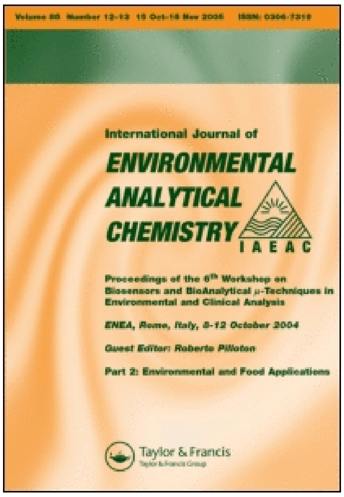

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Spectrophotometric Determination of Copper in Environmental Samples by Solid-liquid Extraction of its 9,10-Phenanthrenequinone Monoximate Complex into Molten Naphthalene

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A fairly selective and sensitive spectrophotometric method has been developed for determination of copper after extraction of its 9,10-phenanthrenequinone monoximate complex into molten naphthalene in the pH range of 6.1–8.4. At room temperature, the solid naphthalene containing the metal complex is separated by filtration, dissolved in dimethylformamide (DMF) and the absorbance measured at 470 nm against the reagent blank. Beer's law is obeyed in the concentration range, 0.0–9.6 μg of copper in 10 ml of DMF. The molar absorptivity and sensititivty are 6.30×10^4 l mol^{-1} cm^{-1} and 0.001 μg cm^{-2}, respectively. The interference of various

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ions has been studied and the method has been applied for the determination of copper in various standard reference materials, beers, wines, human hair and environmental samples.

KEY WORDS: Solid-liquid separation, naphthalene, 9, 10-phenanthrenequinone monoxime; spectrophotometry, copper determination, standard reference materials, biological materials, environmental samples.

INTRODUCTION

9, 10-Phenanthrenequinone monoxime (PQM) has been synthesized and used as an analytical reagent in the spectrophotometric determination of a few metal ions[1–4]. In this work, PQM has been employed in the extraction and spectrophotometric determination of copper by the technique of solid-liquid separation after liquid-liquid extraction. The main advantages of this method are that equilibrium distribution in the two phases is attained in a few seconds owing to the high temperature (85–90°C) and the metal chelates are dissolved merely by contact with molten naphthalene. Metal complex can be quantitatively extracted into 1–2 g of naphthalene even from 60 ml of the aqueous phase. This small amount of naphthalene containing the metal complex can easily be dissolved in 3–5 ml of the organic solvent and all of it can be taken for the analysis; thus resulting in a highly sensitive method. The technique is especially useful for those metal ions which form complexes with the reagent at a high temperature[5–8] or have low solubility in non-aqueous organic solvents at room temperature. Metal ions which form thermally unstable complexes may interfere in the usual liquid-liquid extraction spectrophotometric methods but they cannot interfere in the present case. The proposed method is found to be more sensitive and selective than many of the recent spectrophotometric methods[9–17] (Table I) and has been employed for the determination of copper in various complex materials.

EXPERIMENTAL

Reagents

Phenanthrenequinone monoxime was prepared and purified accord-

TABLE I
Sensitivities (S) of different reagents for copper

Reagent	$S/\mu g\,cm^{-2}$	Wavelength nm	Reference
Dithizone	0.0022	533	9
2, 2′-Biquinoline	0.0100	542	9
1-Pyrrolidinecarbodithioate	0.0053	435	10
3′, 5′-Dimethyl-2′-hydroxyazobenzene-4-sulphonic acid	0.0130	480	11
Morpholine-4-carbodithioate	0.0059	440	12
4-(2-Quinolylazo)phenol	0.0012	440	13
1-(2′-Amino-3′-hydroxy-pyridyl-4′-azo)venzene-4-sulphonic acid	0.0022	540	14
1-Phenyl-4, 4, 6-trimethyl-(1H, 4H)pyrimidine-2-thiol	0.0081	400	15
2-(2-Benzothiazolylazo)-5-dimethylaminobenzoic acid	0.0011	440	16
2, 4-Dihydroxyacetophenone-thiosemicarbazone	0.0045	360	17
2, 4-Dihydroxyacetophenone semicarbazone	0.0060	345	17
9, 10-Phenanthrenequinone monoxime	0.0010	470	This work

ing to the method in our previous papers[5,6] and its 1×10^{-3} M solution was prepared in ethanol. Copper sulphate solution was prepared from sample (analytical grade) in double-distilled water and standardized by known methods. Dilute solution of perchloric acid (0.2 M) or ammonia (0.2 M) was used to adjust pH. Naphthalene and DMF (analytical grade) were checked spectrophotometrically before use. To study the interference of various ions 10 mg of anions and 500 μg of cations were prepared in double-distilled water.

