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ARTICLE

Solvent Extraction and Separation of Silver(I) in Real Sample Using Hexaacetato Calix[6]arene

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Abstract: In this study, silver(I) was extracted at pH 11.5 into organic phase using 0.0001 M hexa-*p*-t-butyl-hexaacetato calix[6]arene solution in xylene after a five min equilibration period. Silver(I) was back extracted with 1 M HNO_3 and determined photometrically. Log-log plot gives 1:1 stoichiometry of extracted species indicating that one ligand reacts with one mole of silver(I). The values of ΔG, ΔH and ΔS were determined by studying the extraction equilibrium at different temperatures. Quantitative separation of binary and synthetic mixtures of silver from associate elements was effectively carried out. The extraction and separation of silver(I) from real and multicomponent samples were also studied. The RSD was $\leq$ 0.5%.

Keywords: Solvent extraction, Acetyl derivative, Calix[6]arene, Separation, Silver(I).

Introduction

Ores of copper, copper-nickel, lead-zinc, argentite, chlorargyritepyrargyrite and alloys with gold are main sources of silver.Their compounds have been widely used in pharmaceuticals, industrial, printed circuitry, superconductors, electroplating, brazing, soldering, solar energy, photovoltaic cells, photographic films, water purification and microbiocides. In the medical field, silver has been used as an antiseptic and disinfectant in medical appliances [1-3].

Calixarene is the macrocyclic compound having hydrophobic cavity which can form host-guest type of complex. Cavity size of calixarene can be varied by substituting lower rim. Acetyl derivatives of calix[6]areneare formed by acylation of calix[6]arene and have a variety of applications. The present study deals with the extraction and separation of silver(I) using acetyl derivative of calix[6]arene. Also, it is applied to determine trace level quantity of silver present in real samples.

There are very few methods available for the selective separation and extraction of silver(I) using supramolecular compounds, like calixarenes, cryptands and crown ethers. Liquid-liquid extraction of Ag(I) was carried out using tetraspirocyclohexylcalix[4]pyrrole, calix[4] arenetetramide and its thio analog [4-6]. However, for the quantitative extraction, high reagent concentrations were required and stripping efficiency was low. The structural effects of the three isomers, 2, 3 and 4-pyridino calix[4]arenes on the extraction of silver have been examined. It was observed that the position of the pyridyl nitrogen, conformation and the size of calix[4]arene affect the quantitative extraction [7]. A new calix[4]arene-based podand incorporating two 2, 2'-bipyridine and two benzyl units in alternate positions at the lower rim showed quantitative extraction of silver(I) from neutral aqueous solution containing a mixture of lead and silver nitrates [8].

Makrlik groups reported the extraction of Ag(I) using the two-phase water/nitrobenzene system and determined the stability constant of the5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-methyl thio)ethoxy]calix[4]arene)-Ag(I)complex in

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nitrobenzene saturated with water [9]. Also, studies have been carried out on the extraction of silver using ionic liquids containing calixarene [10]. The calix[4]arene bearing four pyridine groups in the lower rim was used for the solvent extraction of silver and it was observed that this compound showed 230-fold enhancement of the extractability of Ag(I) in ionic liquid over that in chloroform [11]. Ketonic derivatives of calixarenes were found to be selective extractants for Ag(I) over Pd(II), but the extraction of both metals was found to be suppressed in highly acidic media [12,13]. The extraction capacity of tetraallyloxy and tetrabenzyloxy derivatives of calix[4]arenes in the cone and 1,3-alternate conformations was also investigated to extract thallium(I) and silver(I) ions [14].

The kinetics of complicated ion-pair extraction was studied by using Ag(I)-specific thia-crown ether compounds as ion-association reagents by adding fluorescent anions [15,16]. It was found that the extraction capacities of poly cyclic crown ethers were higher than for monocyclic crown ethers.

A simple and practical extraction method of supramolecular solvent was developed for separation and enrichment of trace amounts of palladium (Pd) and silver (Ag) in water samples,where the limits of detection were 2.8 and 1.9 µg/L for Pd and Ag [17].

Newly synthesized chelating resins have been used for on-line solid-phase extraction and preconcentrationfor the determination of trace levels of Ag(I) from water, by flame atomic absorption spectrometry. The detection limits for Ag(I) were found to be2.4 µg/L and 0.3 µg/L [18-19].

Experimental

Reagents and Chemicals

All reagents used in this study were purchased from Merck and Sd-fine. A standard solution of silver(I) was prepared by dissolving 0.03175 g of silvernitrate in double distilled water containing 1 mL HNO_3 and diluted to 500 mL. 0.1 M EDTA was prepared by dissolving 3.73 gm of di-sodium salt of EDTA in 100 mL. 0.001M 1,10phenanthroline was prepared by dissolving 0.020 g in 100 mL. 20% ammonium acetate was prepared by dissolving 20 g in 100 mL. 0.0001M bromopyragallol red was prepared by dissolving 0.006 g in 100 mL. All these solutions were diluted to adequate volume using double distilled water.For extraction of silver(I), 1 x 10^{-4} M solution of reagent was prepared in xylene. Working solutions were prepared by appropriate dilution.

