

Synergistic solvent extraction of copper, cobalt, rhodium and iridium into 1, 2-Dichloroethane at trace level by newly synthesized 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetra-[4-(*N*-hydroxyl-3-phenylprop-2-enimidamido) phenylazo] calix[4]arene

Ashok Kumar · Pratibha Sharma · Lal Kumar Chandel ·
Bhagwan Lal Kalal · Sandor Kunsagi-Mate

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Abstract A spectrophotometric method for determination of copper, cobalt, rhodium and iridium ions from nitric acid media after extraction of these ions by 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetra-[4-(*N*-hydroxyl-3-phenylprop-2-enimidamido) phenylazo] calix [4] arene (THPAC) has been developed and possible synergistic effect has been investigated. The maximum enhancement was obtained in the presence of 30% 1, 2-dichloroethane in DMF and 3M nitric acid. The trace amounts of the metal were determined spectrophotometrically. Beer's law was obeyed in concentration range 5.0–10.0 µg, 6.0–120.0 µg, 12.0–100.0 µg, and 10.0–130.0 µg/10 mL of the final solution of copper, cobalt, rhodium and iridium, respectively. The molar absorptivities ($\text{l mol}^{-1} \text{cm}^{-1}$) and Sandell's sensitivities ($\mu\text{g cm}^{-1}$) were calculated: Cu (II) = 0.96×10^4 , 0.0066; Co (II) = 1.13×10^4 , 0.0052; Rh (III) = 0.98×10^4 , 0.012; and Ir (III) = 2.03×10^4 , 0.0095, respectively. Seven replicate analyses containing of 20.0 µg of Cu (II), 24.0 µg of Co (II), 36.0 µg of Rh (III) and 25.0 µg of Ir (III) gave mean absorbance 0.302, 0.462, 0.344, 0.264; and relative standard deviation 0.65, 0.85, 1.10, 1.08%, respectively. The interference of various ions was studied and optimum conditions were developed for determination

of metals in certain alloys, environmental, pharmaceutical and synthetic samples.

Keywords Synergistic extraction · Spectrophotometric determination · Copper · Cobalt · Rhodium · Iridium · Calixarene · Diluents

Introduction

The development of supramolecular chemistry has been dominated by the design and synthesis of macrocyclic compounds with potential receptor capabilities [1]. Calix[*n*]arene is a class of molecules with pronounced binding affinity towards various ligands, which depends on type of substituents at the upper and lower rim. A large number of substituted calix[4]arenes have already been synthesized with the aim of modifying their binding properties [2–4]. Lower rim modifications through out the phenolic oxygen atom have been explored widely in design and synthesis of metal cation receptors [5].

Calix[*n*]arenes play an increasingly important role in host–guest chemistry, largely because they can provide a well organized platform for the attachment of pendant groups [6]. Moreover, azo compounds are the most widely used class of dyes due to their versatile applications in various fields such as dyeing of textile fibers, coloring of different materials and in advanced applications in organic synthesis [7, 8]. Also, azo group brings to calixarenes a chromogenic activity. These compounds make an important class of organic colorant, consisting of at least a conjugated chromophore of azo (–N=N–) functionality.

Furthermore, synergistic extraction of metal ions has various advantages over ordinary solvent extraction system, such as enhancement of extractability, widening the

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A. Kumar (✉) · P. Sharma · L. K. Chandel · B. L. Kalal
School of Chemical Sciences, Devi Ahilya University,
Takshashila Campus, Indore 452 001, India
e-mail: drashoksharma2001@yahoo.com

S. Kunsagi-Mate
Department of General and Physical Chemistry, University of
Pecs, Ifjusag 6, Pecs 7624, Hungary

optimum extraction pH range, stabilization of extracted species by forming an adduct [9]. The continued interest in the field can be seen from various reviews published by different authors [10, 11]. Hence, in view of variegated importance associated with the azocalix[*n*]arenes and in continuation of our enduring research on calix[4]arenes [12], azo substituted heterocyclic compounds [13, 14] and solvent extraction [15], efforts have been laid down to under take comprehensive synergistic extraction of metals using hitherto uninvestigated synthesized calix[4]arenes containing azo functionality. The interference of various ions was studied and optimum conditions were developed for determination of the metals in certain alloys, environmental, pharmaceutical samples and synthetic mixtures.

Experimental

Reagents and apparatus

All the chemicals used were of analytical grade purity. Melting points were taken in open capillary tubes using an electric melting point apparatus. All the melting points reported are uncorrected. IR spectra were recorded on a Shimadzu 460 FTIR-spectrometer in KBr disks. ¹H NMR spectra were recorded on Jeol NMR 200 MHz spectrometer in CDCl₃. The chemical shifts are quoted in ppm value on the δ scale using TMS as an internal reference and coupling constants (J) in Hz. A Shimadzu 1700 Pharma Spec UV–Vis spectrophotometer with 10 mm quartz cell was used for the absorbance spectra of organic extractants. Reaction monitoring and purity of all the synthesized compounds was checked using silica gel G plates (E. Merck) and ethyl acetate/xylene (3:7 v/v) as eluting system.