Equipment

Elico pH meter, SP-700/500 spectrophotometers (Pye Unicam) and a

Pye Unicam 191-atomic absorption spectrophotometer (for direct determination of copper) were used.

General procedure

To an aliquot of copper solution (0.0–9.6 μg) taken in a 100 ml beaker was added 1.0 ml of PQM solution. The pH was adjusted to 6.1–8.4. The solution was transferred to a 100 ml round bottomed flask and warmed on a water-bath at about 60°C. Naphthalene (2 g) was added and the mixture was heated on a water-bath at 85–90°C to melt naphthalene completely. The solution was shaken vigorously until naphthalene separated out as a solid mass. Naphthalene was separated from the aqueous phase by filtration, dissolved in DMF and made exactly 10 ml in a standard flask. A portion of this solution was taken in a 1 cm cell and the absorbance measured against the reagent blank. This was referred to the calibration curve constructed under similar conditions.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of phenanthrenequinone monoxime and its copper complex was recorded in naphthalene-DMF solution against water and reagent blank, respectively (Figure 1). It was observed that the complex gave absorption maximum at 470–475 nm where the reagent absorbed negligibly. All absorbance measurements were made at 470 nm.

Effect of pH

Extraction was carried out at different pH, keeping other conditions constant. The absorbance of the extract was constant in the pH range 6.1–8.4 (Figure 2).

Effect of reagent concentration

Extraction was carried out at optimum pH and varying amounts of reagent. It was found to be quantitative in the volume range 0.4–

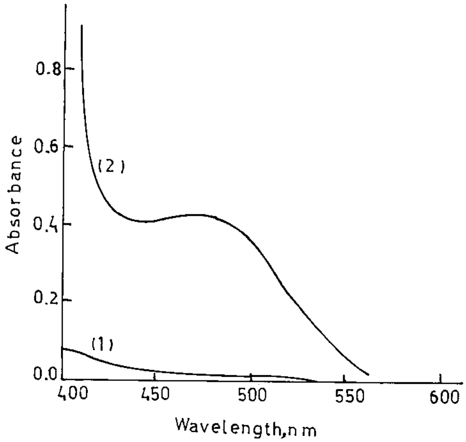

FIGURE 1 Absorption spectra of PCM and its copper complex in naphthalene-DMF solution. Cu: 4.3 μg, 1×10^{-3} M PQM: 1.0 ml, pH: 7.5 naphthalene: 2 g, reference: water for PQM (1) and reagent blank for Cu-PQM (2).

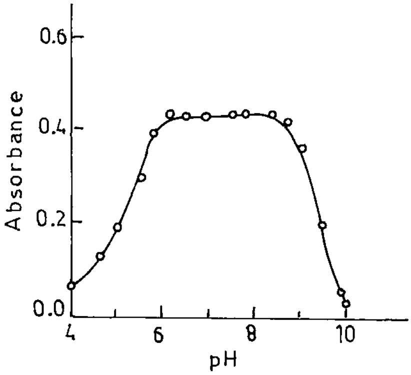

FIGURE 2 Effect of pH. Cu: 4.3 μg, 1×10^{-3} M, PQM: 1.0 ml, wavelength: 470 nm, naphthalene: 2 g, reference: reagent blank.

4.0 ml of 1×10^{-3} M PQM solution. Thus 1.0 ml of the reagent was used for subsequent studies.

