

Calixarene hexaacetato derivative for solvent extraction of chromium (III)

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Trace concentrations of chromium(III) have been quantitatively extracted with 0.0001M hexaacetato calix(6)arene in toluene at pH 6.5. Chromium(III) was stripped from the organic phase with 4M hydrochloric acid and determined spectrophotometrically at 520 nm as its complex with xylenol orange. Various parameters influencing the extraction such as pH, reagent concentration, nature of diluents and stripping agents and effect of diverse ions have been examined. The novelty of the proposed method is that chromium in different oxidation states can be separated from each other, apart from its separation from iron(III), manganese(II), cobalt(II) and molybdenum(VI). The method has been extended to analysis of chromium(III) in real samples such as stainless steel.

Amongst supramolecules, calix(4)arene has been extensively used for solvent extraction separation of transition elements^{1,2}. Picric acid³ or thiocyanate⁴ are favoured as the counter-anions during extractions. Actinium(III)⁵ and uranium(VI)⁶ have been extracted with carboxylate derivatives of calixarene. Chromium(III) shows strong interference during extraction with the hydroxamic acid⁷ derivative of calixarene. Lanthanides have been extracted with diamide⁸ and tetrasulphonate⁹ derivatives of calixarenes. Hexaacetyl calix(6)arene have been used for the quantitative extraction of cobalt(II)¹⁰, palladium(II)¹¹, and iron(III)¹². In this note we report a novel method for the solvent extraction of chromium(III) using a hexaacetate derivative of calixarene.

Experimental

A Jasco V-530 UV- visible spectrophotometer with matched 10 mm quartz cuvettes and a digital pH meter (Elico, model LI-120) with glass and calomel electrodes were used.

Stock solution of chromium(III) was prepared by

dissolving 0.153g of chromium chloride in 250 ml distilled water and standardized complexometrically¹³. It contained 200 µg/ml of chromium (III). A diluted solution containing 10µg/ml of chromium(III) was prepared by twenty-fold dilution. A 0.0001M solution of hexaacetato *p*-tert-butyl calix(6)arene in toluene was also prepared.

Aqueous solution of xylenol orange (0.001M) was used for determination of the extracted chromium(III). Buffer solution of pH 3.0 was prepared with sodium acetate and monochloroacetic acid.

Hexaacetato calix(6)arene was synthesized¹⁴ by the following procedure: About 10g (0.666 mol) of *p*-*t*-butylphenol was dissolved in potassium hydroxide (6 ml, 5M) and 37% formaldehyde solution. The mixture was heated at 110-120°C for 2h to give a light yellow taffy like precursor. This precursor was mixed with xylene (40 ml) and heated to 210-220°C for 3h in an atmosphere of nitrogen with a Dean and Stark collector. The cooled mixture was filtered and suspended in 300 ml of chloroform, and then shaken with 100 ml of 1M hydrochloric acid. The organic layer was separated, washed with water, dried over anhydrous sodium sulphate and concentrated to 100 ml. The addition of methanol caused precipitation of a colourless solid which was filtered off. Recrystallization was carried out from chloroform and methanol (yield, 80%; m.p. 380-388°C). The spectral characteristics are as follows: IR (KBr): 3400, 3150 cm⁻¹ (OH stretching). ¹H NMR (CDCl₃): 10.2 (s, 1, ArOH), 7.10 (s, 2, ArH), 7.10 (s, 2, ArH), 3.88 (s, 2, CH₂), 1.25 (s, 9, C(CH₃)₃). ¹³C NMR (CDCl₃): 147.2 (15% Ar), 144.2 (15%Ar), 126.1 (65% Ar), 34.0 (17%Ar CH₃Ar), 33.1 (25% C(CH₃)₃).

The synthesis of hexaacetato calix(6)arene derivative was carried out as follow. About 2.0 g of *t*-butylcalix(6)arene was treated with a 1:3 mixture of pyridine and acetic anhydride. The mixture was refluxed for one hour at room temp to get the crude product, which on recrystallization from chloroform/methanol gave white platelets (yield, 84%; m.p. 360-362°C). The spectral characteristics of the derivative are as follows: IR (KBr): 1760 cm⁻¹

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(>C=O stretching). ^1H NMR (CDCl_3): 6.9 (s, ArH), 3.6 (Br, CH), 1.9 (s, OCOCH_3), 1.2 (s, $\text{C}(\text{CH}_3)_3$).

