

Determination of Trace Copper by FAAS after Solid Phase Extraction and Preconcentration onto Amberlite XAD-2 Loaded with Nitroso-R Salt

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A procedure for the separation and preconcentration of trace amounts of copper is proposed. It is based on the adsorption of copper(II) ions solution onto a column of Amberlite XAD-2 resin loaded with disodium 1-nitroso-2-naphthol-3, 6-disulfonate (nitroso-R salt). Copper is quantitatively retained on the column in the pH range 5.5-7.8 at a flow rate of 2 mL min⁻¹. The copper complex eluted with 5 mL of dimethylformamide (DMF) and copper was measured by flame atomic absorption spectrometry (FAAS) at 324.8 nm. In this case, 0.10 µg of copper can be concentrated in the column from 800 mL of aqueous sample, where its concentration is as low as 0.125 ng mL⁻¹. Eight replicate determinations of 1.0 µg mL⁻¹ of copper in the final DMF solution gave a relative standard deviation of 1.8%. The sensitivity for 1% absorption was 27.5 ng mL⁻¹. The interference of a large number of anions and cations was studied and the optimized conditions developed were utilized for the trace determination of copper in various environmental and standard samples.

Key Words: Amberlite XAD-2, flame atomic absorption spectrometry, solid phase extraction of copper, standard alloys and biological samples.

Introduction

Disodium 1-nitroso-2-naphthol-3,6-disulfonate (nitroso-R salt) was introduced in 1921 by Van Klooster for the detection of cobalt¹ and then subsequently used by various investigators for the determination of small quantities of metals in various samples²⁻⁵. Preliminary experiments indicated that metal ions like Cu²⁺ also react with this reagent and form colored water soluble anionic complex.

Copper is an essential element not only for life in mammals but also for plants and lower forms of organisms. Copper is important not only because of its toxicity at high levels but also because it is an essential element. It is usually used as an algacide and herbicide^{6,7}. In natural water and biological samples its level is low, and previous steps of separation and enrichment are usually required for its determination. Many

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preconcentration procedures for copper determination⁸⁻¹⁹ have been developed and they involve different analytical techniques and several materials. Among the methods of preconcentration reported are liquid-liquid extraction using dithiocarbamate⁸ and trioctylmethylammonium chloride⁹ as complexing reagents, coprecipitation with magnesium hydroxide as collector¹⁰, precipitation as rubeanic acid complex and filtration using a membrane filter¹¹, and also several systems of adsorption that use sorbents such as polyurethane foam loaded with diethyldithiocarbamate¹², activated carbon^{13,14}, Amberlite XAD resins^{15,16}, naphthalene¹⁷⁻²¹, benzophenone²² and silica gel loaded with diethyldithiocarbamate²³. Solid phase extraction¹²⁻²³ has received more acceptance due to a number of possible advantages including availability and easy recovery of the solid phase, achieving high preconcentration factors and ease of separation and enrichment using continuous flow systems. This paper proposes an analytical procedure for the determination of trace copper by FAAS, using a column packed with Amberlite XAD-2 resin loaded with nitroso-R for preconcentration and separation. Amberlite XAD-2 (polystyrene-divinylbenzene polymer) is a widely used resin in preconcentration procedures, because of its good physical and chemical properties such as porosity, high surface area, durability and purity¹⁵. The metal complex can easily be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and then the copper is determined by atomic absorption spectrometry. The interference of a number of metal ions and anions in the determination of copper has been studied in detail. The developed method is found to be highly sensitive and selective and has been employed for the determination of copper in complex materials.

Experimental

Apparatus and reagents

A Shimadzu AA 670 flame atomic absorption spectrophotometer was used in the following conditions: wavelength: 324.8 nm, lamp current: 3.0 mA, slit width: 0.5 nm, burner height: 6.0 mm, acetylene flow: 1.8 L min⁻¹, air flow: 8.0 L min⁻¹. A Beckman pH meter was employed for pH measurements. The glass column, having a stopcock and a porous disk, was 6 cm long and 6 mm in diameter. A small amount of glass wool was placed on the disk to prevent the loss of resin beads during sample loading. All glassware and the column were washed with a mixture of concentrated sulfuric acid and concentrated nitric acid (1+1) before use. All reagents were of analytical reagent grade. A standard copper solution was prepared from copper(II) nitrate in distilled water and standardized by known methods²⁴. A 0.1% solution of 1-nitroso-2-naphthol-3,6-disulfonate acid (nitroso-R) was prepared in distilled water. Buffer solutions of pH 3-6, 6-8 and 8-11 were prepared by mixing appropriate ratios of 0.5 M acetic acid and 0.5 M sodium acetate, 0.1 M sodium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate, and 0.5 M ammonia and 0.5 M ammonium acetate, respectively. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively. Dimethylformamide (DMF) was obtained from Merck.