Apparatus

A systronics UV-Visible spectrophotometer (Model No-108) with matched 10 mm quartz cuvettes was used for the absorbance measurements. The calibration of the spectrophotometer was checked by measuring the absorption spectrum of 0.004% solution of potassium chromate in 0.05 M KOH solution and also with 0.0058 % solution of $KMnO_4$ in 1M H_2SO_4. The observed spectra are reported in literature.

A digital pH meter (Systronics Model No-361) with combined glass and calomel electrodes was used to measure the H^+ ion concentration. The pH meter was standardized using the buffer of pH 4.01, 6.0, 7.0, 9.2 at room temperature.

Experimental Procedure for Determination of Silver(I)

For solvent extraction of silver(I), 25 ppm of 10 mL aqueous solution at pH 11.5 and10 mL of 0.0001 M of hexa-*p*-t-butyl-hexaacetato calix[6]arene (HR) in xylene were shaken vigorously for five min in a 60 mL separatory funnel. After equilibrium, two phases allowed to settle and separate. The amount of silver(I) present in the organic phase was back extracted with 10 mL of 1 M nitric acid solution. It was evaporated to dryness and concentration of silver(I) presentwasdeterminedspectrophotometricallywithbromo-pyragallolred [20]. From the concentration of silver in each phase, distribution ratio and percentage extraction values were calculated.

$$D = \frac{\text{Total concentration of solute in the organic phase}}{\text{Total concentration of solute in the aqueous phase.}}$$

where, D=Distribution ratio, assuming that there is no association, dissociation or polymerization in the phases, under idealized condition K_D =D.

UV-Visible spectrophotometer (Systronics-108) and digital pH meter (Systronics-361) were used during the study.

Results and Discussion

Effect of pH on Extraction of Silver(I)

To study the effect of pH, silver(I) was extracted at pH varying from 1.0 to 13.5 with acetyl derivative of calix[6]arene. It was observed that pH over 11.0 -12.0 gives maximum extraction. Hence, for routine work, pH of 11.5 was ensured (Fig. 1).

Effect of Contact Time

The contact time also affects the extraction of silver. It was studied by equilibrating aqueous silver from 30 sec to 15 min with organic phase-containing ligand. It was found that at four min, the percentage extraction was more. In general, five min contact time was taken for further extraction studies (Fig. 2).

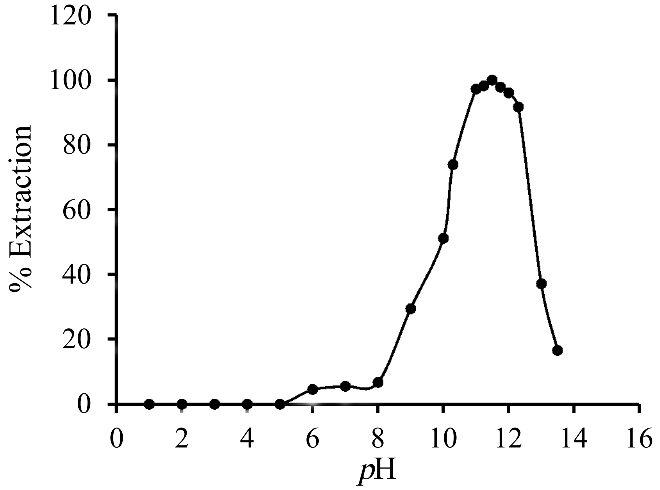

FIG. 1. Effect of pH on the percentage extraction of silver(I) with hexaacetato calix(6)arene.

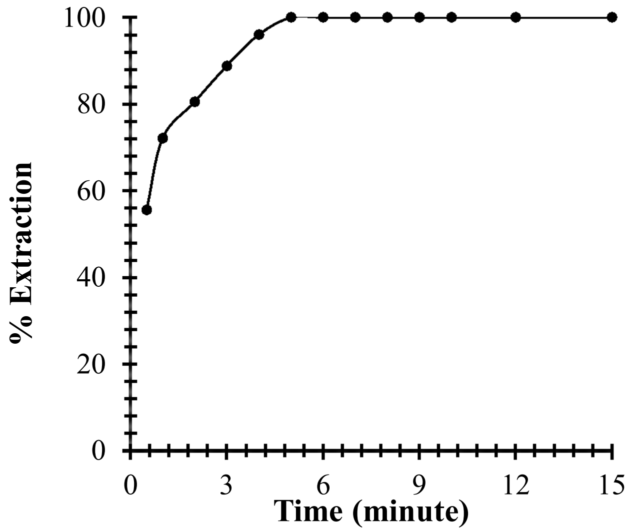

Fig.2. Kinetic study of silver extraction with hexaacetatocalix(6)arene in xylene; pH = 11.5; Ag(I) = 25 ppm; O/A = 1:1.