General procedure

An aliquot of solution containing $30\mu\text{g/ml}$ chromium (III) was taken and its pH was adjusted to 6.5 with dil. hydrochloric acid or ammonium hydroxide. The total volume of the solution was made up to 10ml with distilled water and it was transferred to separatory funnel. Then 10 ml of hexaacetato calix(6)arene in toluene ($1 \times 10^{-4}M$) was added to it and shaken vigorously for 5 min. The two phases were allowed to settle and separate. Chromium (III) was stripped with 10ml of 4M hydrochloric acid from the organic phase and determined spectrophotometrically at 520 nm as its complex with xylene orange¹⁴. The concentration of chromium (III) was computed from the calibration curve.

Results and discussion

When chromium (III) was extracted in the pH range of 1.0-8.5 with $1 \times 10^{-4}M$ hexaacetato calix(6)arene in toluene the extraction was < 50% at pH 2.0 and ~75% at pH 4.0. From pH 6.0-7.5 extraction was quantitative and after pH 8.0 it decreased. Therefore all extraction experiments were carried out at pH 6.5.

Chromium (III) was extracted with varying concentration of reagent ranging from 5×10^{-4} - $5 \times 10^{-6}M$. The extraction was quantitative with $1 \times 10^{-4}M$. Hence this concentration was employed throughout the investigations.

Various solvents having different dielectric constants, viz., benzene, toluene, xylene, cyclohexane, hexane, carbon tetrachloride, chloroform, dichloroethane and dichloromethane were tested as the diluents. The extraction was quantitative only with toluene, xylene and carbon tetrachloride, with all other diluents it was incomplete. Since, toluene offers better phase separation and is relatively less toxic, it was preferred as the diluent.

After extraction chromium(III) was stripped with varying concentration of several mineral acids, viz, hydrochloric, nitric, sulphuric and perchloric acid. The stripping was > 98% with 3M perchloric acid and 85.3% with 4M acetic acid. However with 2M sulphuric and 4M hydrochloric acid, the stripping was quantitative. Since it facilitated subsequent spectrophotometric determination of chromium(III),

Table 1— Effect of diverse ions on the extraction of Cr (III)
[Cr(III) 20 μg]

Foreign ions	Amount tolerated (μg)	Ratio
Li(I), Na(I), K(I), Cs(I), Rb(I)	1000	1:50
Ba(II), Ca(II), Sr(II)	500	1:25
In(III), Se(IV), Te(IV), Ga(III)	300	1:15
Ce(III), Sn(IV), Sb(III), As(III)	200	1:10
Pt(IV), Bi(III), Tl(III), Au(III)	100	1:5
Zn(II), Mg(II), Cu(II), Pb(II), Al(III), UO ₂ (II), Mo(VI), Th(IV)	60	1:3
Mn(II), Co(II), Fe(III), Pd(II)	40	1:2
Cl^- , I^- , SCN^- , SO_3^{2-} , NO_2^- , SO_4^{2-}	800	1:40
Cd(II), Ni(II), Ag(I)	Interference	—

4M hydrochloric acid was preferred as the stripping agent.

The extraction of chromium(III) was carried out with varying shaking time from 1-15 min. The optimum period of equilibration was 3 min; hence equilibration period was kept at 3 min.

To ascertain the nature of extracted species, plots of log D versus log [HR] were constructed. A linear plot with a slope of 2.74 suggests the probable composition of the extracted species as 1:3, i.e., $\text{Cr}(\text{HR})_3$ where HR represents the extractant.

As the calix(6)arene derivative exists in the 'winged' conformation, i.e. 1,4-alternate conformer, it gives rise to a conformation where the aryl groups in the 1- and 4-positions project outwards like a pair of wings perpendicular to the aryl groups in the 2-, 3-, 5- and 6-positions. Since they are co-linear, they form a channel where other molecules are comfortably placed. It is assumed that there is no true covalent bond formation in these supramolecular compounds. Chromium (III) is probably held firmly among three calixarene molecules by real ionic attraction due to the substituted oxygen¹¹.

