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Extractive Spectrophotometric Determination of Cu(II) with Phosphoryl Derivative of *p-tert*-butylthiacalix(4)arene

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A spectrophotometric method has been developed for the determination of Cu(II) using a phosphoryl derivative of *p-tert*-butylthiacalix(4)arene as an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted in toluene at pH 8.3. The method obeys Beer's law over a range from 1 to 19 ppm. The molar absorptivity and Sandell sensitivity were 1.046×10^3 L mol^{-1} cm^{-1} and 1.6×10^{-5} µg cm^{-2}, respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Key Words: Copper, Spectrophotometric determination, Toluene, *p-tert*-butylthiacalix(4)arene.

INTRODUCTION

A number of reagents such as hydrazone[1], thiosemicarbazone[2,3], oxime[4,5], thiourea[6,7], *etc.* have been used for the determination of Cu(II). Cyclic ligands such as crown ethers[8-10] has also been used. But there is a limited number of calixarenes has been applied as an analytical reagent[11]. The synthesis of sulphur containing calix(4)arenes and their application as selective extractants towards metal ions have been reported by Yordonov *et al.*[12-14]. In almost all the cases of solvents extraction of metal ions using calixarenes, after extraction stripping of the metal ion in the aqueous phase is required for quantative determination of the metal ion. In present studies a simple, rapid and sensitive direct spectrophotometric method for the determination of Cu(II) using calix(4)arene derivative is developed.

EXPERIMENTAL

The reagent phosphorous diester amide thiacalix(4)arene (PDATCA) IUPAC nomenclature: 9,13-diepithiotetrabenzo[d,g,l.o][1,3,9,11,6,14,2,10]-tetraoxadithiadiphosphacyclohexadecin-11,23-diamine,3,7,15,19-*tetrakis*(1,1-dimethyl ethyl)-N,N,N´,N´-tetraethyl sterioisomer was synthesized by the given procedure[15]. The stock solution of Cu(II) was prepared by dissolving a weighed amount of sulphate in double distilled water containing dilute sulphuric acid, which was diluted to the desired volume with double distilled water and standardized by sodium diethyl dithiocarbamate method[16]. Absorbance and pH measurements were carried out on a Shimadzu UV-Visible 2100 spectrophotometer with 1 cm quartz cells and a digital pH meter with combined glass electrode, respectively.

General procedure for the extraction: The pH of an aliquot of Cu(II) solution was adjusted to 8.3 with dil. NH_4OH/HCl. This aqueous phase was diluted to 10 mL and equilibrated with 10 mL toluene containing 1 mL of 0.2 % PDATCA in toluene for 1 min. The organic phase was separated out and dried over sodium sulphate. The absorbance of the organic phase was taken at a wavelength of 480 nm. The aqueous phase was analyzed for its copper content by a known method.

RESULTS AND DISCUSSION

Effect of pH on the extraction of Cu(II): The extraction of copper with PDATCA has been studied over the pH range of 1.0-12.0. It was observed that the percentage extraction of copper increases up to pH 8.3 and further it decrease. Hence all the other studies were carried out at the pH of 8.3.

Absorption spectrum: The absorption spectrum of the complex Cu: PDATCA in toluene shows maximum absorption at a wavelength of 480 nm. At this wavelength, the absorption due to the reagent is negligible. Hence a wavelength of 480 nm was selected for further absorbance measurements of the complex.

Effect of salting out agents: The presence of 0.1 M salts of various alkali and alkaline metals does not show any effect on the absorbance of the Cu(II): PDATCA complex. Therefore, no salting out agent was required during the extraction.

Effect of reagent concentration: To study the effect of concentration of PDATCA on the extraction of a fixed amount of copper, varying amounts of PDATCA was added and the absorbance was measured. It was found that 1 mL of PDATCA (0.2 %) was sufficient to extract 1.5 μg of copper solution from the aqueous phase.

Effect of equilibration time and stability of the complex: The study of change in absorbance with variation in equilibration time of extraction of complex in organic solvent shows that equilibration time of 1 min is sufficient for the extraction of copper. The study of stability of colour of the complex with respect to time shows that the colour was stable for 36 h.

Calibration plot: A calibration plot of absorbance against varying copper concentration and fixed PDATCA concentration gives a linear graph in the concentration range 10-190 μg of copper (Fig. 1). This shows that the Beer's law is obeyed in this range. The molar absorptivity and Sandell sensitivity of the extracted species was calculated to be 1.046 × 10^3 L mol^{-1} cm^{-1} and 1.6 × 10^{-5} µg cm^{-2}, respectively.