Preparation of Amberlite XAD-2 column loaded with nitroso - R

Amberlite XAD-2 was treated with an ethanol:hydrochloric acid:water (2+1+1) solution overnight at ambient temperature. Then the resin was rinsed with deionized water until the supernatant water pH became neutral. The packing of the column must be done using ethanol as eluent since water makes resin beads

float. The resin was saturated with the reagent by passing 3.0 mL of a 0.1% nitroso-R solution at a flow rate of 1 mL min⁻¹. The resin was loaded with 13 mg of nitroso-R per gram of resin. The flow rate of the solution was controlled using the stopcock of the column. Afterwards it was washed with water until reagent excess was eliminated from the resin. All experiments were done in the glass column (60 mm × 6 mm), having a stopcock and a porous disk. It was plugged with glass wool and then filled with the XAD-2 to a height of 1.0-1.2 cm (0.2 g). Before sample loading the column must be preconditioned by passing a buffer solution through it. Then the column can be used repeatedly at least 10 times.

Procedure for the sorption of copper on the column

Sample solution (25 to 800 mL) containing 0.25 to 30.0 µg of copper ions was put into a beaker and 2 mL of buffer solution pH 6.5 was added. This solution was passed through the column at a flow rate of 2.0 mL min⁻¹. The flow rate of the solution was controlled using the stopcock of the column. Then the column was washed with 10 mL of deionized water and the adsorbed copper chelate on the column was eluted with 5.0 mL of DMF at a flow rate of 1.0 mL min⁻¹. The eluent was collected in a 5.0 mL volumetric flask and copper was determined by flame atomic absorption spectrometry.

Results and Discussion

In order to determine the optimum conditions for the quantitative extraction of copper using Amberlite XAD-2 resin loaded with nitroso-R, several parameters were assessed.

Reaction conditions

These were established with the use of 5.0 µg of copper. The sorption of copper on the column was found to be maximum in the pH range 5.5-7.8 (Figure). In subsequent studies, the pH was maintained at approximately 6.5. Addition of 0.5-10 mL of the buffer did not affect the retention of copper and the use of 2 mL is recommended.

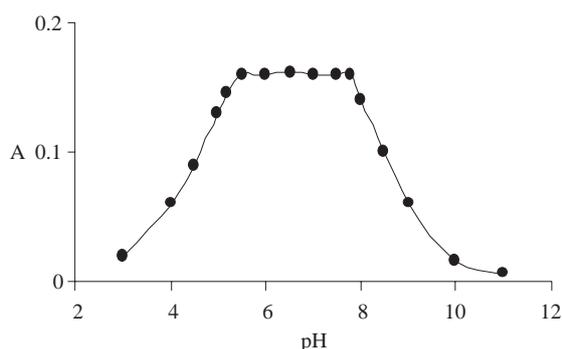


Figure. Effect of pH on sorption of copper on the column. Conditions: Cu, 5.0 µg in 40 mL of aqueous solution; flow rate of sample, 2 mL min⁻¹; eluent, 5.0 mL of DMF.

The flow rate of the sample solution was varied from 0.2 to 5.0 mL min⁻¹. The flow rate of the solution was controlled using the stopcock of the column. It was found that a flow rate of 0.2-4.0 mL min⁻¹ did not affect adsorption. A flow rate of 2 mL min⁻¹ was used in all experiments.

The volume of the aqueous phase was varied in the range 10-900 mL under the optimum conditions, keeping the other variables constant. It was observed that the signal height was almost constant up to 800 mL (preconcentration factor of 160). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase.

Sorption capacity

The sorption capacity of the Amberlite XAD-2 resin loaded column with nitroso-R for copper was also evaluated. In this case, a column containing 0.2 g of Amberlite XAD-2 resin was used and different volumes of 20.0 mg L⁻¹ copper solution were passed through the column. Copper was determined in fractions of solution until the analyte concentration became detectable. The resin had a sorption capacity of 1.2 mg of copper per gram of XAD-2 resin.