Effect of diverse ions

Chromium (III) was extracted in the presence of a large number of foreign ions (Table 1). The tolerance limit was set as the amount of foreign ion causing an error of +2% in the recovery. Most of the anions were

Table 2—Separation from multicomponent mixture. [Extractant $1 \times 10^{-3}M$]

Sr.No.	Metal	Conc. (μg)	pH	Stripping agent	Recovery (%)	Chromogenic Reagent
1	Cr(VI)	100	6.5	Unextracted	100	Diphenyl carbazide
	Cr(III)	30	6.5	2M H ₂ SO ₄	99.5	Xylenol orange
2	Sr(II)	200	7.5	Unextracted	100	Muroxide
	Cr(III)	30	7.5	4.0M HCl	99.5	Xylenol orange
	Th(IV)	50	7.5	0.005M H ₂ SO ₄	98.0	Thoron.
3	Cs(I)	100	7.0	Unextracted	100	
	Th(IV)	50	7.5	0.005M H ₂ SO ₄	98.0	Thoron
	Cr(III)	30	7.0	5.0M HCl	99.5	Xylenol orange
	Fe(III)	30	7.0	1.0M HCl	99.7	Thiocyanate
4	Mg(II)	250	7.5	Unextracted	100	Eriochrome black T
	Th(IV)	50	7.5	0.005M H ₂ SO ₄	98.0	Thoron
	Co(II)	30	7.5	1.5M NH ₄ SCN	99.9	Nitroso-R-salt
	Cr(III)	30	7.5	4M HCl	99.5	Xylenol orange
5	Th(IV)	50	7.5	0.005M H ₂ SO ₄	98.0	Thoron
	Co(II)	30	7.0	1.5M NH ₄ SCN	99.9	Nitroso-R-salt
	Cr(III)	30	7.0	5.0M CH ₃ COOH/4.0M HCl	99.5	Xylenol orange
	Pd(II)	30	7.0	3M HNO ₃	99.7	Stannous chloride
	Pb(II)	50	6.0	4M HNO ₃	99.5	PAR.

tolerated in the ratio 1:40. Alkali metals were tolerated in the ratio 1:40, while main group elements were tolerated in the ratio 1:15. A few of the transition elements were tolerated in the ratio 1:2 but cadmium(II), nickel(II) and silver(I) showed strong interference. However it is possible to eliminate such interference by selective extraction¹⁵.

The difference in extraction and stripping was fully exploited to develop a novel method of separation of chromium(III) from several metals in multicomponent mixtures. The details of various separation developed are described in Table 2.

When chromium(III) was extracted, most metals like strontium(II), caesium(I) and chromium(VI) were not extracted and consequently separated. Although metals like thorium(IV), cobalt(II), iron(III), palladium(II) and lead(II) were coextracted with chromium(III), they could be stripped with different stripping agents either before or after stripping chromium (III) depending upon extractability of the said cation.

The mixture of strontium(II), chromium(III), and thorium(IV) was resolved by stripping chromium (III) with 4M hydrochloric acid, thorium (IV) with 0.005M sulphuric acid while strontium (II) remained unextracted.

The separation of caesium(I), thorium(IV), chromium(III) and iron(III) was accomplished as caesium(I) was not extracted while thorium (IV) was stripped with 0.005M sulphuric acid, chromium (III) with 5.0M hydrochloric acid and iron (III) with 1.0M hydrochloric acid.

The separation of magnesium(II), thorium(IV), cobalt(II) and chromium(III) was achieved, as magnesium(II) was not extracted, thorium(IV) was stripped with 0.005M sulphuric acid, cobalt(II) with 1.5M ammonium thiocyanate, and finally chromium(III) with 4.0M hydrochloric acid.

The separation of thorium(IV), cobalt(II), chromium(III) and palladium(II)/lead(II) in quaternary mixture was accomplished by first stripping thorium(IV) with 0.005M sulphuric acid, cobalt(II) with 1.5M ammonium thiocyanate, chromium(III) with 5.0M acetic acid and palladium(II) or lead(II) with 3-4M hydrochloric acid.

It was possible to separate chromium(VI) from chromium(III) as the former was not extracted under the conditions for extraction of chromium(III) and was thus separated. This facilitated the separation of chromium(III) from several metals generally associated with it in mineral and alloys.

Analysis of chromium (III) in real samples

A sample of austenitic stainless steel (0.4g) was dissolved in a mixture of nitric and perchloric acid. The solution was evaporated to near dryness, extracted with water and the volume made up to 1000ml. An aliquot of the solution was taken from which iron(III) was extracted with ethylacetate with 4M nitric acid followed by selective extraction of nickel(II) at pH 5.5 with 0.1M dimethylglyoxime in chloroform. Chromium(III) was extracted as usual by the proposed method. The results indicated 18.1% of chromium (III) in the sample against the certified value of 18.0%.

The proposed method is simple rapid and selective. Total time required for separation and determination is 30 min. It is suitable for separation of chromium(III) from lead(II), iron(III), palladium(II), cobalt(II), thorium(IV) and chromium(VI) with which it is generally associated in minerals and alloys.

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