Effect of naphthalene

Extraction was carried out by varying the amounts of naphthalene from 0.2–4.0 g at optimum pH and under constant conditions. It was found that the absorbance remained constant for 1.3–3.5 g of naphthalene. Below 1.3 g the extraction was incomplete and above 3.5 g it was difficult to dissolve naphthalene in limited amount of DMF (10 ml). Thus 2 g of naphthalene was used for subsequent studies.

Effect of aqueous phase

Since the amount of the organic phase is very small as compared to that of the aqueous phase the effect of the latter on extraction was studied. Extraction was quantitative when the aqueous phase did not exceed 60 ml.

Effect of standing time

Absorbance of the extract in naphthalene-DMF was constant for at least 18 hours.

Effect of electrolytes

Various electrolytes such as sodium chloride, potassium chloride, sodium nitrate and sodium acetate (0.01–0.1 M) caused no improvement in extraction indicating the absence of salting out effect.

Beer's law and sensitivity

Under the optimum conditions described above Beer's law is obeyed up to 9.6 μg of copper in 10 ml of the DMF solution. The molar absorptivity and sensitivity in terms of Sandell's definition are calculated to be 6.30×10^4 $1\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$ and 0.001 μg/cm^2. Ten replicate solutions containing 4.3 μg of copper gave a mean absorbance of 0.427 with a relative standard deviation of 0.96%.

Effect of diverse ions

Different amounts of anions and metal ions were added separately to 1.0 ml of the reagent in the presence of copper (4.3 μg) and then copper was determined according to the general procedure. Among the anions examined (Table II) oxalate, citrate, tartrate, orthophos-

TABLE II
Effect of diverse anions

Alkali salt added	Amount of annion added (mg)	Absorbance at 470 nm
—	—	0.430
Sodium fluoride	10	0.425
Sodium chloride	10	0.425
Sodium sulphate	10	0.430
Sodium nitrate	10	0.428
Potassium bromide	10	0.426
Potassium iodide	10	0.428
Sodium oxalate	10	0.398
	7	0.425
Sodium citrate	10	0.390
	6	0.423
Sodium potassium tartrate	10	0.388
	4	0.425
Sodium orthophosphate	10	0.380
	2.5	0.423
Sodium carbonate	10	0.428
Potassium thiocyanate	10	0.425
EDTA (disodium)	10	0.001
	1	0.008
	0.1	0.010

Cu: 4.3 μg, 1×10^{-3} M, PQM = 1.0 ml, naphthalene = 2.0 g.

phate and EDTA interfered in the determination of copper but their relatively low amounts could be tolerated except EDTA probably due to higher stability of copper-EDTA complex. Of the metal ions examined (Table III) Fe(III), Co(II), Ni(II), Pd(II), Os(VIII) form complexes with the reagent so they interfered seriously in the determination of copper, but their interference was eliminated by pre-extraction at pH (Fe: 2.0, Co: 3.5, Ni: 10.5, Pd: 2.0 and Os: 10.5). Thus the method is fairly selective and has been applied to the determination of copper in complex materials.

TABLE III
Effect of diverse cations

Metal salt added	Amount of cation added (μg)	Absorbance at 470 nm	Remarks
—	—	0.430	—
Iron(III)chloride	500	0.424	Eliminated by pre-extraction at ph 2.0
	250	0.428	Eliminated by pre-extraction at pH 2.0
Palladium(II)nitrate	500	0.426	Eliminated by pre-extraction at pH 2.0
	250	0.430	Elimiated by pre-extraction at pH 2.0
Cobalt(II)chloride	500	0.425	Eliminated by pre-extraction at pH 3.5
	250	0.429	Eliminated by pre-extraction at pH 3.5
Nickel(II)nitrate	500	0.426	Eliminated by pre-extraction at pH 10.5
	250	0.428	Eliminated by pre-extraction at pH 10.5
Osmium(VIII)tetraoxide	500	0.224	Eliminated by pre-extraction at pH 10.5
	250	0.228	Eliminated by pre-extraction at pH 10.5
Lead(II)nitrate	500	0.430	—
Magnesium(II)chloride	500	0.430	—
Zinc(II)sulphate	500	0.428	—
	250	0.430	
Manganese(II)sulphate	500	0.430	—
Tin(II)chloride	500	0.429	—
Silver(I)nitrate	500	0.433	—
	250	0.430	