Synthesis of 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetra-[4-(*N*-hydroxy-3-phenylprop-2-enimidamido) phenylazo] calix [4] arene (THPAC)

The typical synthesis of THPAC was performed in following reaction steps (Scheme 1).

Preparation of 4-(4'-hydroxy) phenyl azoacetanilide (1)

In a small beaker, 3.82 g (0.015 mol) of *p*-amino acetanilide (prepared as per the literature procedure [16]) in 15 mL of conc. hydrochloric acid and 15.0 mL of water were taken. Diazotization was performed by the drop wise addition of a solution of 4.0 g (0.005 mol) of sodium nitrite in 20.0 mL water with maintaining the temperature of the vessel below 5 °C. Now, in a another 200 cc beaker, a solution of 4.7 g (0.05 mol) of phenol in 30 mL of 10% sodium hydroxide solution was prepared and allowed to cool down to 5 °C by immersing in an ice bath, assisted by

the direct addition of about 25.0 g of crushed ice. The phenol solution was stirred vigorously and to this the cold diazonium salt solution was added very slowly. Reddish orange crystals of 4-(4'-hydroxyl) phenyl azo acetanilide (**1**) were appeared soon. The mixture was allowed to stand in an ice-bath for 30 min with occasional stirring, filtered through a Buchner funnel, washed well with water and drained. Further washing was done with ethanol and dried. Recrystallization of the product was performed by glacial acetic acid. Yield 75%, m.p.176–178 °C

IR (ν cm⁻¹, KBr): 3441 (O–H), 3110 (N–H), 3025 (=C–H, sp²), 2868 (–C–H, sp³), 1676 (N=N), 1705 (C=O), 1595, 1481, 1398 (C···C ring str.), 1143 (C–O), 910,740 (sub phenyl); ¹H NMR (δ _H, CDCl₃): 2.12 (s, 3H, CH₃), 6.53 (bs, NH), 7.12–7.42 (m, 8H, Ar–H), 8.41 (s, OH); Anal calc.(%) for C₁₄ H₁₃ N₃ O₂: C, 65.87; H, 5.13; N, 16.46; Found C, 65.54; H, 4.95; N, 15.94

Preparation of *N'*-hydroxy-[4-(4'-hydroxyl) phenylazo] phenylethanimidamide (2)

