1364 © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***54***, *1364—1367 (1981)* [Vol. 54, No. 5

A Sensitive Atomic Absorption Spectrometric Method for Copper Employing the Direct Introduction of Chelating Resin into a Carbon Tube Atomizer

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(Received May 14, 1980)

A new and simple method for the determination of ppb levels of copper by electrothermal atomic absorption spectrometry was established. The main feature of the proposed method is that chelating resin, a preconcentration agent for copper, is introduced directly as a "resin-suspension" into the carbon tube atomizer without drying and weighing of the resin. To a 250 cm^3 sample solution containing up to 1.0 μg of copper, 0.10 g of chelating resin (below 400 mesh) is added, and the mixture is stirred for about 20 min. After the separation of the resin from the aqueous phase through a membrane filter, 5.0 cm^3 of resin-suspension is prepared by adding water to the resin. Then, 10 μdm^3 (resin: 0.2 mg) of the suspension is introduced into an atomizer, and the copper peak-height is measured under the optimum operating conditions. The calibration graph was linear over the concentration range from 0.1 ppb to 4.0 ppb of copper. The relative standard deviation was 2.3% from 10 repeated measurements; a mean value of 1.08 ppb copper was obtained for a sea water sample.

Atomic absorption spectrometry with an electrothermal atomizer and a deuterium background corrector is today an useful analytical tool: the determinations of trace metal elements in both liquid and solid samples can be carried out rapidly and easily. The direct analysis of a solid sample has been applied to biological tissues[1,2] and plastic containers.[3]

Chitosan,[4] a natural chelating polymer with anion-exchange behavior, has been used for the separation of transition elements from alkali and alkaline-earth salts. By combining the concentration of vanadium (VO_3^-) on chitosan with the direct introduction of its powder into the atomizer, Muzzarelli *et al.*[5] proposed a sensitive method for the determination of vanadium in sea water; however, the method requires the drying and weighing of VO_3-adsorbed chitosan powder. Atomization methods which use direct heating of the metal-adsorbed ion-exchange resin have also been examined as ways to determine copper[6] and mercury[7] concentrations; these methods make it possible to analyze an extremely dilute solution, but the precisions are not satisfactory.

For the preconcentration and separation of trace metal ions in sample solution, the chelating resin[8] has been used because of its selectivity in forming stable chelates: for instance, Sato *et al.*[9] proposed a determination method for copper by Flameless A. A. S. which included preliminary treatment by the resin.

The present authors[10] have briefly reported a determination method for copper in which chelating resin was introduced as a "resin-suspension" into a carbon tube atomizer, after the adsorption of copper ions on it under a batchwise operation. Highly purified chelating resin contains no copper, and its smoke does not affect the value of the atomic absorption of copper or the base line. The method does not require drying and weighing of the resin, nor elution of copper from the resin. We did some experiments on the effect of foreign ions on the method: magnesium and calcium ions in as small an amount as 0.1 ppm caused lower results for the atomic absorption of copper. It was found that the interferences of these ions can be eliminated by adding cobalt nitrate to the sample solution; there will be no adsorptions of these ions on the resin.

The proposed method for the determination of copper in a matrix of chelating resin was studied in detail and applied to determine copper ion concentrations in water samples.

Experimental

Apparatus. A Nippon Jarrell-Ash FLA-100 carbon tube atomizer was used in conjunction with a Nippon Jarrell-Ash Model AA-8500 two channel atomic absorption spectrophotometer. A single-element copper hollow cathode lamp (Hamamatsu TV. Co. L-233) was employed as a light source, and peak-heights were recorded with a Rikadenki Co. B-34 recorder. Resin-suspension was injected into the atomizer by using a micropipette (Eppendorf Co. Model 3130) fitted with disposable plastic tips. A centrifuge tube (volume: 15 cm^3) with a glass stopper was used, and a 5.0 cm^3 mark was etched on the tube.

Reagents. All chemicals were of super-special grade. Deionized water was passed through a column packed with Chelex-100 (NH_4-form, 50—100 mesh) prior to use.

Standard Copper Solution: The copper stock solution (1000 ppm) was made by dissolving 0.5000 g of copper metal grain (99.99% purity) in nitric acid and then diluting to 500 cm^3 with water. The working solutions were prepared by diluting the stock solution properly.