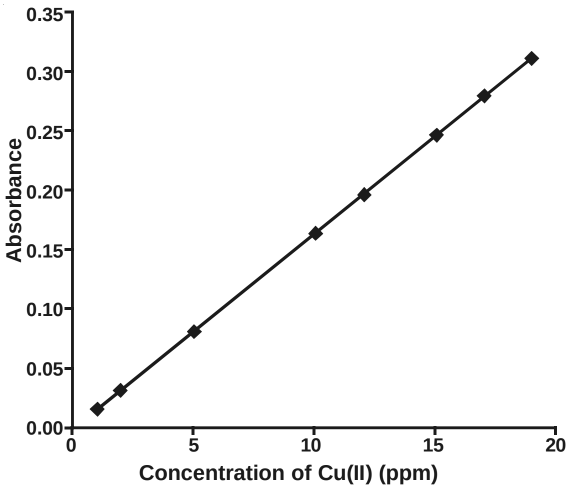

Fig. 1. Calibration plot of Cu(II) with PDATCA

Nature of extracted species: The composition of the extracted complex has been determined by Job's continuous variation method, slope ratio method (Fig. 2) and mole ratio method. From all these methods it is observed that the composition of the Cu(II): PDATCA complex is 1:1.

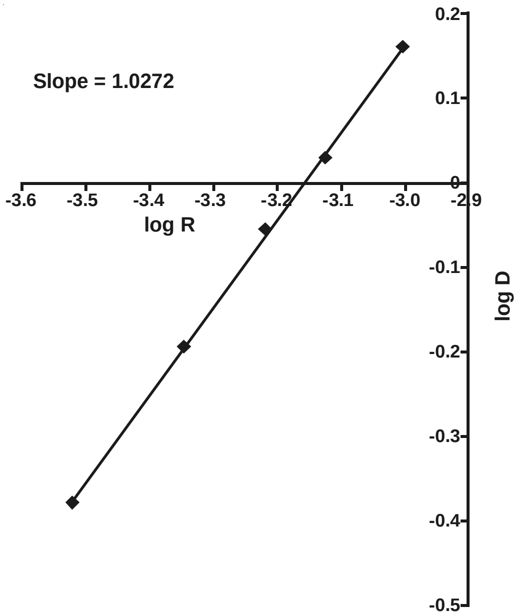

Fig. 2. log-log plot for stoichiometric ratio of metal to reagent

Effect of divalent ions and foreign ions: A number of foreign ions when present in different amounts do not interfere during the extraction. The ions which interfered were masked by an appropriate masking agent (Table-1).

TABLE-1
EFFECT OF DIVALENT IONS AND FOREIGN IONS

Ion	Tolerated ratio	Ion	Tolerated ratio	Ion	Tolerated ratio
Cl^-	1:30	$C_2O_4^{2-}$	1:15	Zn^{2+}	1:10
Br^-	1:30	I^-	1:25	Ag^+	1:5
F^-	1:30	$S_2O_3^{2-}$	1:25	Th^{4+}	1:25
ClO_3^-	1:20	Li^+	1:40	Na^+	1:30
BrO_3^-	1:15	Mg^{2+}	1:15	Co^{2+}	Masked
IO_3^-	1:20	Ca^{2+}	1:20	Ni^{2+}	Masked
SO_3^{2-}	1:25	K^+	1:30	Pd^{2+}	Masked
SO_4^{2-}	1:25	Ba^{2+}	1:35	Fe^{3+}	Masked
NO_2^-	1:30	Sr^{2+}	1:25	EDTA	Masked
NO_3^-	1:30	Al^{3+}	1:15	Tartarate	Masked
PO_4^{3-}	1:25	Be^{2+}	1:40	U^{6+}	Masked
$P_2O_7^{2-}$	1:25	Bi^{3+}	1:40	Mn^{2+}	Masked
ClO_4^-	1:20	As^{3+}	1:25	Cr^{3+}	Masked
Thiourea	1:10	W^{2+}	1:20	–	–

TABLE-2
SEPARATION OF Cu(II) WITH PDATCA FROM VARIOUS SYNTHETIC AND REAL SAMPLES

Sample	Copper found*	
	Certified value	Present method
Synthetic mixture		
Cu(100) Pt(100) Mn(100)	100 µg	99.99 µg
Cu(100) Zn(100) Cd(100)	100 µg	99.80 µg
Cu(100) Zr(100) Ag(100)	100 µg	99.50 µg
Pharmaceutical samples		
Suparadyn (Nicholas Piramal)	6.7 mg	6.6 mg
Multivitamin Capsule (Mayer Organics Ltd.)	5.0 mg	4.9 mg
Alloys		
Mg alloy BCSCRM 307	0.048 %	0.049 %
Nimonic 901 BCSCRM 387	0.28 %	0.27 %
Brass	80 %	80.05 %
Monel metal	90 %	90 %
Beer	5.48 %	5.49 %
Wine	3.70 %	3.65 %
Human hair	3.52 %	3.55 %

*Average of three independent determinations.

Precision and accuracy of the method: The precision and accuracy of the developed spectrophotometric method have been tested by analyzing ten solutions containing 150 µg of copper in the aqueous phase. The average of 10 determinations was 150.16, variance 0.36 and variation from mean at 95 % confidence limit was ± 0.42.

The proposed method was successfully applied for the analysis of the real samples such as pharmaceutical samples, alloys and many synthetic mixtures. The results were found to be in good agreement with those obtained by standard methods (Table-2).

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