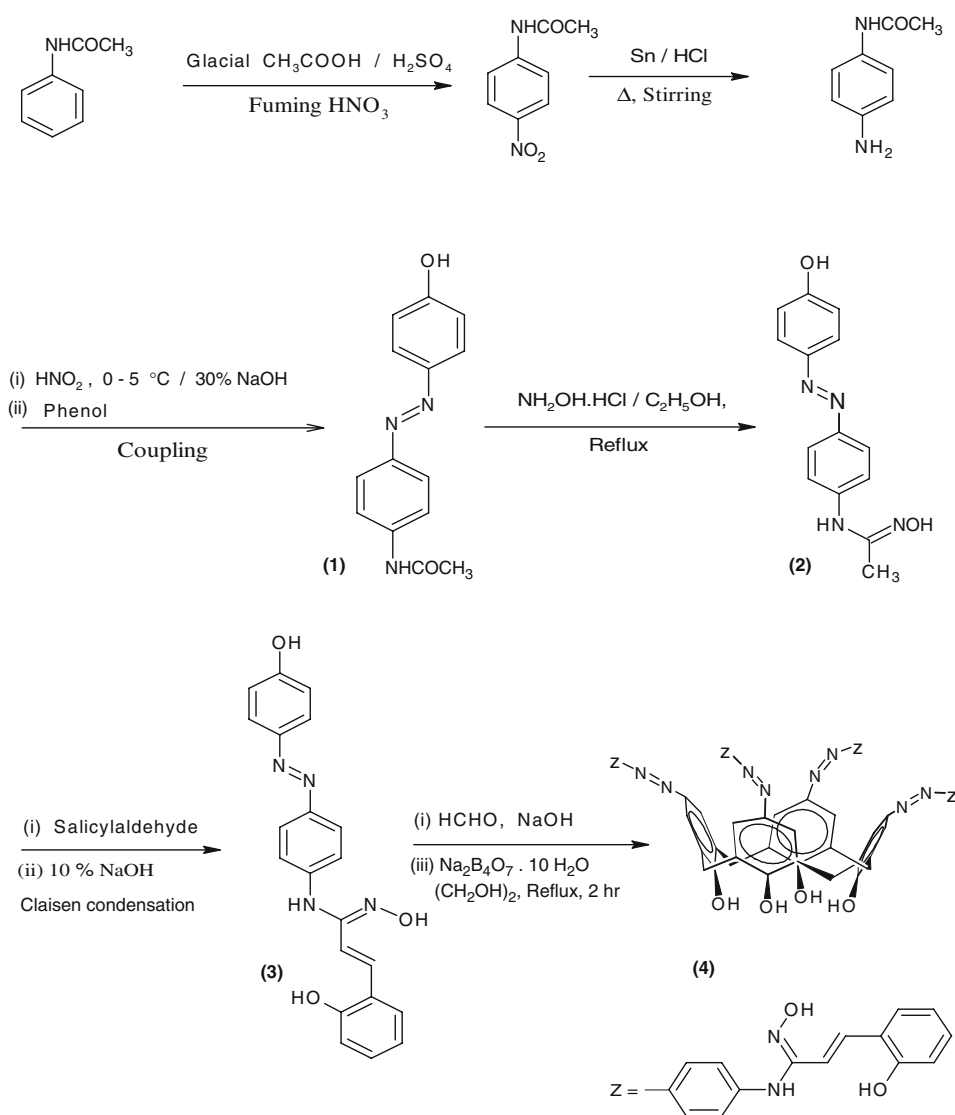
In a 100 cc conical flask, a solution of 12.5 g of hydroxylamine hydrochloride in 20.0 mL of water was prepared. To this, a cold solution of 7.0 g of sodium hydroxide prepared in 20.0 mL of water, was added. The contents were chilled down to 5 °C by placing the beaker in ice bath. Now, 4.0 g of 4-(4'-hydroxyl) phenyl azoacetanilide (**1**) was added slowly with gentle shaking. When the addition was complete, the mixture was allowed to stand in ice bath for 15 min and then filtered off to obtain the crystals of *N'*-hydroxyl-[4-(4'-hydroxyl) phenylazo] phenyl phenylethanimidamide (**2**) in good yield. Recrystallization was done from petroleum ether (60–80 °C). Yield 79%, m.p. 178–180 °C

IR (ν cm⁻¹, KBr): 3360 (O–H), 3212 (N–H), 3042 (=C–H, sp²), 2890(–C–H, sp³), 1681 (N=N), 1640 (C=C/C=N) 1605, 1512, 1470(C···C, ring str.), 845, 720 (sub.phenyl); ¹H NMR (δ _H, CDCl₃): 2.23 (s, 3H, CH₃), 5.79 (NH), 7.41–7.74 (m, 8H, Ar–H), 8.81 (bs, 2 OH); Anal calc.(%) for C₁₄ H₁₄ N₄ O₂: C, 62.21; H, 5.22; N, 20.73; Found C, 62.15; H, 4.88; N, 20.49

Preparation of *N'*-hydroxy-[4-(4'-hydroxy) phenylazo] phenyl-3-phenylprop-2-enimidamide (3)

As per the synthetic strategy of Claisan reaction conditions, 1.35 g (0.005 mol) of (**2**) and 5.30 g (0.005 mol) of salicylaldehyde i.e., equimolar quantity were taken together in a 200 cc stoppered conical flask containing 25.0 mL of methylated spirit. To this, 5.0 mL of 10% aqueous sodium hydroxide was added. The mixture in securely corked flask was shaken vigorously for 15 min (releasing the pressure from time to time, as necessity), and then allowed to stand for 1 h. During the shaking, compound (**3**) separated at first

Scheme 1 An overview of synthetic pathway of 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetra-[4-(*N*-hydroxyl-3-phenylprop-2-enimidamido) phenylazo] calix [4] arene



as a fine emulsion which then rapidly turned into pale yellow crystals. The precipitate obtained was filtered at the pump, washed well with water to eliminate the traces of alkali, drained and then recrystallized from hot rectified spirit. Yield 76%, m.p. $163-165^\circ\text{C}$

IR: ($\nu \text{ cm}^{-1}$, KBr): 3542 (O–H), 3348 (N–H), 3042 ($=\text{C}-\text{H}$, sp^2), 2890 ($-\text{C}-\text{H}$, sp^3), 1680 (N=N), 1595 (C=C/C=N), 1590, 1480, 1371 (C \cdots C, ring str.), 1205 (C–O), 820, 710 (sub. phenyl); ^1H NMR (δ_{H} , CDCl_3): 5.23 (d, 1H, $\text{CH}=\text{CH}-\text{Ar}$), 5.65 (d, 1H, $\text{CH}=\text{CH}-\text{Ar}$), 6.66 (NH), 7.21–7.53 (m, 8H, Ar–H), 7.82 (m, 4H, Ar–H), 8.51 (bs, 3 OH). Anal calc.(%) for $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_2$: C, 70.38; H, 5.06; N, 15.63; Found C, 70.18; H, 4.89; N, 15.22