Chelating Resin: Chelex-100 (Bio-Rad laboratories, Richmond, Calf., Na-form) prepared to grain size below 400 mesh was used. After the removal of fine particles in the resin by decantation, 500 cm^3 of 2 mol dm^{-3} hydrochloric acid was added to about 50 g of resin in a beaker. The mixture was stirred for about 30 min, and the resin was washed with water by decantation. Then, 500 cm^3 of 4 mol dm^{-3} ammonia water was added to the resin, and the mixture was stirred for 2 h. The resin was filtered through a glass filter (3G4), washed with water, and dried in vacuum for four hours at 60 °C.

Ammonium Tartrate Solution (10%): Ammonium tartrate was dissolved in water to give a 20% solution. The solution was passed through a column packed with Chelex-100 (NH_4-form), and diluted to 10%.

Buffer Solution: 0.8 mol dm^{-3} sodium acetate solution was purified by use of Chelex-100 (Na-form), and diluted to 0.4 mol dm^{-3}. 0.2 mol dm^{-3} acetic acid-sodium acetate solution was used as a buffer solution (pH: 4.7), *Cobalt Nitrate Solution (2.5%)*: 5.0% cobalt nitrate solution was purified by use of Chelex-100 (Co-form), and diluted to 2.5%.

Water Samples. Samples were acidified to about pH 2 with nitric acid, and stored in polyethylene bottles.

Analytical Procedure. To a sample solution (250 cm^3) containing less than 1.0 μg of copper, 5 cm^3 of 2.5% cobalt nitrate solution and 10 cm^3 of 10% ammonium tartrate solution are added. The solution is adjusted to about pH 5 with (1+10) ammonia water and acetic acid, and 5 cm^3 more of buffer solution is added to the solution. Then, 0.10 g of chelating resin is added to the solution, and the mixture is stirred for 20 min by a magnetic stirrer. After the resin has been separated from the mixture through a membrane filter (pore size: 2.0 μm) or glass filter (3G4), the resin is transferred into a centrifuge tube by using about 10 cm^3 of water and the tube is centrifuged. The supernatant liquid is decanted, being careful to leave the resin in the tube, and 5.0 cm^3 of "resin-suspension" is prepared by adding water to the resin in the tube. Then, 10 μdm^3 (resin: 0.2 mg) of the suspension, which has been mixed thoroughly to prepare a uniformly suspended solution, are introduced into a carbon tube atomizer. The atomic absorption of copper, its peak-height, is measured under the instrumental operating conditions shown in Table 1.

TABLE 1. INSTRUMENTAL OPERATING CONDITIONS

Operating step	Current A	Time s	Mode	Final temp °C
Drying	35	20	Ramp	*ca.* 300
Ashing	110	60	Ramp	*ca.* 1200
Atomization	250	10	Flash	*ca.* 2500

Wavelength: 324.75 nm, lamp current: 5 mA, argon gas flow rate: 3 dm^3/min, damping: 1, sensitivity: 0.

The calibration graph was linear over the concentration range from 0.1 ppb to 4.0 ppb of copper. It was confirmed by using standard copper solution that the copper ions in a sample solution (250 cm^3) are almost all adsorbed by the chelating resin (resin-suspension: 5.0 cm^3) under the conditions of this procedure; that is, the concentration ratio is found to be about 50:1.

Results and Discussion

Ashing of Chelating Resin. Figure 1 shows the typical profiles of absorption for copper-adsorbed resin and copper-free resin in a carbon tube under the instrumental operating conditions. In the case of copper-adsorbed resin, the first peak appeared in an ashing step owing to a smoke evolution of the resin, and then the second peak, which is based on the atomization of copper, was obtained. In copper-free resin, although the first peak appeared as before, there were neither the second peak nor any absorption by the deuterium lamp during the atomization step. Therefore, no correction is necessary for background absorption in measuring the second peak.