TABLE III (continued)

Metal salt added	Amount of cation added (μg)	Absorbance at 470 nm	Remarks
Cadmium(II)chloride	500	0.430	—
Mercury(II)nitrate	500	0.431	—
Aluminium(III)nitrate	500	0.431	—
Ammonium molybdate	500	0.430	—
Ammonium vanadate	500	0.428	—
	250	0.430	
Bismuth(III)nitrate	500	0.429	—
Sodium arsenite(III)	500	0.426	—
	250	0.429	
Tartar emetic	500	0.427	—
	250	0.429	
Rhodium(III)chloride	500	0.438	—
	200	0.431	
Ruthenium(III)chloride	500	0.436	—
	200	0.430	
Iridium(III)chloride	500	0.440	—
	200	0.432	
Platinum(IV)chloride	500	0.433	—
	250	0.431	
Chromium(III)chloride	500	0.435	—
	200	0.431	
Gold(III)chloride	500	0.440	—
	200	0.432	
Sodium tungstate	500	0.431	—

Condition same as Table II.

Determination of copper in standard reference materials

A 0.1–1.0 g sample of the alloy was completely dissolved in 20–30 ml of hydrochloric acid (1:1) on a water-bath. Then 3–5 ml of 30% hydrogen peroxide were added to it. The excess of peroxide was decomposed by heating the solution on a water-bath. The mixture was cooled and filtered through a filter paper. The filtrate was diluted to 500 ml with distilled water in a flask. An appropriate volume of this solution was taken and the copper was determined by the general procedure. The results are given in Table IV.

Determination of copper in beers and wines

A 50 ml of beer or wine sample was evaporated to dryness. The residue was ashed and dissolved in 1000 ml of 1:1 nitric acid solution. Four ml of this sample solution were taken and analyzed by the general procedure. The results are given in Table V.

Determination of copper in human hair

A 10 g sample of human hair was taken and dissolved in 30 ml of concentrated nitric acid and 3.0 ml of concentrated perchloric acid by heating. This solution was cooled, filtered and diluted to 1000 ml with distilled water in a standard flask. Two ml of this solution were taken and the copper was determined by the general procedure (Table V).

Determination of copper in flyash

A 10 g of flyash sample of I.P. thermal power station (New Delhi) was digested with nitric acid for half an hour and its solution diluted to the mark in a 500 ml standard flask. Two ml of this solution were taken and copper determined by the proposed method (Table V).

Determination of copper in waste water

A 500 ml of the composite sample of waste water (Shantivana drain, I.P. Thermal power station and Okhla Sewage, New Delhi) was reduced to 100 ml by evaporation in the presence of a few drops of nitric acid. One ml of this solution was taken for the analysis of these samples. The results are given in Table V. In all the cases the results were compared with atomic absorption spectrophotometric method (AAS).

TABLE IV

Determination of copper in alloys

Complex material	Certified composition (%)	Amount of copper taken (μg)	Amount of copper found (AAA) (μg)	Amount of copper found by present method (μg)	Average (μg)	Relative error (%)
N.B.S., SRM-85b Aluminium alloy	Ni:0.084, Mg:1.49 Mn:0.61, Cr:0.21 Si:0.18, Fe:0.24 Zn:0.03, Ti:0.022 Pb: 0.021, Ga:0.019 V:0.006, Cu:3.99	3.99	4.00	4.05 3.95 4.10 3.95 4.10	4.03	1.00
N.B.S., SRM-94c Die casting alloy	Mn:0.014, Al:4.13 Sn:0.006, Fe:0.018 Cd:0.002, Mg:0.042 Pb:0.006, Cu:1.01 Ni:0.006	5.05	5.10	4.95 5.15 5.10 5.20 5.15	5.11	1.18
N.B.S., SRM-627 Zinc base alloy	Al:3.88, Pb:0.0082 Fe:0.023, Sn:0.0042 Cd:0.0051, Mn:0.014 Cr:0.0038, Ni:0.0029 Si:0.021, Mg:0.030 Cu:0.132	6.60	6.65	6.75 6.80 6.50 6.60 6.65	6.66	0.90
N.B.S., SRM-629 Zinc base alloy	Al:5.15, Pb:0.0135 Fe:0.017, Sn:0.012 Cd:0.0155, Mn:0.0017 Cr:0.0008, Si:0.078 Ni:0.0075, Mg:0.094 Cu:1.50	7.50	7.45	7.80 7.45 7.60 7.40 7.70	7.59	1.20

Samples standardized by AAS.

