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Original Scientific Paper

The Use of Phenanthrenequinonedioxime Supported on Naphthalene for the Preconcentration and Determination of Copper in Alloys and Human Hair

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Solid chelating compound, phenanthrenequinonedioxime (PQDO), supported on naphthalene, provides a simple, rapid and economical means of preconcentrating copper in alloys and biological samples. Copper forms a chelate with PQDO supported on naphthalene in the column at pH 1.8~8.4. The metal complex and naphthalene are dissolved out of the column with 5 ml of dimethylformamide (DMF) and the absorbance is measured by an atomic absorption spectrometer at 324 nm. A calibration curve is linear over the concentration range 0.5~12.0 μg of copper in 5 ml of the final solution. The preconcentration factor is 80. The sensitivity for 1% absorption is 0.039 μg/ml (0.153 μg/ml for the direct AAS method from the aqueous medium). The method has been used for the determination of copper in various standard alloys and biological samples.

INTRODUCTION

Vicinal α-dioximes, such as dimethylglyoxime (DMG), α-furldioxime, α-benzildioxime, 1,2-cyclohexanedionedioxime (Nioxime) and 1,2-cycloheptanedionedioxime (Heptoxime), have drawn a considerable attention of many researchers because of their high selectivity to diverse metal ions. They have been widely used as analytical reagents for the analyses of transition metals, especially nickel and palladium since the discovery of dimethylglyoxime by Tshugaeff.[1] Nickel and palladium are coordinated to the functional group C(NOH)–C(NOH) of two dioxime molecules, forming a four membered chelate ring of high stability.[2,3]

Recently, some adsorbents such as thiol cotton,[4] siland glass beads,[5,6] C_{18}-bonded silica gel,[7] amberlite XAD-4,[8] cellulose,[9] silica gel[10] and a few metal oxides and hydroxides[11] have been reported for the preconcentration of some metal ions. Although some of these are fairly effective, their preparation is sometimes lengthy and requires rigid control of the conditions. Furthermore, the desorption of the metal complex is carried out by the slow process of eluation, making the procedure more time consuming.

A chromatographic method has been developed in this laboratory for the separation and preconcentration of metals by using various types of chelating agents and ion-pairs supported on naphthalene.[12-14] In the present communication, the analytical procedure for the preconcentration of copper with phenanthrenequinonedioxime (PQDO) supported on naphthalene is described. The developed procedure is so simple that only the metal solution has to be passed through the column. The metal ion retained on the adsorbent is not eluted even after washing with water but can be dissolved out with a suitable solvent from the column along with naphthalene. Interference due to diverse ions has been studied and conditions have been developed for the determination of copper in alloy and biological samples.

EXPERIMENTAL

Reagents

Standard copper solution (2 ppm) was prepared by diluting 1000 ppm atomic absorption standard copper chloride solution with double-distilled water. Buffer solutions were prepared by mixing an appropriate ratio of 1 M aqueous ammonia and 1 M ammonium acetate solution. Naphthalene, DMF and all other reagents were of analytical reagent grade. Double-distilled water was used throughout.

Preparation of PQDO

In a 500 ml flask, 4 g of phenanthrenequinone was taken, and it was mixed with 4.5 g of hydroxylamine hydrochloride, 4.8 g of barium carbonate and 100 ml of ethanol. The mixture warmed was stirred with a constant hot plate stirrer and then refluxed for 5 hours. After filtration, the filtrate was allowed to stand for one night. The dioxime compound was recrystallized twice from ethanol and dried (m.p. 203±1 °C; yield, 55%).[15]

Preparation of Loaded PQDO Naphthalene Materials

Acetone solution of PQDO (3 g in 80 ml) was stirred on a hot plate stirrer arrangement at 40 °C, along with 10 ml of distilled water. Then to it 10 g naphthalene was added. This acetone solution of the chelating agent and naphthalene was added to 1000~1500 ml of distilled water with constant stirring at room temperature. The coprecipitated mixture was stirred for 3 hours and allowed to stand for 12 hours. The supernatant solution was aspirated by a siphon and then the mixture was washed twice with distilled water. This was a slurry of PQDO-naphthalene in water.