Synthesis of THPAC (4)

Compound (3) (0.60 g, 0.0017 mol), *p*-formaldehyde (5.37 g, 0.18 mol) and solid sodium hydroxide (0.27 g,

0.0067 mol) were dissolved in 25.0 mL *i*-propanol. The reaction mixture was refluxed for 2 h under stirring. It was neutralized with hydrochloric acid and was transferred into a round bottomed three-neck flask, equipped with a stirrer and thermometer. Then, 2.27 g (0.006 mol) of sodium tetraborate decahydrate and 50.0 mL of hot ethylene glycol were added with stirring. The reaction mixture was refluxed for 2 h. Then, the mixture was cooled down to 80°C and poured into 500 mL of cold water. The precipitate obtained was filtered off and dried under vacuum at 40°C . The dried product was recrystallized from a mixture of chloroform–methanol (3:7, v/v). Yield 78%, m.p. 262°C (decomposed)

IR ($\nu \text{ cm}^{-1}$, KBr): 3472–3348 (bs, O–H), 3335 (N–H), 3042 ($=\text{C}-\text{H}$, sp^2), 2885 (C–H, sp^3), 1678 (N=N), 1655 (C=C/C=N), 1595, 1480, 1410 (\cdots , ring str.), 1190 (C–O), 810, 720, 675 (sub. phenyl); ^1H NMR (δ_{H} , CDCl_3): 3.41 (d, 4 H, Heq of Ar– CH_2 –Ar), 4.22 (s, NH \times 4), 4.48 (d, 4 H, Hax of Ar– CH_2 –Ar), 5.25 (d, 4H, $\text{CH}=\text{CH}-\text{Ar}$), 5.58 (d,

4H, $\text{CH}=\text{CH}-\text{Ar}$), 6.21–6.66 (m, 16 H, Ar-H \times 4), 6.92–7.65 (m, 24 H, Ar-H \times 8), 7.79 (s, 4 OH), 8.85 (s, 4 OH), 9.62 (bs, 4 OH). Anal. calc.(%) for $\text{C}_{88} \text{H}_{72} \text{N}_8 \text{O}_{12}$: C, 73.73; H, 5.06; N, 7.82; Found C, 73.45; 5.88; N, 7.62.

Extraction procedure

Picrate extraction experiments were performed following Wong's procedure [17]. A solution of 10 mL of a 2.5×10^{-4} M THPAC in 30% dichloroethane in DMF was vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. In all extractions, aqueous phase was adjusted to a desired nitric acid molarity (3M). After mixing the aqueous phase (containing metal picrate of studied metal ion, interfering metal ions and anions) and organic phase, the whole mixture was mechanically stirred in thermostated water bath at 25 °C for 1 h and finally left standing for additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically against the blank. Blank experiments showed that no picrate extraction was occurred in the absence of calixarene. The metal picrate was prepared by stepwise addition of a 1.0×10^{-2} M of metal nitrate/chloride solution to a 1.5×10^{-5} M aqueous picric acid solution and shaken at 15 °C for 30 min.

Results and discussion

Dependence of distribution on nitric acid concentration

The effect of water miscible interfering ions on extraction was investigated at increasing nitric acid molarities. The distribution ratio (D), defined as the ratio of the metal in the organic phase per mL and the concentration of the metal in aqueous phase per mL was calculated. From knowledge concerning 'D', the volume of the aqueous phase (V_a) and that of the organic phase (V_o), the percentage of extraction (E %) was calculated as: $E (\%) = 100 D / (D + V_a/V_o)$. The distribution ratio (D) was considerably enhanced by the presence of organic additive. The maximum extractability was shifted towards lower acidity in the presence of organic additive (Fig. 1). At higher acid concentration, the extraction was less influenced by organic additive, while higher D values were obtained by low acid concentration (2–3M HNO_3). This phenomenon had been observed earlier for extraction from mixed aqueous organic media [18].