TABLE V

Determination of copper in beers, wines, human hair and environmental samples

Sample		Copper found by present method (μg/ml)	Average (μg/ml)	Relative error (%)	Copper found by AAS method[a] (μg/ml)
Beer	A	5.60, 5.45, 5.35, 5.40, 5.50	5.45	1.11	5.40
	B	3.85, 3.90, 3.80, 3.85, 3.80,	3.84	1.05	3.80
	C	6.45, 6.40, 6.40, 6.50, 6.55,	6.46	0.61	6.50
	D	7.40, 7.50, 7.35, 7.65, 7.55	7.49	0.79	7.55
	E	6.30, 6.25, 6.40, 6.10, 6.35	6.28	1.10	6.35
Wine	A	4.50, 4.60, 4.35, 4.60, 4.55	4.52	0.66	4.55
	B	3.75, 3.80, 3.70, 3.85, 3.80	3.78	0.80	3.75
	C	6.00, 6.20, 6.05, 5.90, 6.15	6.06	1.00	6.00
	D	5.50, 5.55, 5.30, 5.40, 5.35	5.42	1.30	5.35
	E	4.30, 4.10, 4.40, 4.35, 4.20	4.27	0.70	4.30
Human hair	A	2.10, 1.95, 2.00, 2.00, 2.15	2.04	0.48	2.05
	B	2.45, 2.40, 2.50, 2.40, 2.60	2.47	1.20	2.50
	C	3.15, 3.20, 3.25, 3.10, 3.15	3.17	0.93	3.20
	D	2.30, 2.20, 2.40, 2.35, 2.45	2.34	1.26	2.37
	E	4.50, 4.35, 4.40, 4.60, 4.45	4.46	0.88	4.50

TABLE V (continued)

Sample		Copper found by present method (μg/ml)	Average (μg/ml)	Relative error (%)	Copper found by AAS method[a] (μg/ml)
Environmental samples					
Flyash	A	4.90, 5.00, 5.15, 4.80, 4.95	4.96	0.80	5.00
	B	4.80, 4.60, 4.80, 4.70, 4.50	4.68	1.05	4.73
	C	5.45, 5.50, 5.35, 5.60, 5.55	5.29	1.12	5.35
	D	5.10, 5.20, 5.00, 5.05, 4.95	5.06	0.78	5.10
Waste water Shantiva drain, Delhi	A	4.95, 4.80, 4.80, 4.90, 4.65	4.78	1.035	4.83
	B	4.40, 4.35, 4.50, 4.35, 4.50	4.42	0.67	4.45
	C	3.40, 3.50, 3.40, 3.50, 3.25	3.41	1.15	3.45
	D	4.25, 4.10, 4.35, 4.25, 4.40	4.27	0.92	4.31
I.P. thermal power station, Delhi	A	1.20, 1.15, 1.20, 1.25, 1.30	1.22	0.82	1.21
	B	1.50, 1.45, 1.45, 1.55, 1.40	1.47	1.39	1.45
	C	1.00, 1.10, 1.10, 1.00, 1.10	1.06	0.95	1.05
	D	1.65, 1.70, 1.75, 1.65, 1.70	1.69	0.58	1.70
Okhla sewage, Delhi	A	1.95, 2.00, 1.95, 1.95, 2.00	1.97	1.02	1.95
	B	1.50, 1.55, 1.50, 1.45, 1.50	1.50	1.31	1.52
	C	2.10, 2.15, 2.10, 2.20, 2.15	2.14	0.94	2.12
	D	2.25, 2.30, 2.35, 2.20, 2.35	2.29	0.88	2.27

[a] Average of fine determinations.

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