Apparatus

A Perkin-Elmer, Model 403 atomic absorption spectrophotometer and a Toa-Dempa HM-5A pH meter were used. All the absorption measurements were carried out under the operating conditions given below: Wavelength, 324 nm; slit setting, 4 (7 nm); current, 15 mA; acetylene flow, 35 (pressure 0.6 kg/cm^2), and air flow, 57 (pressure 2.1 kg/cm^2). A funnel-typed glass tube of 60 mm in length and 6 mm i.d. was used as a chromatographic column. The column was fitted with cotton wool and then filled with the naphthalene-chelating agent material to give a height of 0.5~0.7 cm.[13]

General Procedure

An aliquot of the copper solution containing 0.5~12.0 μg of copper was placed in a 20 ml beaker and to this *ca.* 0.5 ml of the acetate buffer (pH 4.3) was added. The sample solution was diluted to 18 ml with distilled water. Before this solution was passed through the column packed with PQDO-naphthalene material at a flow rate of 0.5 ml/min, the column was conditioned to pH 4.3 by passing 3~4 ml of the buffer. After the sample solution was passed through the column, the packing was washed with a small volume of distilled water and then aspirated strongly for a few minutes by pushing the naphthalene material with the flatted glass rod till naphthalene crystals appeared from the outlet of the column on dissolving it with solvent. The metal complex along with naphthalene was dissolved out with 5 ml of DMF. This solution was aspirated into an air-acetylene flame and the absorbance measured at 324 nm.

RESULTS AND DISCUSSION

Retention Characteristics of PQDO

Copper forms the chelate with 2 moles of the dioxime molecule on the surface of naphthalene after passing through the column. The amount of copper retained is proportional to the amount of PQDO. The colored band of the chelate was clear when PQDO was more than 2 g.

Reaction Conditions

The retention of copper was constant and maximal on PQDO-naphthalene material in the pH range 1.8~8.4. The retention of copper was *ca.* 100%. In subsequent work, the pH was adjusted to 4.3 with the buffer. Addition of 0.2~4.0 ml of the acetate buffer (pH 4.3) caused no variation in the retention of copper and 1.0 ml of the buffer was used for further study.

The flow rate was varied from 0.2~4 ml/min. The retention of copper did not cause any effect up to 1.3 ml/min. The flow rate of 0.5 ml/min was selected.

The retention capacity of the chelating agent supported on naphthalene was determined by the batch method. This experiment was carried out by taking 500 μg of copper.[14] The maximum capacity was 5.3 mg/g of PQDO. The retention capacity of copper was proportional to the amount of PQDO on naphthalene.

The effect of the volume of aqueous phase on the retention of copper was studied between 10 and 1000 ml. The retention remained constant and maximal when the volume of the aqueous phase did not exceed 400 ml whereas it decreased gradually with increasing the volume of aqueous phase. This may be due to the increase of the solubility of the chelate for water. In this experiment, 20 ml of aqueous phase was used for convenience.

An attempt was made to dissolve the copper-PQDO chelate along with naphthalene from the column. The solid mass was insoluble in many nonaqueous solvents. The chelate is soluble in *n*-butylamine, dioxane and DMF. As a small volume of solvent is required for dissolution of the chelate, it is essential to select the solvent which has high solubility to the chelate. DMF was found to be the most suitable solvent. It was found that 2~3 ml of this solvent was enough to dissolve the mixture, further enhancing the sensitivity of the method. It is also necessary to eliminate the surplus water attached to naphthalene because of the appearance of naphthalene crystals.

Under the optimum conditions described above, a calibration curve for copper was constructed at 324 nm. It was found to be linear over the concentration range 0.5~12

μg in 5 ml of DMF solution. The sensitivity for 1% absorption was 0.039 μg/ml for the direct AAS method from the aqueous medium). Eight replicate determinations of 6 μg of copper gave a mean absorbance of 0.136 with a relative standard deviation of 0.7%.

Effect of Diverse Ions

Different amounts of metal ions and alkali metal salts were added individually to a solution containing 6 μg of copper, and the general procedure applied. The tolerance limit (error < 3%) is given in Table I. Many of the salts can be tolerated up to g~mg levels. EDTA (5 μg) and KCN (100 μg) could be tolerated in the determination of copper. Among the metal ions studied, most metal ions did not interfere with mg-levels. Fifty μg of V(V) could also be tolerated. Hence, the proposed method is highly selective and can be directly applied to the analysis of copper in various complex materials without any preliminary separation.