Dependence of D on the THPAC concentration

Dependence of D on the THPAC concentration was studied at $[\text{HNO}_3] = 3\text{M}$. The extraction process was occurred as follows:

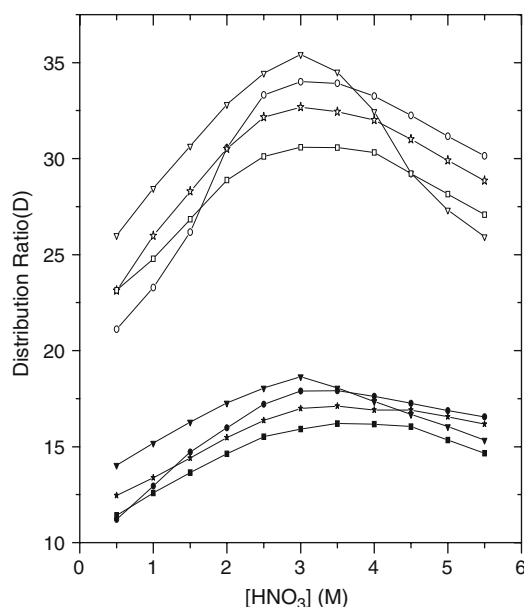
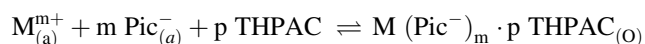


Fig. 1 Effect of the nitric acid concentration on the extraction of Cu (II), Co (II), Rh (III) and Ir (III) with 0.02M THPAC from a pure nitric acid solution, Cu (II):●, Co (II):▲, Rh (III):■ and Ir (III):◆, to a solution containing 30% (v/v) 1, 2-Dichloroethane in DMF [Cu (II):○, Co (II):△, Rh (III):Ψ and Ir (III):□]



where $p = 1, 2, \dots$ and the subscripts (a) and (o) refer to the species present in aqueous and organic phase, respectively. Assumptions are made that the partition of the ligand to the aqueous phase is negligible ($[\text{THPAC}]_{(a)} \sim 0$). The presence of $\text{M}(\text{Pic})_m$ and $\text{M} \cdot (\text{X})_m \cdot (\text{THPAC})_p$ [with $\text{X} = \{\text{NO}\}_3^{-}$; the anion present in the aqueous phase] in the organic phase and the extraction of mixed complexes $[\text{M}(\text{Pic})_n \cdot \text{X}_{(m-n)} \cdot (\text{THPAC})_p]$ is also negligible, as conformed by blank experiments. The extraction coefficient for $p:1$ complexation (K_{ex}) is given by:

$$K_{\text{ex}} = \frac{[\text{M} \cdot (\text{Pic}^{-})_m \cdot p \text{THPAC}]_{(o)}}{[\text{M}^{m+}]_{(a)} [(\text{Pic}^{-})]_{(a)}^m [\text{THPAC}]_{(o)}^p}$$

By introducing the distribution ratio D as

$$D = [\text{M}(\text{Pic}^{-})_m \cdot p \text{THPAC}]_{(o)} / [\text{M}^{m+}]_{(a)}$$

We obtained

$$\log D = \log K_{\text{ex}} + m \log [\text{Pic}^{-}]_{(a)} + p \log [\text{THPAC}]_{(o)}$$

Where D is defined as ratio of the analytical concentration of cation in both phase:

$$D = [\text{A}]_{\text{org}} / [\text{A}]_{\text{aq}}$$

Consequently, a plot of the $\log D$ vs. $\log [\text{THPAC}]_{(o)}$ may lead to a straight line whose slope allows accessing the stoichiometry of the extracted species. The slope for all the

Table 1 Extraction of the metals by THPAC from acidic solution; Organic Phase: 1.0×10^{-2} M THPAC in 30% 1, 2-Dichloroethane in DMF; Aqueous Phase: 3M HNO_3

[HNO_3] (M)	Distribution ratio (D)							
	Copper (II)		Cobalt (II)		Rhodium(II)		Iridium(III)	
	I	II	I	II	I	II	I	II
0.5	11.21	21.12	14.03	26.00	12.46	23.12	11.42	23.15
1.0	12.95	23.28	15.18	28.45	13.38	25.98	12.59	24.78
1.5	14.72	26.18	16.28	30.65	14.40	28.29	13.66	26.84
2.0	15.98	30.56	17.28	32.82	15.47	30.52	14.62	28.88
2.5	17.21	33.32	18.05	34.45	16.36	32.16	15.52	30.12
3.0	17.90	34.00	18.65	35.42	16.99	32.68	15.91	30.60
3.5	17.91	33.92	18.05	34.52	17.12	32.45	16.21	30.58
4.0	17.62	33.25	17.35	32.46	16.91	32.02	16.18	30.32
4.5	17.25	32.26	16.69	29.23	16.90	31.01	16.05	29.22
5.0	16.87	31.16	16.05	27.32	16.55	29.90	15.35	28.16
5.5	16.55	30.15	15.35	25.94	16.18	28.85	14.65	27.08

I, Extraction without organic additive

II, Extraction with organic

extracted species was found near about 1. It indicates that the extracted species would be $\text{Cu}(\text{Pic}^-)_2 \cdot \text{THPAC}$, $\text{Co}(\text{Pic}^-)_2 \cdot \text{THPAC}$, $\text{Rh}(\text{Pic}^-)_3 \cdot \text{THPAC}$ and $\text{Ir}(\text{Pic}^-)_3 \cdot \text{THPAC}$. The intercept of the plot with the log D-axis equals $\log K_{\text{ex}} + m \log [\text{Pic}^-]_{(\text{a})}$.