Effect of Polar and Non-polar Solvents

In non-polar solvents toluene, xylene and cyclohexane, extraction was found to be quantitative. Distribution ratio has a high value (∞). We know that a very high value of distribution ratio indicates the formation of the ion–pair complex. On the other hand, chloroform (22.22%), dichloromethane (3.33%) and 1,2 dichloroethane (5.56%) were found to be poor solvents. The percentage of extraction was more for the non-polar solvent having lower dielectric constant with aromatic nature. The present study was carried out using xylene as an extraction solvent.

Effect of Extractant and Loading Capacity

Varying reagent concentration distribution ratio shows different values. The extraction of silver(I) from 1 x 10^{-6} M to 5 x 10^{-6} M was in the range of 25-50%. For 1 x 10^{-5} M, extraction was

57.22 %. For the reagent concentration 0.2 x 10^{-4} M, it was found to be 69.45%. In the reagent concentration range of 0.4 x 10^{-4} to 0.85 x 10^{-4},the percentage extraction was in the range of 80-90%. For 0.95 x 10^{-4},it was found to be 92.22. The percentage extraction was found to be quantitative from 1x10^{-4} and above reagent concentration (Fig.3). The loading capacity of proposed concentration of reagent was found to be 100 ppm of metal ion (Fig. 4).

The stoichiometry of the extracted species can be depicted by conventional slope analysis method [21]. The graph between log *D* and log of the ligand concentration (Fig. 3) shows a slope of 0.96. Therefore, the expected nature of extracted species is 1:1; i.e., $[Ag(HR)]_{org}$ indicating that one ligand reacts with one mole of silver(I) ions. Again, the graph of log *Dversus*pH (Fig. 5) shows a linear plot with a slope of 1.01 nearly equal to integer one, which clearly shows that one ligand is being associated with one mole of metal ion in the organic phase [22].Hence, we can conclude that the probable structure of complex in the organic phase is $AgNO_3$. (HR); where HR is the acetyl derivative of calix(6)arene. The overall reaction can be represented as:

$$Ag^{+} + NO_3^{-} + HR \rightarrow AgNO_3.\ (HR)$$

The equilibrium constant for the extraction of silver in the basic medium (pH 11.5) is given by:

$$\{[Ag(HR)]^{+}, OH^{-}\}_{aq} \rightleftharpoons \{[Ag(HR)]^{+}, OH^{-}\}_{org}$$

The equilibrium constant K_{ex} is defined as:

$$K_{ex} = \frac{\{[Ag(HR)]^{+}, OH^{-}\}_{org}}{[Ag^{+}]_{aq}\,[HR]_{org}[OH^{-}]_{aq}}.$$

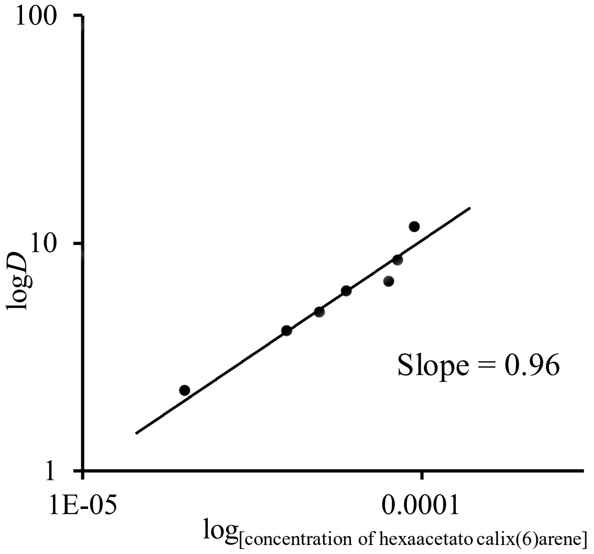

FIG. 3.Effect of reagent concentration on the extraction of silver(I).

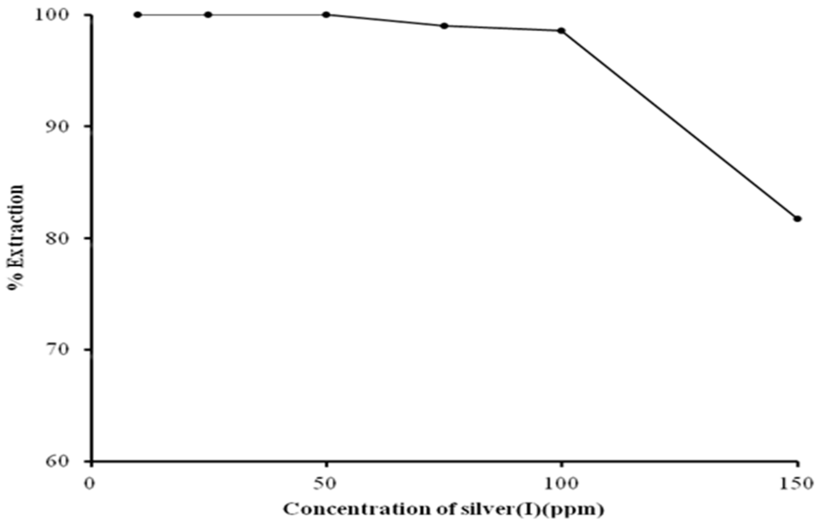

FIG.4. Effect of metal loading on percentage extraction of silver(I)