Choice of solvent

A number of solvents were tried, to elute the metal complex from the XAD-2 resin. Since the metal complex is dissolved in a small volume (3-5 mL) of solvent, it is essential to select a solvent in which the chelate is highly soluble and one which is also sensitive for atomic absorption spectrometric measurements. DMF was preferred because of the high solubility and stability of the metal complex. It was found that 2-5 mL of this solvent was sufficient to elute the entire mixture, thus further enhancing the sensitivity of the method. All of the optimized parameters are given in Table 1.

Table 1. Optimized parameters for method.

Optimized parameters	Found
pH	6.5
Eluent	DMF
Volume of the eluent	5.0 mL
Volume of the buffer	2.0 mL
Volume of the aqueous phase	10-800 mL
Flow rate of sample	2.0 mL min ⁻¹

Calibration and sensitivity

Since it is possible to retain 0.10 µg of copper from 800 mL of solution passing through the column, elution with 5.0 mL of DMF gives a detection limit of 0.125 ng mL⁻¹ for copper at the optimal instrumental settings. The linearity was maintained in the concentration range 0.31 ng mL⁻¹ to 3.0 µg mL⁻¹ copper in aqueous solution if copper was collected from 800 mL and 10 mL aqueous solutions for the lowest and highest concentration or 0.05 to 6.0 µg mL⁻¹ copper in the final DMF solution with a correlation factor of 0.9995. Eight replicate determinations of 5.0 µg of copper in 5.0 mL of DMF solution gave a mean absorbance of 0.160 with a relative standard deviation of 1.8%. The sensitivity for 1% absorption was 27.5 ng mL⁻¹.

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 5.0 µg of copper (40 mL solution) and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ion required to cause -3% errors in the determination of copper. The results obtained are given

in Table 2. Among the salts examined, most could be tolerated up to gram or milligram levels except for EDTA. Thus, the proposed method is relatively selective and can be used for the determination of copper in alloys and biological samples without any prior separation.

Table 2. Tolerance limits for diverse salts and metal ions on the determination of 5.0 μg of copper*.

Salt or ion	Tolerance limit
$\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$, KNO_3	1 g
K_2SO_4	200 mg
KI, NaF	95 mg
NH_4Cl , $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$, K_2CO_3	65 mg
Sodium potassium tartrate	25 mg
Thiourea, KSCN, NaClO_4	16 mg
Sodium oxalate, $\text{Na}_2\text{S}_2\text{O}_3$	32 mg
Trisodium citrate	10 mg
Na_2 EDTA	70 μg
Mg(II) from $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	190 mg
Ca(II) from $\text{Ca}(\text{NO}_3)_2$	95 mg
Cd(II) from $\text{Cd}(\text{NO}_3)_2$, Sb(III) from SbF_3 , Pb(II) from $\text{Pb}(\text{NO}_3)_2$	30 mg
Ti(IV) from TiS_2	30 mg
Zn(II) from $\text{Zn}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, Al(III) from $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$	13 mg
Cr(VI) from CrO_3 , Cr(III) from $\text{Cr}_2(\text{SO}_4)_3$	9.5 mg
Se(VI) from SeF_6 , Ga(III) from $\text{Ga}_2(\text{SO}_4)_3$	8.5 mg
Mo(VI) from MoO_2F_2 , U(VI) from UF_6 , Mn(II) from $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$	7.8 mg
Pd(II) from $\text{PdSO}_4\cdot 2\text{H}_2\text{O}$, Te(IV) from TeI_4	7.0 mg
Os(VIII) from OsO_4 , Bi(III) from $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$	5.5 mg
Rh(III) from $\text{Rh}_2(\text{SO}_4)_3\cdot 12\text{H}_2\text{O}$, V(V) from V_2O_5 , Ag(I), Ni(II)	4.5 mg
Ru(III), Hg(II), Co(II), Fe(III)	3.0 mg

*Volume of aqueous solution is 40 mL and final solution in DMF is 5.0 mL.

Validation of the method and applications

Determination of copper in standard alloys and steel samples

The proposed method was applied to the determination of copper in Nippon Keikinokogyo (NKK) CRM 916 and No. 920 Aluminum Alloy and NKK No. 1021, Al, Si, Cu, Zn Alloy and Japanese Standards of Iron and Steel (JSS) CRM 651-7 and 653-7 Stainless Steel. A 0.1 g sample of the standard aluminum alloy or steel was dissolved in 6-14 mL of hydrochloric acid (1+1) by heating in a water bath and then 1 mL of 30% (v/v) hydrogen peroxide was added. The excess peroxide was decomposed by heating the sample in the water bath. The solution was cooled, filtered if needed and diluted to 100 mL with distilled water in a standard flask. An aliquot (1-2 mL) of this sample was taken in a 20 mL beaker and the general procedure

was applied. The results obtained are given in Table 3. These results are in agreement with the certified values.