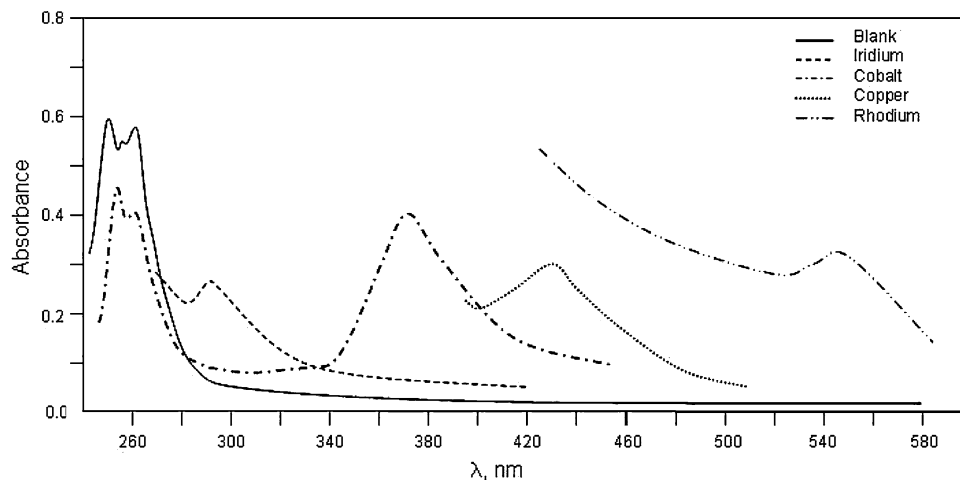
Influence of diluents

The extractability and selectivity of metals by organic extractants are greatly affected by the nature of the solvent. To study the influence of commonly available organic solvents such as benzene, xylene, chloroform, cyclohexane and 1,2-dichloroethane the extractability of the metals from 3.0M HNO_3 was investigated with (1.0×10^{-2} M)

THPAC dissolved in various solvents (Table 1). A significant enhancement in extraction was obtained by introducing 30% 1, 2-dichloroethane in DMF.

Beer's law and sensitivity

Under optimum conditions described above, a calibration graph for copper, cobalt, ruthenium, iridium was obtained at 432, 370, 545 and 290 nm against reagent blank, respectively. Beer's law obeyed in concentration range 5.0–110.0 μg , 6.0–120.0 μg , 12.0–100.0 μg , and 10.0–130.0 $\mu\text{g}/10$ mL of the final solution of copper, cobalt, rhodium and iridium, respectively. The molar absorptivities ($\text{l mol}^{-1} \text{cm}^{-1}$) and Sandell's sensitivities ($\mu\text{g cm}^{-1}$) were calculated: $\text{Cu}(\text{II}) = 0.96 \times 10^4$, 0.0066; $\text{Co}(\text{II}) = 1.13 \times 10^4$, 0.0052; $\text{Rh}(\text{III}) = 0.98 \times 10^4$, 0.012; and $\text{Ir}(\text{III}) = 2.03 \times 10^4$, 0.0095; respectively. Seven replicate analyses containing of 20.0 μg Cu (II), 24.0 μg Co (II), 36.0 μg Rh (III), and 25.0 μg Ir (III) gave mean absorbance of 0.302, 0.462, 0.344, and 0.264 (Fig. 2) with relative standard deviation of 0.65, 0.85, 1.10, and 1.08%, respectively. The proposed method was found to be more sensitive and selective than many of recent spectrophotometric methods. It is probably because of complex ion pair formation between big size inclusion compound and picrate ion (picrate is a large charge—diffusion anion) effectively. Furthermore, both picrate and ligand has lipophilic exterior and therefore no limiting factor in extraction from aqueous to organic phase. Intra molecular hydrogen bonding among four hydroxyl groups at lower rim of calixarene provides a stable cone conformation to it. Basic calixarene skeleton provides a pre-organization to four azo groups for complexation with metal ion. Presences of oxime group at upper rim substituent decreases the solubility of compound in organic solvent and make it water soluble to some extent. Furthermore,

Fig. 2 Absorption spectra of Cu: 20.0 μg ; Co: 24.0 μg ; Rh: 36.0 μg ; Ir: 25.0 μg ; extracted with 0.2M calix[4]arene from 3M HNO_3 

interaction between oxime group and metal ion pull the letter towards cavity from aqueous media. The interference of various ions was studied and optimum conditions were developed for the determination of metals in certain alloys, environmental and pharmaceutical and synthetic samples.