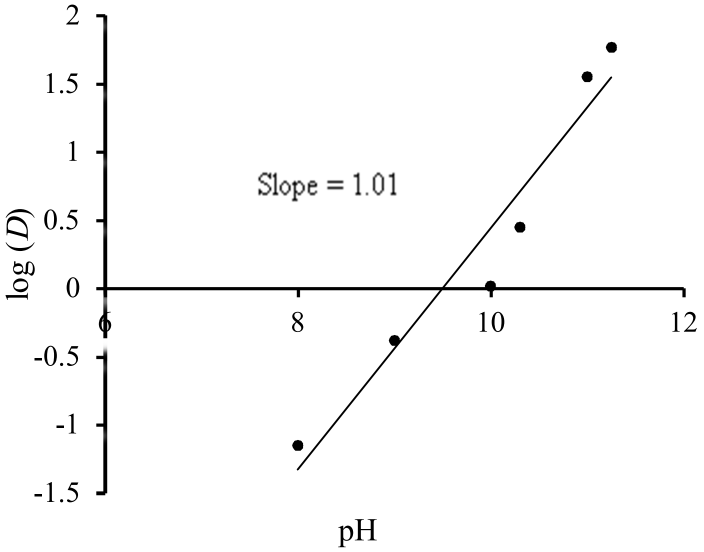

FIG 5. Plot of log *D* against pH for the extraction of silver(I).

Thermodynamic Study

The extraction of Ag(I) with hexaacetato calix[6]arene was carried out in the range of 298 to 328 K. The extraction of Ag(I) decreases with increased temperature. According to Van't Hoff, the K'_{ex} related with temperature is expressed by the equation, $\frac{d\ln K'_{ex}}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^0}{R}$. The graph of $\ln K'_{ex}$ against 1000/T was linear with a slope of 18.69. The values of thermodynamic parameters ΔG^0 = -111.26 kJ mol^{-1}, ΔH^0 = -155.39 kJ mol^{-1}, and ΔS^0 = -148.07 J K^{-1} mol^{-1} (Table 1) for the solvent extraction of Ag(I) were calculated. Formation of ion–pair complex is favored by a high negative value of standard Gibb's free energy. The reaction was favored with decrease of temperature supported by a negative value of entropy. The negative value of enthalpyindicated the exothermic reaction.

TABLE1. Effect of temperature on solvent extraction of silver(I) with hexaacetato calix[6]arene.

Temp / (K)	log K_D	dlogK'_{ex}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
298	3.999	19.50	-155.39	-111.26	-148.07
308	1.771	17.271		-101.85	-173.82
313	1.279	16.779		-100.55	-175.2
318	0.954	16.454		-100.19	-173.59
323	0.415	15.915		-98.426	-176.35
328	0.196	15.696		-98.578	-173.2

Effect of Back Extracting Agents

Solvent extraction of silver(I) was carried out at pH 11.5 using ligand in xylene witha contact time of five min. Then, the metal ions in the organic phase were back extracted using various concentrations of mineral acids from 0.1 to 2 M. For nitric acid and hydrochloric acid from 0.1 M to 0.5 M, the extraction was incomplete. For 1 M, it was found to be quantitative and for 1 M and 2 M, it was 77.78 and 75.0, respectively. It was found that with increase in the concentration the percentage extraction was decreased. For acetic acid, the percentage extraction was incomplete from 0.1 M to 0.5 M and from 1 M to 2 M, it was found to be quantitative. When perchloric acid was used as a stripping agent, then for 0.1 M, the extraction was found to be quantitative and again with increasing concentration up to 2 M, it was found that the percentage extraction was decreased. Using sulphuric acid, it was found that from 0.1 M to 2 M, the extraction was incomplete. Hence, for the ease of extraction, stripping was carried out by using 1 M nitric acid (Table 2).

TABLE 2. Effect of concentration of back extractant on percentage extraction of silver(I).