TABLE I

Effect of diverse salts and metal ions

Salt or ion	Tolerance limit
KNO_3, NaCl, $CH_3COONa \cdot 3H_2O$, NH_4Cl, Na_2SO_4, KH_2PO_4 potassium sodium tartrate, ammonium citrate	1 g*
$NaClO_4 \cdot H_2O$	400 mg*
NH_4F	300 mg*
KI	100 mg*
KSCN	10 mg*
$K_2C_2O_4$	1 mg*
thiourea	500 μg
KCN	100 μg
disodium EDTA	5 μg
Mg(II), Ca(II), W(VI), Mn(II), Pb(II), Al(III), Co(II), Ag(I)	10 mg*
Ni(II)	7 mg*
Zn(II), Cr(III), Cr(VI)	5 mg*
Pb(II), Cd(II)	1 mg*
Au(III)	1 mg*
Fe(II)	500 μg*
V(V)	50 μg

* Maximum amount tested. Cu(II): 6 μg. The pH of the solution was adjusted to 2.0~2.5 to avoid precipitation of metal hydroxides. Wavelength: 324 nm.

Determination of Copper in Standard Alloys and Human Hair

A 0.1~1.0 g sample of the standard alloy (aluminium alloy, zinc alloy and magnesium alloy) was completely decomposed with HCl (1+1) by heating on a water-bath. After dissolution, 1 ml of H_2O_2 (30%) was added. The excess of H_2O_2 was decomposed by heating. The solution was cooled, filtered and diluted to 100 ml with distilled water in a standard flask.

Human hair (5 g) was washed with ethanol and detergent and dried in desiccator. This was placed in a 100-ml Kjeldahl flask. 15 ml of concentrated nitric acid was added and allowed to stand for one night. This was washed on a sand bath. Then, 1.5 ml of concentrated perchloric acid was added to it and digested completely. The solution was cooled, filtered and diluted to 50 ml with distilled water in a standard flask. An aliquot of the solution was placed in a beaker and copper was determined by the general procedure. The results (Table II) are in agreement with those obtained by the DDTC-MIBK method.[16]

TABLE II

Determination of copper in alloys and human hair

Sample	Composition %	% copper	
		certified value	found[a]
N.B.S., SRM-85b	Mn:0.61, Si:0.18, Ni:0.084, Cr:0.211 V:0.006, Ti:0.022, Ga:0.019, Fe:0.24, Pb:0.021,Mg:1.49,Zn:0.030	3.99	3.93±0.07
N.B.S., SRM-94c zinc alloy	Mn:0.014, Ni:0.006, Sn:0.006, Al:4.13, Cd:0.002, Fe:0.018, Pb:0.006, Mg:0.042	1.01	1.01±0.03
N.B.S., SRM-171 magnesium alloy	Mn:0.45, Si:0.0118, Ni:0.0009, Al:2.98, Pb:0.0033, Fe:0.0018, Zn:1.05	0.0112	0.0117±0.0005
Human hair			22.818±0.256(μg/g) 19.694±0.529(μg/g)[#]

[a] Mean of four determinations. pH:2.0~2.5. [#] DDTC-MIBK method.[13]

CONCLUSION

The combined use of the column and some chelating agents such as PQDO for the chromatographic preconcentration of metal ions offers many advantages: economical, only a small amount of the naphthalene (0.1 g) was used and this too can be dissolved in 2~3 ml of organic solvent; rapid, the retained metal in the column is dissolved by organic solvent instead of eluation. The selectivity of the method may be further improved by the use of other optical and electroanalytical techniques of analysis. The column preconcentration procedure has proved effective for the determination of trace metals in alloys and biological samples and may be employed safely for environmental samples. The characteristic of the proposed method is that it requires only a simple funnel of funnel-shaped column.

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SAŽETAK

Upotreba fenantrenkinondioksima na naftalenu za predkoncentriranje i određivanje bakra u legurama i ljudskoj kosi

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Kruta kelatizirajuća tvar, fenantrenkinondioksim (PQDO), nanesen na naftalen kao nosač, jednostavno je, brzo i ekonomično predkoncentriranje bakra u legurama i biološkim uzorcima. Bakar tvori kelate s PQDO na naftalenskom nosaču u koloni kod pH 1,8-8,4. Metalni kompleks i naftalen otapaju se s kolone s 5 mL dimetilformamida te se aspsorpcija mjeri atomskim apsorpcijskim spektrometrom pri 324 nm. Kalibracijska krivulja ima linearni dio u koncentracijskom području od 0,5 do 12,0 μg bakra u 5 mL otopine. Faktor predkoncentriranja iznosi 80. Osjetljivost za 1% apsorpciju je 0.039 μg/ml (0.153 μg/L za direktnu AAS metodu iz vodenog medija). Metoda je korištena za određivanje bakra u raznim standardnim referentnim materijalima i biološkim uzorcima.