Effect of diverse ions

The interference of various ions in the estimation of the metal ions has been studied in detail. In general, a 1,000 μg of the anion or amount equivalent to 500 μg of metal ion was added individually to an aliquot containing 20.0 μg Cu (II), 24.0 μg Co (II), 36.0 μg Rh (III), and 25.0 μg Ir (III). Among the anions examined acetate, chloride, citrate and thiocyanate did not interfere in the determination of all these metal ions. Iodide interfered seriously in the determination of copper; EDTA interfered in all the cases. Obviously, the stability constant of these metal EDTA complexes must be higher than metal calix[n]arene complexes. Among the cations examined Ce^{+3} , Ce^{+4} , Mg^{+2} , Ca^{+2} , VO_2^{+2} , Cr^{+3} , Mn^{+2} , Co^{+2} , Zn^{+2} , Rh^{+3} , Pd^{+2} , Cd^{+2} , Ir^{+3} , Sb^{+3} , Bi^{+3} did not interfere in the determination of all the metal ions; Fe^{+3} and Ni^{+2} interfered in the determination of copper. The interference of Fe^{+3} was masked by 5 mL of 5% ascorbic acid and interference of Ni^{+2} was masked by 5 mL of 5% of hydroxyl amine solution in the determination of copper. The interference of Fe^{+3} , Cu^{+2} and Ni^{+2} in the determination of cobalt (II) was masked by 5 mL of 5% hydroxyl amine solution, respectively. In the determination of rhodium (III) and iridium (III) Fe^{+3} , Cu^{+2} , Ni^{+2} also interfered. The interference was eliminated by using ascorbic acid, thiourea and hydroxyl amine as masking agent, respectively. Thus interference due to various ions was studied and optimum conditions were developed for the determination of metals in standard alloys, environmental, pharmaceutical and synthetic samples.

Determination of copper and cobalt in alloys

In order to assess the analytical applicability of proposed method copper and cobalt were determined in certain ferrous and non ferrous alloys such as JSS-607 high speed steel, JSS-655 stainless steel and NLK-920 aluminum alloy. The alloys were dissolved separately in HCl (30.0 mL) containing a few drops of conc. nitric acid. The mixture was gently heated and the excess acid was evaporated and the requisite volume was made up by distilled water and then metals were assayed by recommended procedure. Various interfering metal ions were masked by suitable masking agents. All consistent resultant data were presented in Table 2.

Table 2 Sequential determination of copper and cobalt in some standard alloys

Sample	Taken (μg)		Found (μg)		RSD (%)	
	Cu	Co	Cu	Co	Cu	Co
JSS 607 high speed steel	2.80	2.36	2.78	2.33	0.96	1.04
	5.60	3.54	5.57	3.51	0.74	1.12
JSS 655-4 stainless steel	–	3.36	–	3.3	–	0.84
	–	3.92	–	3.8	–	0.98
NLK 920 aluminium alloy	2.90	–	2.87	–	0.96	–
	1.45	–	1.44	–	0.48	–

JSS 607 high speed steel contain (%) Si: 0.32, V:0.86, W:16.96, Mn: 0.006, S:0.006, C: 0.75, P: 0.012, Cr: 4.14, Co: 4.72, Ni: 0.58+, Cu: 0.28^a

JSS 655-4 stainless steel contain (%) Si: 0.60, Nb: 0.60, Te: 0.03, W: 0.024, Cr: 0.008, Mn: 1.58, S: 0.006, P: 0.003, C: 0.055, Cu: 0.008*, Co: 0.28, Ni: 11.48^b

NLK 920 aluminium alloy contain (%) Sn: 0.20, V: 0.05, Si: 0.78, Mg: 0.46, Zn: 0.80, Mn: 0.20, Sn: 0.20, Bi: 0.06, Pb: 0.10, Ti: 0.15, Cr: 0.27, Fe: 0.72^c, Ca: 0.03, Ga: 0.05, Cu: 0.29*

^a Interference of copper is masked by 1 mg of thiourea in the determination of cobalt

^b Interference of nickel is masked by 5 mL of 5% hydroxyl amine solution in determination of copper and cobalt

^c Interference of iron is masking with 5 mL of 5% ascorbic acid

Determination of copper in environmental sample

Vehicle exhaust particulate (1.0 g) dissolved in 18.0 mL of conc. HNO_3 , 8.0 mL of conc. HClO_4 and 2.0 mL of conc. HF in a 100 mL teflon beaker, were evaporated to a small volume, filtered through a filter paper and volume was made up to 50.0 mL by distilled water. Copper concentration was determined by recommended procedure. The interference of nickel ion was masked by 5 mL of 5%