Stripping agents /Concentration	% Extraction 0.1 M	0.25 M	0.5 M	1 M	2 M
HNO_3	13.89	29.45	48.89	100	77.78
HCl	32.22	40.56	55.0	100	75.0
CH_3COOH	58.33	64.45	71.11	100	100
$HClO_4$	100	69.45	60.56	52.78	40.0
H_2SO_4	28.89	36.67	38.89	51.67	78.33

Mass Spectrometric Analysis

Hexaacetatocalix[6]arene was synthesized in laboratory by reported mehod. It is the cone-shaped compound having cavity inside and its anular space varring from 1.0 A^0 to < 4.8 A^0 [23]. The ionic radii of silver(I) fall under this range, so that it was easily trapped in the cavity of hexaacetatocalix[6]arene through ion-pair interaction. The stoichiometry of the extracted species was determined by LCMS spectra of the pregenant organic phase. The acetyl derivative of calix[6]arene (HR) has m/e 1226.9 and its complex with silver(I) supposed to be [Ag(HR)] in the organic phase has m/e 1326.9. This enhanced the value of the complex formed in the organic phase clearly supporting 1:1 metal:ligand stoichiometry in the organic phase. Mass: m/z, 1326.9 (M+2) parent ion. 1324.6 (M+1), 1282 (M+2)-$COCH_3$,1267.3 (M+1)-$COCH_3$, (M. F. Ag-$C_{78}H_{96}O_{12}$). The comparative mass spectra of acetyl derivative of calix[6]arene and its complex with silver(I) are depicted below in Figs. 6 and 7,respectively. Also, the possible structure of the complex is shown in Fig. 8.

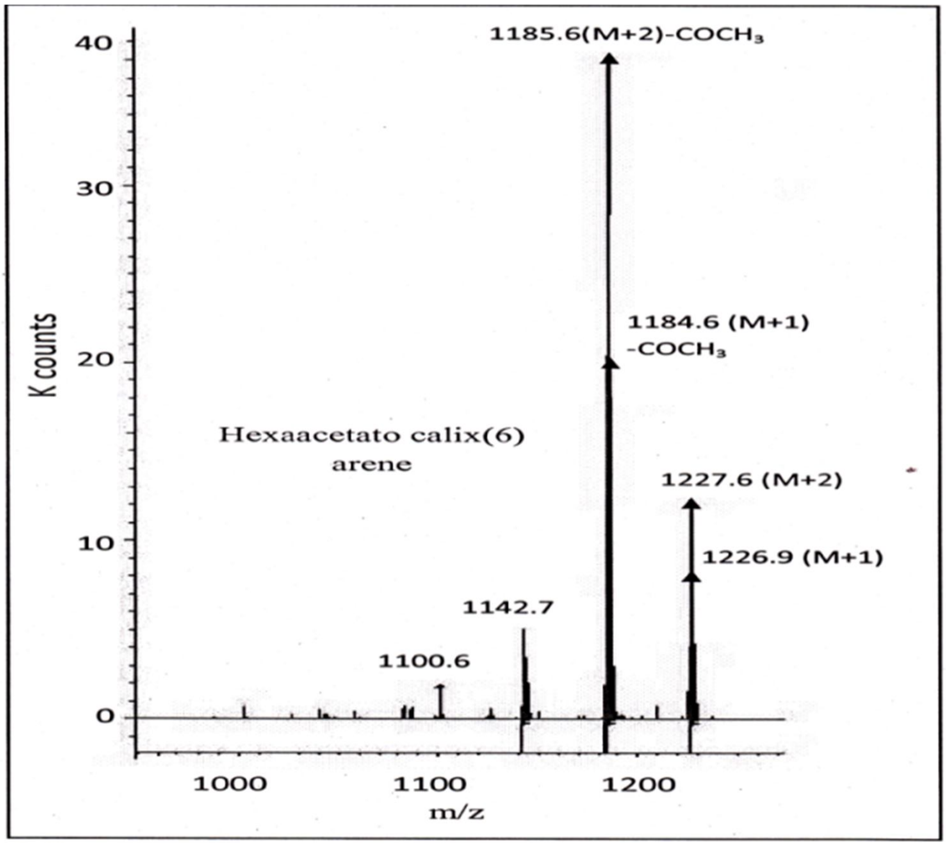

FIG. 6. Representative mass spectra of hexaacetatocalix[6]arene.