Table 3. Determination of copper in standard alloys.

Sample	Composition%	Concentration%	
		Certified Value	Found*
JSS 651-7 Stainless Steel	C, 0.047; Si, 0.072; P, 0.028; Cr, 18.60; S, 0.0063; Mo, 0.84; Al, 0.002; N, 0.0312; Co, 0.22; Mn, 1.72; Ni, 9.20	0.082	0.079 ± 0.005
JSS 653-7 Stainless Steel	C, 0.068; Si, 0.63; Cr, 22.53; Co, 0.35; Mn, 1.72; Ni, 13.91; N, 0.0276	0.030	0.032 ± 0.002
NKK No. 916 Aluminum Alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Zn, 0.30; Ti, 0.10; Sn, 0.05; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Co, 0.03; Mn, 0.11; Ni, 0.06; V, 0.02	0.27	0.29 ± 0.02
NKK No. 1021 Al, Si, Cu, Zn, Cr, Alloy	Si, 5.56; Fe, 0.99; Mg, 0.29; 0.03; Zn, 1.76; Ti, 0.04; Sn, 0.10; Pb, 0.18; Sb, 0.01; Zr, 0.01; Bi, 0.01; V, 0.007; Ca, 0.004; Mn, 0.11; Ni, 0.14;	2.72	2.76 ± 0.09
NKK No. 920 Aluminum Alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Sn, 0.20; Pb, 0.10; Sb, 0.10; Bi, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.10; Mn, 0.20; Ni, 0.29; V, 0.15	0.71	0.75 ± 0.04

*Average of five determinations ± standard deviation
Conditions were the same as in Table 2.

Determination of copper in biological samples

The accuracy and applicability of the proposed method were applied to the determination of copper in National Institute for Environmental Studies (NIES) No.1 Pepperbush; NIES No.3 Chlorella; NIES No.5 Human Hair; NIES No.7 Tea Leaves. Some 0.1 g of sample was taken in a beaker and dissolved in concentrated nitric acid (≈5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 100 mL with water in a calibrated flask. NIES No.8 Vehicle Exhaust Particulates (0.1 g) was dissolved in 18 mL of concentrated nitric acid, 18 mL of concentrated perchloric acid and 2 mL of concentrated hydrofluoric acid in a 100 mL Teflon beaker, and evaporated to a small volume, filtered through a filter paper and made up to 100 mL with distilled water. An aliquot (10-50 mL) of the sample solution was taken individually and copper was determined by the general procedure. The results are given in Table 4, and are in good agreement with the certified values.

Table 4. Determination of copper in biological samples.