Table 3 Determination of copper in vehicle exhaust particulates

Sample	Copper (II)		Copper found by AAS Method (μg)
	Certified value (μg)	Found ^a (μg)	
NIES, No. 8 ^b Vehicle exhaust particulate	67	67.25 \pm 1.2	67.2

NIES, No. 8^b Vehicle Exhaust Particulate contain (%) K: 0.115 \pm 0.008, Ca: 0.530 \pm 0.08, Zn: 0.104 \pm 0.005, Mg: 0.101 \pm 0.005, Al: 0.330 \pm 0.020, Na: 0.192 \pm 0.008, Sr: 89.0 \pm 3.0, Cu: 67.0, Ni: 18.5^c, Cd: 1.1 \pm 0.1, Pb: 219 \pm 9.0, As: 2.6 \pm 0.2, Cr: 25.5 \pm 1.5, V: 17.0 \pm 2.0

Sb: 6.0 \pm 0.4, Cs: 0.24 \pm Rb: 4.6, Sc: 0.55, La: 1.2, Bi: 56.0, Ag: 0.2, Se: 1.3, Mo: 6.4, Ce: 3.1, Th: 0.35, Sm: 0.20, Eu: 0.05, Lu: 0.02

^a Average of five replicate determinations \pm standard deviation

^b NIES No. 8 Iron and steel Institute of Japan, Tokyo, Japan

^c Nickel is masked by 5 mL of 5% hydroxyl amine solution for determination of copper

Table 4 Determination of copper in pharmaceutical samples

Sample	Copper (II) (mg)		
	Certified value	Proposed method ^a	AAS
Supradyn (Roche, India)	3.39	3.34 ± 0.08	3.37
Edinol capsule (Bayer, India)	6.6	6.55 ± 0.009	6.58
Multivitamins (Mayer organics, India)	18.08	18.14 ± 0.062	18.1

Supradyn (Roche, India) composition; Dried ferric sulphate^b IP : 32 mg, Zinc sulphate IP: 2.20 mg + Copper sulphate ± IP^c

Edinol capsule (Bayer, India) composition; Dried Ferrous sulphate^b IP: 30 mg + Copper sulphate IP^c

Multivitamins (Mayer organics, India) composition; Zinc sulphate IP^c: 20 mg, Manganese sulphate IP: 1.0 mg, Magnesium hydroxide IP: 30 mg + Copper sulphate IP^c

^a Average of triplicate analyses ± standard deviation

^b Interference of iron (III) is masked with 5 mL of 5% ascorbic acid

^c IP Indian Pharmacopoeia

Table 5 Sequential determination of rhodium and iridium in synthetic mixtures

Synthetic Mixture	Taken (ppm)		AAS (ppm)		Parent method (ppm)		RSD (%)	
	Rh	Ir	Found		Found		Rh	Ir
			Rh	Ir	Rh	Ir		
A	20.00	15.50	20.05	15.42	19.92	15.34	1.06	0.95
B	22.00	24.50	21.94	24.55	21.88	24.32	0.65	0.75

Synthetic Mixture A; Pd (II): 9.5, Pt (IV): 26.0, Ir (III) : 15.5, Rh (III): 20.0, Mn (II) : 20, Cu (II)^a: 9.0

Synthetic mixture B; Pd (II) : 10.0, Fe (II)^b : 9.0, Pt (IV) : 6.0, Ir (III) : 24.5, Rh (III) : 22.0, Co (II):15.00, Cu (II)^a : 13.50

^a Interference of copper is masked by 1 mg of thiourea

^b Interference of iron is masked by 5 mL of 5% ascorbic acid

hydroxylamine solution in determination of copper. All results are given in Table 3.

Determination of copper in pharmaceutical sample

The proposed method was applied for the determination of copper (II) in pharmaceutical samples such as Supradyn (Roche, India), Multivitamins (Mayer, organics) and Edinol (Bayer, India). The capsule/tablets were ignited in a muffle furnace at 250 °C for 1 h. The ash was dissolved in conc. HCl, filtered and solution was diluted by distilled water. By taking suitable aliquots of above solution, copper concentration was determined by present method and by ASS method (Table 4). The results are in good agreement.

Sequential determination of rhodium and iridium

Various synthetic mixtures containing rhodium and iridium together with other metals were prepared. These metals were determined by a general procedure after masking the interference of metal ions by using suitable masking agents. The results are presented in Table 5.

Conclusion

The main focus of our work was to synthesize a new chromogenic calixarene which is useful for multiple applications such as laboratory, environmental, pharmaceutical and industrial processes for determination of copper, cobalt, rhodium and iridium through two-phase synergistic solvent extraction. The developed method would be proved to be convenient, highly selective and accurate.

Supporting information available

A comparison of proposed method to recent spectrophotometric methods is given as supporting information.

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