The Effect of Ashing Current. Figure 2 shows the effect of ashing current on the absorbance of copper. In the case of copper-adsorbed resin, the absorbance at an ashing current of 70 A was higher than those at the current range from 100 to 130 A, and the absorbance at 140 A was lower. The increase of absorbance at 70 A is due to an absorption by smoke evolution of the resin resulting from an incomplete ashing. This is seen by observing that the copper-free resin also has an absorption at the same current. On the other hand, the decrease of absorbance at 140 A is due to the loss of copper by its partial volatilization during the ashing step; in the case of an aqueous solution, the absorbance of copper also shows a similar decrease. As shown in Table 1, an ashing current of 110 A was adopted before the atomization step. It was observed that the resin acts as a sensitizer for copper during the atomization step; that is, the absorbance of copper-adsorbed resin at an ashing current of 110 A increases about 35% in comparison with that of copper in an aqueous solution. Similar sensitization was observed when a fine activated carbon was added instead of the resin to the aqueous solution. Yoshimura and Noda[11] have reported that an activated carbon is effective for the deoxidation of metal oxides (Cu_2O, CuO, PbO_2, ZnO, ZnO_2) in the direct atomization of these oxides during the flame A. A. S.

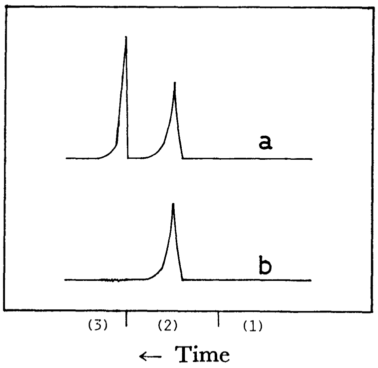

Fig. 1. Typical profiles of absorption for copper-adsorbed resin and copper-free resin.
(a): Cu-adsorbed resin (b): Cu-free resin (1): Drying, (2): Ashing, (3): Atomization.

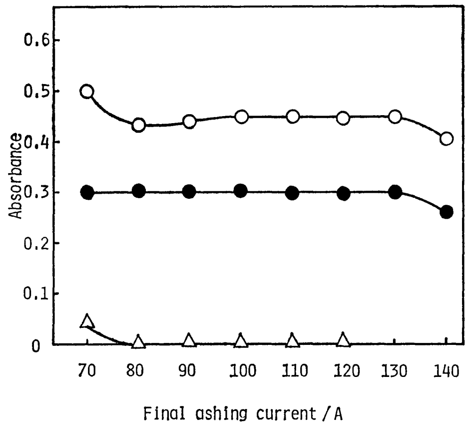

Fig. 2. Effect of ashing current on absorbance of copper. Resin-suspension: 0.10 g/5 cm^3 H_2O, injecting volume: 10 μdm^3. ○: Cu-adsorbed resin (Cu: 0.75 μg), △: Cu-free resin, ●: aqueous soln (Cu: 0.75 μg/5 cm^3).

The Effect of the Amount of Chelating Resin and of the Stirring Time. We examined the effects of the amount of chelating resin and of the stirring time in the procedure on the adsorption of copper on the resin. Since the absorbance of copper gave a constant value for amounts from 0.05 to 0.50 g, 0.10 g of the resin was added to a 250 cm^3 sample solution. Stirring for 20 min by a magnetic stirrer was sufficient to allow copper and cobalt ions to be adsorbed on the chelating resin from a sample solution. The resin transformed into NH$_4$-form was used in the procedure, because the rate of adsorption for copper ion on NH$_4$-form resin was faster than that on H-form resin.

The Effect of the Amount of Cobalt. Chelex-100[8] has a very strong attraction for transition metals. The selectivity series for cations in an acetate buffer system at pH 5 is:

$$Hg^{2+} > Cu^{2+} \gg Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} \gg Mg^{2+} = Ca^{2+} \gg Na^{+} > NH_4^{+} > H^{+}.$$

In general, when a large amount of cobalt ion exists in a sample solution containing the resin, magnesium or calcium ions are not adsorbed by the resin, but a small amount of copper ion is quantitatively adsorbed by it. From some experiments, the addition of 5.0 cm^3 of 2.5% cobalt nitrate solution to a 250 cm^3 sample solution showed satisfactory results for copper ions in the presence of about 100 ppm of magnesium ions.