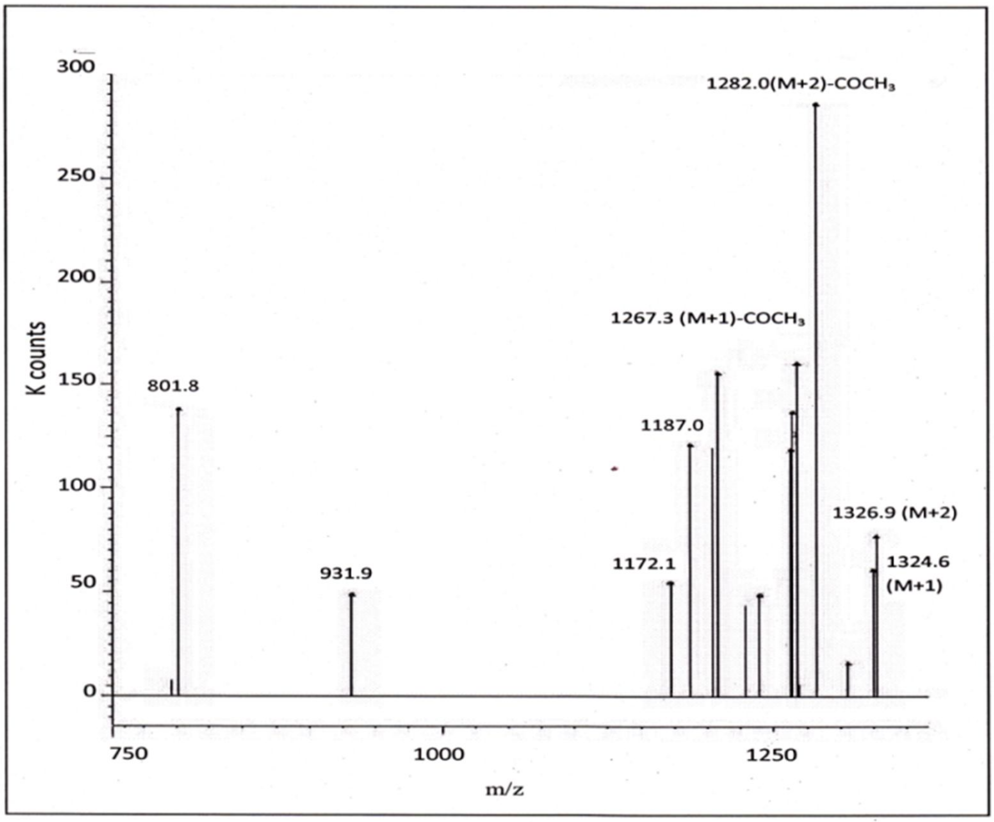

FIG. 7. Representative mass spectra of hexaacetatocalix[6]arene with silver(I).

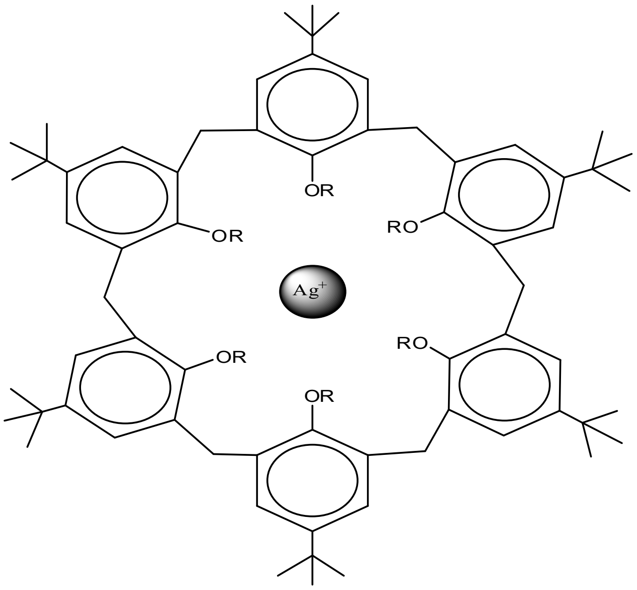

FIG 8.Possible structure of hexaacetatocalix[6]arene with the silver(I) (R = -COCH$_3$).

Applications

Foreign Ions Effect

After successful extraction and stripping of silver using the proposed experimental conditions,the effect of large number of foreign ions on its extraction was studied. Initial interference was studied by adding large excess of foreign ions (say 500 ppm), then theconcentration was decreased up to the tolerance limit. It was observed that the method is free from interference of large number of transition, non-transition metal ions and anions. Only some metal ions Cd^{2+}, Hf^{4+}, Au^{3+}, Hg^{2+}, Ga^{3+} and In^{3+} interfered strongly. Also, the anions Br^{-}, I^{-}, thiocynate, thiosulphate and EDTA ions strongly interfered during the extraction (Table 3).

TABLE 3. Effect of diverse ions on the extraction and determination of silver(I).

