99.65	0.59
Polyethylene	2.76	2.80	98.57	3.92

*Average of five determination

Figure1. Effect of pH on percentage extraction of aluminium(III) with acetyl derivative of calix(6)arene in toluene.
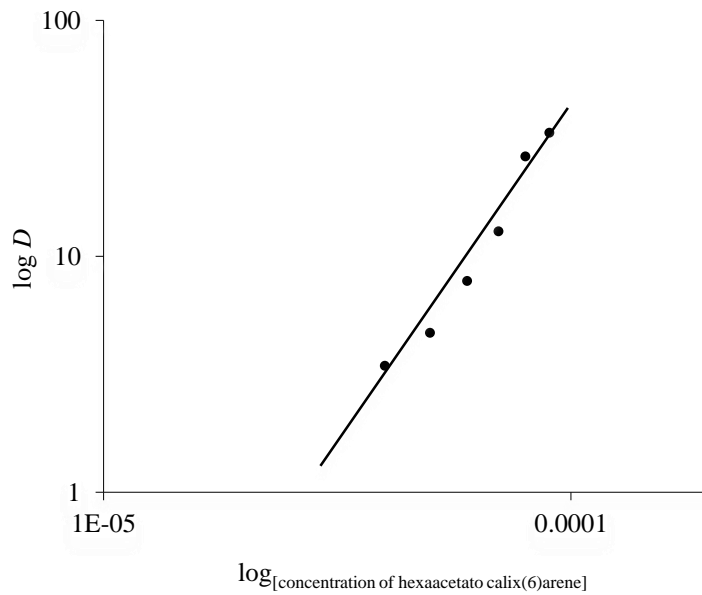
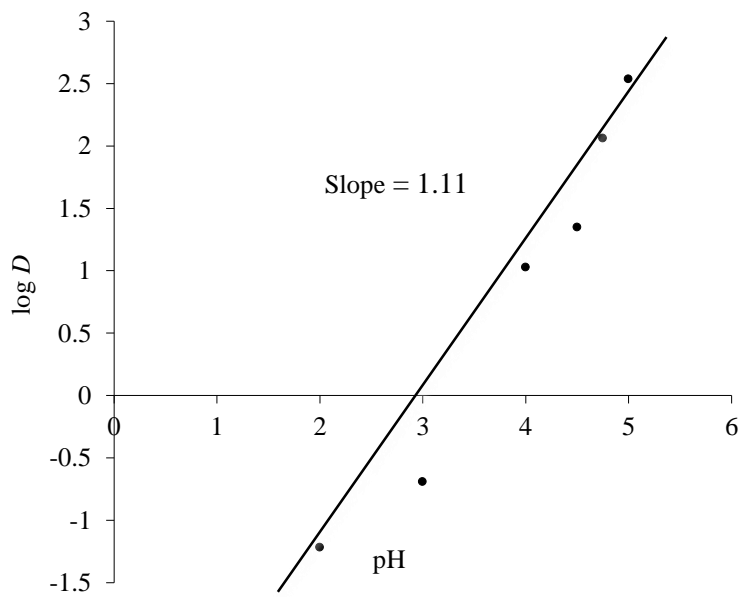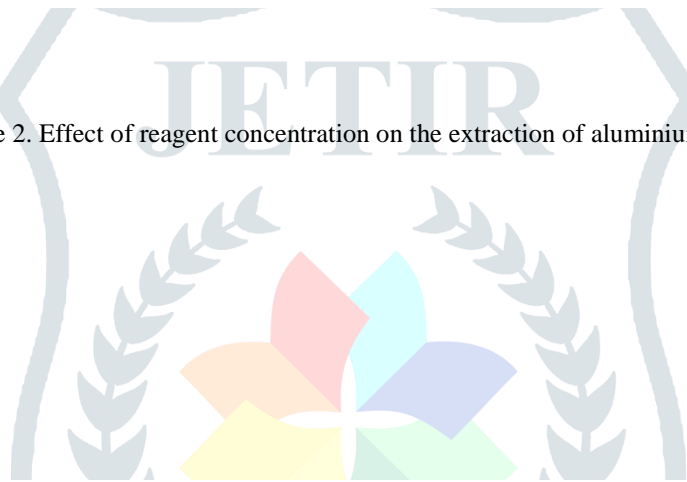Figure 2. Effect of reagent concentration on the extraction of aluminium(III)

Figure 3. Plot of log D against pH for the extraction of aluminium(III)
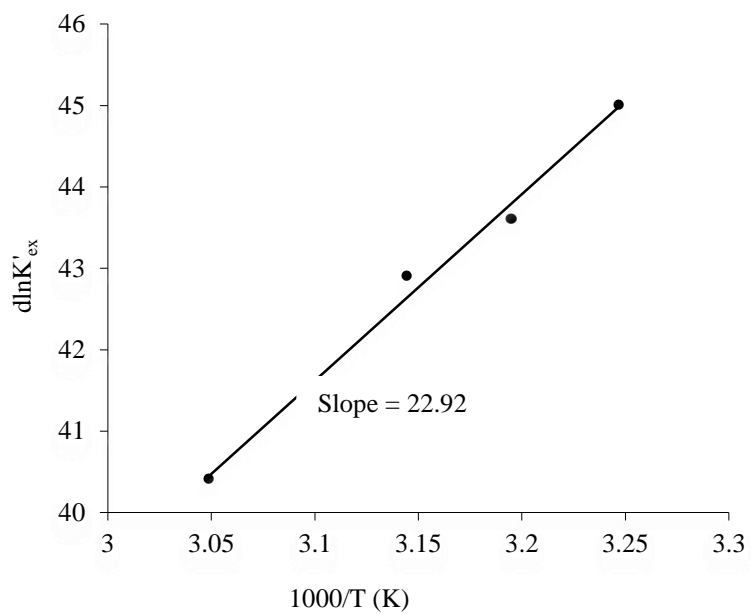
Figure 4. Temperature effect on the extraction of aluminium(III) with hexaacetato calix(6)arene in toluene (pH = 5.0, reagent concentration 1 x 10^{-4} M)