Sample	Composition	Concentration ($\mu\text{g g}^{-1}$)	
		Certified Value	Found*
NIES, No.1 Pepperbush	K, 1.51 ± 0.06 ; Mn, 0.203 ± 0.107 ; Mg, 0.408 ± 0.020 ; Ca, $1.38 \pm 0.07\%$ Cd, 6.7 ± 0.5 ; Ni, 8.7 ± 0.6 Fe, 205 ± 17 ; Co, 23 ± 3 ; Pb, 5.5 ± 0.8 ; Zn, 340 ± 20 ; Rb, 75 ± 4 ; Ba, 165 ± 10 ; Na, 106 ± 13 ; Sr, 36 ± 4 ; As, 2.3 ± 0.3 ; P, (1100); Cr, (1.3); Cs, (1.2); Tl, (0.13); Hg, (0.056) $\mu\text{g g}^{-1}$	12 ± 1	11 ± 1
NIES, No.3 Chlorella	K, 1.24 ± 0.06 ; Ca, 0.49 ± 0.03 ; $3.5 \pm$ Fe, 0.185 ± 0.010 ; Mg, 0.33 ± 0.02 ; P, (1.7)% Zn, 20.5 ± 1.0 ; Sr, 40 ± 3 ; Co, 0.87 ± 0.05 ; Mn, 69 ± 5 ; Cd, (0.026); Pb, (0.60); Sc, (0.013) $\mu\text{g g}^{-1}$	0.3	3.3 ± 0.2
NIES, No.5 Human Hair	Pb, 6.0; Cd, 0.20; Sb, 0.07; Zn, 169; Al, 240; Fe, 225; Mg, 208; Hg, 4.4; K, 34; Rb, 0.19; Sc, 0.05; Se, 1.4; Na, 26; Sr, 2.3; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Ni, 1.8; Co, 0.10 $\mu\text{g g}^{-1}$	16.3	16.24 ± 0.09
NIES, No.7 Tea Leaves	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.221; Co, 0.12; Mn, 7.00; Ni, 6.5 $\mu\text{g g}^{-1}$	7.0	7.08 ± 0.08
NIES, NO. 8 Vehicle Mg, Exhaust Zn, Particulates	K, 0.115 ± 0.008 ; Ca, 0.53 ± 0.02 ; 0.101 ± 0.005 ; Al, 0.33 ± 0.02 ; 0.104 ± 0.005 ; Na, $0.92 \pm 0.008\%$ Sr, 89 ± 3 ; Co, 3.3 ± 0.3 ; Ni, 18.5 ± 1.5 ; Cd, 1.1 ± 0.1 ; Pb, 219 ± 9 ; As, 2.6 ± 0.2 ; Cr, 25.5 ± 1.5 ; V, 17 ± 2 ; Sb, 6.0 ± 0.4 ; Cs, (0.24); Rb, (4.6); Sc, (0.055); La, (1.2); Br, (56); Ag, (0.2); Se, (1.3); Mo, (6.4); Ce, (3.1); Th, (0.35); Sm, (0.20); Eu, (0.05); Lu, (0.02) $\mu\text{g g}^{-1}$	67 ± 3	66 ± 2

*Average of five determinations \pm standard deviation

+Standard addition method was applied.

NIES: National Institute of Environmental Studies reference materials.

NIES, No. 1, No. 3 & No. 8 (Values in parentheses were approximate and not certified).

Conditions were the same as in Table 2.

Determination of copper in natural waters and hair

The method was employed for the determination of copper in hot spring, coastal, river, ground and lake water samples at levels as low as ppb. A 500 mL water sample was adjusted to pH 1.5 with nitric acid, filtered to remove suspended material and then analyzed by the general procedure. The results given in Table 5 are comparable to those of the standard DDTC-MIBK method²⁵.

The method was also applied to the determination of copper in human hair. Some 1.0 g of sample was decomposed by heating with 30 mL of concentrated nitric acid and 3 mL of 60% perchloric acid in a Kjeldahl flask. The solution was cooled, filtered and diluted to 200 mL with water in a calibrated flask. An aliquot of this solution was taken and copper was determined by the general procedure. The results obtained for these samples are shown in Table 5.

Table 5. Determination of copper in natural waters and human hair.

Sample	Copper found ^a (ng mL ⁻¹)	
	Present method	Alternative Method ^b
Coastal water	1.3 ± 0.2	1.4 ± 0.2
River water, A	1.7 ± 0.3	1.6 ± 0.3
River water, B	1.9 ± 0.2	1.8 ± 0.3
River water, C	5.8 ± 0.4	5.7 ± 0.5
River water, D	1.6 ± 0.2	1.7 ± 0.2
Hot spring water	11 ± 0.7	10 ± 0.8
Lake water	12 ± 0.5	13 ± 0.6
Human hair (male) ^c	12.3 ± 0.7	12.8 ± 0.9
Human hair (female) ^c	23.9 ± 0.8	24.3 ± 1.0

a) Mean of five determinations ± standard deviation

b) DDTC - MIBK method after vacuum evaporator concentration.

c) Results are given in $\mu\text{g g}^{-1}$.

Conditions were the same as in Table 2.

Conclusion

The main advantages of this procedure are: (i) the preparation of the extractor system is simple and can be performed in a short period of time; (ii) a good enrichment factor (160 ×) can be achieved. The achieved recovery measured by the standard addition technique showed that the proposed procedure had good accuracy. The proposed procedure has been applied for copper determination in various samples. This reagent is fairly sensitive and selective for copper but, with the preconcentration step and the use of flame atomic absorption spectrometry, its sensitivity and selectivity have been further improved. It is not possible to develop selective spectrophotometer methods for metal ions using this adsorbent, since many metal-nitroso-R complexes absorb at close wavelengths. However, with the use of FAAS this problem can be easily solved. The proposed procedure was applied for copper determination in various samples.

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