Forgien ion	Added as	Tolerance limit	Forgien ion	Added as	Tolerance limit
Li^+	$LiCl$	200	Th^{4+}	$Th(NO_3)_4.5H_2O$	50
Na^+	$NaCl$	150	Al^{3+}	$AlK(SO_4)_2.12H_2O$	50
K^+	KNO_3	350	Ga^{3+}	$GaCl_3$unhydrous	Interfere
Be^{2+}	$BeCl_2.2H_2O$	350	In^{3+}	$InCl_3$unhydrous	Interfere
Mg^{2+}	$MgCl_2.6H_2O$	150	Sn^{2+}	$SnCl_2.2H_2O$	10
Ca^{2+}	$CaCl_2.2H_2O$	250	Pb^{2+}	$Pb(NO_3)_2$	10
Ba^{2+}	$BaCl_2.2H_2O$	100	As^{3+}	As_2O_3	100
Sc^{3+}	Sc_2O_3	30	Sb^{3+}	$SbCl_3$	30
V^{5+}	V_2O_5	10	Bi^{3+}	$Bi(NO_3)_3.5H_2O$	10
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	10	Cl^-	Potassium chloride	350
Mn^{2+}	$MnCl_2.4H_2O$	30	Br^-	Potassium bromide	Interfere
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	50	I^-	Potassium iodide	Interfere
Fe^{2+}	$FeSO_4.7H_2O$	30	Nitrite	Sodium nitrite	200
Co^{2+}	$Co(NO_3)_2.6H_2O$	30	Nitrate	Sodium nitrate	350
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	30	*o*-phosphate	Sodium dihydrogeno-phosphate	100
Cu^{2+}	$CuSO_4.5H_2O$	50	Thiocynate	Ammthiocynate	Interfere
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	50			
Y^{3+}	Y_2O_3	30	Thiosulphate	Sodium thiosulphate	Interfere
Zr^{4+}	$ZrOCl_2.8H_2O$	30	Acetate	Sodium acetatetrihydrate	50
Mo^{6+}	$(NH_4)_6Mo_7O_{24}.4H_2O$	30	Oxalate	Potassium oxalate	10
Rh^{3+}	$RhCl_3.H_2O$	10	Tartaret	Sodium potassium tartaret	10
Cd^{2+}	$CdCl_2.2H_2O$	Interfere	EDTA	Di sodium salt of EDTA	Interfere
La^{3+}	LaO_3	30	Carbonate	Sodium bicarbonate	100
Ce^{4+}	$(NH_4)_4Ce(SO_4)_42H_2O$	50	Sulphate	Potassium sulphate	350
Sm^{3+}	Sm_2O_3	50	Fluoride	Sodium fluoride	10
Hf^{4+}	$HfCl_4$	Interfere	Bisulphite	Sodium bisulphite	100
Au^{3+}	$HAuCl_4.xH_2O$	Interfere	Citrate	Trisodium citrate	30
Hg^{2+}	$HgCl_2$	Interfere			

Determination of Silver(I) in Synthetic Mixtures

Silver is a precious metal on earth. The synthetic mixture was prepared according to its composition in the real samples or natural source. A solution containing 25 ppm ofAg(I) was taken and a known amount of other metal ions was added. Extraction of silver was carried out using the developed method. The RSD was found to be ≤ 0.5%(Table 4).

TABLE 4. Extraction separation and determination of silver(I) from synthetic mixtures.

Composition (ppm)	Silver(I) found (µg)	Mean (µg)	% Recovery	% [a]RSD
Ag(25)+As(25)+Ni(25)	24.86, 24.86, 24.86, 24.72,24.58	24.78	99.11	0.50
Ag(25)+Cu(25)+Pb(25)	24.87, 24.75, 2462,24.75, 24.87	24.77	99.09	0.43
Ag(25)+Cu(25)+Zn(25)	24.85, 24.85, 24.71, 24.71, 24.85	24.79	99.17	0.33
Ag(25)+Ni(25)+Zn(25)	24.72, 24.72, 24.86, 24.86, 24.72	24.77	99.09	0.32
Ag(25)+Pb(25)+As(25)	24.75, 24.87, 24.87, 24.87, 24.62	24.80	99.19	0.46

[a] Average of five determinations.

Separation and Determination of Silver(I)from Binary Mixtures

This method permits the extraction and separation of Ag(I) from commonly associated metal ions Al(III), Mn(II), Cr(III),Zr(IV) and Y(III) by taking the advantage of differences in the extraction conditions, like pH, equilibration time and stripping agents of the other metal ions. Below pH 6, silver(I) was not extracted; therefore, separation of it from the other metal ions was easily carried out. For the analysis, the mixture of Ag(I) with other metal ions Al(III) or Mn(II) or Cr(III) or Zr(IV) or Y(III)) was taken and its respective pH was maintained at 5.0, 6.0, 6.5, 3.0 and 6.0, respectively and allowed to equilibrate for 10 min. The added metal ionswere quantitatively extracted in the organic phase and silver(I) quantitatively remained in the aqueous phase. The extracted metal ions from the organic phase were stripped by using 1 M HCl, 2 M H_2SO_4, 4 M HCl, 4 M HNO_3 and 1 M HNO_3 as stripping agents, respectively. The aqueous phase was evaporated to moist dryness and the amount of Al(III) or Mn(II) or Cr(III) or Zr(IV) or Y(III) was determined spectro photometrically by using eriochrome cynine-R, periodate, xylenol orange and arsenazo(III), respectively. The concentration of Ag(I) present in the aqueous phase was determined by the recommended procedure (Table 5).

TABLE 5. Extraction separation of binary mixtures.

Metal ion	Amount taken(µg)	pH	Stripping agent	% Recovery	Determination method	Wavelength (nm)
Ag(I)	25	11.5	1 M HNO_3	99.99	b	650
Al(III)	20	5.0	1 M HCl	99.71	c	535
Ag(I)	25	11.5	1 M HNO_3	99.99	b	650
Mn(II)	25	6.0	2 M H_2SO_4	99.50	d	545
Ag(I)	25	11.5	1 M HNO_3	99.99	b	650
Cr(III)	30	6.5	4 M HCl	99.50	e	520
Ag(I)	25	11.5	1 M HNO_3	99.99	b	650
Zr(IV)	20	3.0	4 M HNO_3	99.66	e	560
Ag(I)	25	11.5	1 M HNO_3	99.99	b	650
Y(III)	10	6.0	1 M HNO_3	99.35	f	620

[b]Bromopyragallol red at 650 nm, [c]Eriochromecynine-R, [d]Periodate, [e]Xylenol orange, [f]Arsenazo(III).

Analysis of Real Samples

The applicability of the proposed method was used to extract and separate silver(I) from real samples. The results obtained by this present method were in good agreement with the certified values. The stock solution of samples was prepared as follows.

Pharmaceutical Samples

The silver ion is bioactive and in sufficient concentration readily kills bacteria *in vitro*. For the analysis of amount of silver(I) present in the antibacterial creams, 0.125 g of Silhex (CadilaHealth Care limited) and 1.25 g of Silverex^{TM} ionic (Virchow Biotech limited) were dissolved in 5 mL of 4 M HNO_3 and evaporated to moist dryness. Then, the residue was dissolved in minimum quantity of water and filtered. After that the filtrate was evaporated to moist dryness and finally diluted to 25 mL.

Silver Dental Alloy

Silver dental alloy (0.2 g) used in teeth feeling was dissolved in 10 mL of 4 M HNO_3 and evaporated to moist dryness. Then, the residue was dissolved in minimum quantity of water and filtered. After that,the filtrate was evaporated to moist dryness and diluted to 25 mL.

Silver Alloy

For the analysis of the silver(I) present in the silver alloy, 0.085 g sample was dissolved in 8 mL of 4 M HNO_3 and evaporated to moist drynessThen, the residue was dissolved in minimum quantity of water and filtered. After that,the filtrate was evaporated to moist dryness and diluted to 25.0 mL.

Waste Liquid during Photographic Film Processing

The waste liquid was collected during the photographic film processing. For the analysis, 20 mL of waste liquid was treated with 10 mL of 4 M HNO_3. The solution was kept overnight in dark. Then, it was evaporated to moist dryness, taken into minimum quantity of water and filtered to remove undissolved impurities. Finally, the solution was diluted to 50.0 mL.

Silver Foil (Vark)

Traditional Indian dishes sometimes include the use of decorative silver foil known as vark. For the determination of the amount of silver(I) in the silver foil, one leaf of nearly 0.005 g (Meera brand guaranteed pure silver leaves and company, Delhi) was dissolved in minimum quantity of HNO_3 and kept overnight. Then, the solution was evaporated to moist dryness and taken into minimum quantity of water. Finally, it was filtered and diluted to 50.0 mL.

All the solutions were acidified with drop ofconcentrated HNO_3 before dilution. An aliquot of each of the above solution was taken and then its pH was maintained to 11.5 and extracted with 10 mL of 1 x 10^{-4} M of acetyl derivative of calix[6]arene and determined spectrophotometrically by complexation with bromopyragallol red at 650 nm (Table 6).

TABLE 6.Analysis of silver(I) in real samples.

Samples	Amount found by proposed method (μg)	Mean (μg)	Certified value (μg)	% Recovery	% ^aRSD
Silhex (Cadila Health Care limited)	14.83 15.10 14.96 14.96 14.96	14.96	15.10	99.09	0.65
Silverex^{TM} ionic (Virchow Biotech limited)	63.12 62.93 63.31 63.12 62.74	63.05	63.50	99.29	0.34
Silver dental alloy	24.86 24.86 24.72 24.58 24.72	24.75	25.00	99.00	0.47
Silver alloy	48.86 49.05 48.86 49.05 48.67	48.90	49.24	99.31	0.33
Waste liquid (during photographic film processing)	46.97 47.16 47.16 46.97 46.78	47.01	47.35	99.28	0.34
Silver foil (vark)	79.86 80.06 79.86 79.47 79.67	79.78	80.25	99.42	0.29

[a] Average of five determinations.

Conclusions

Acetyl derivative of calix[6]arene was found to be a novel extractant for analysis of silver(I)in a variety of real samples, binary mixtures and synthetic mixtures. This study was carried out using very low concentration reagent, relatively less toxic solvent and low concentration of back extracting reagent. The values of thermodynamic parameters were also evaluated. Silver complex was formed with the ligands in the organic phase with the stoichiometric formula $[Ag(HR)]_{(org)}$. The large numbers of foreign ions were tolerated in high ratios. The method was free of interference from a large number of foreign ions which were often associated with naturally occurring silver(I). The time required for the extraction and separation was very short, which indicates a high distribution ratio of the complex involved in the quantitative recovery of silver(I). The proposed method involves quantitative extraction in a single step within a very short time.

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