The Effect of PH on the Adsorption of Copper. As is seen in Fig. 3, the absorbance (△) decreased appreciably with the increase in pH, because of incomplete adsorption of copper due to the formation of hydrolysis products such as Cu(OH)$^+$ or Cu(OH)$_2$. The absorbance (●) also decreased as the pH increased from 4 to 7, but those at pH 9 and 10 increased again through the formation of ammine complexes such as $[Cu(NH_3)_4]^{2+}$. The absorbance (○) gave a constant value over the pH range from 2.5 to 10, because the hydrolysis of copper was prevented by the addition of 10 cm^3 of 10% ammonium tartrate solution. The effect of pH on the adsorption of cobalt ion was also examined: the amount of cobalt ion adsorbed by the chelating resin gave a maximum and constant value over the pH range from 4 to 7. Therefore, the buffer solution with pH 4.7 was used in the procedure.

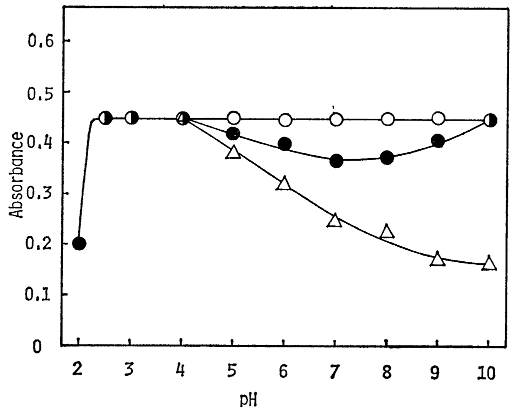

Fig. 3. Effect of pH on the adsorption of copper. Cu: 0.75 μg/250 cm^3, reagents used for pH adjustment; ○: CH$_3$COOH, NH$_3$-water, (NH$_4$)$_2$C$_4$H$_4$O$_6$, ●: CH$_3$COOH, NH$_3$-water, HNO$_3$, △: CH$_3$COOH, NaOH.

The Effect of Foreign Ions. The effect of foreign ions on the procedure were examined under the presence of 3.0 ppb copper ion, both in the case of the addition of a cobalt nitrate solution and in the case of no such addition. The experimental results are given in Table 2. When the cobalt nitrate solution was not added to a sample solution, strontium, iron(II) and chromium(III) ions in small amount such as 1 ppm gave lower results for the absorbance of copper. Further, magnesium and calcium ions interfered remarkably even at 0.1 ppm. On the other hand, the addition of a cobalt nitrate solution was found to be very effective in eliminating the interferences of these ions. Most anions did not interfere, even when 1000 ppm of them were present, regardless of the presence or absence of cobalt ion during the procedure.

Table 2. Effect of foreign ions

	Proposed method		Without Co^{2+}	
Ion	Amount/mg	Absorbance	Amount/mg	Absorbance
—	—	0.450	—	0.450
Na$^+$	2500	0.455	250	0.438
K$^+$	2500	0.445	250	0.439
Mg^{2+}	250	0.460	0.0025	0.449
Ca^{2+}	250	0.458	0.0025	0.446
Sr^{2+}	250	0.447	0.025	0.436
Ba^{2+}	250	0.449	0.25	0.447
Fe^{2+}	250	0.459	0.025	0.452
Mn^{2+}	250	0.452	250	0.442
Ag$^+$	250	0.455	250	0.458
Al^{3+}	250	0.451	2.5	0.441
Cr^{3+}	0.25	0.452	0.025	0.452
Zn^{2+}	25	0.445	25	0.449
Pb^{2+}	2.5	0.443	2.5	0.455
Hg^{2+}	25	0.449	25	0.454

Copper ion: 0.75 μg, Sample volume: 250 cm^3.
The amount of foreign ions means the amount of those ions which does not show any deviation larger than the error allowed(of ±3%) from the absorbance(0.450) of copper.

Table 3. Analytical results of copper in various water samples

Sample	Cu added ppb	Cu found ppb
Town water; Chiyoda-ku, Tokyo (Feb. 12, 1980)	—	3.40
River water; Kamuiwatsuka-river Hokkaido (Aug. 15, 1979)	—	3.36
Sea water;[a)] Aburatsubo-bay	—	1.08
Kanagawa Pref. (Nov. 24, 1979)	1.0	2.07
Deionized water[b)]	—	0.12

a) Sample was taken about 2 km away from the coast.
b) Sample volume taken: 1000 cm^3,

The Determination of Copper in Various Water Samples. The results obtained by the procedure for water samples are shown in Table 3. The mean copper content of a sea water sample was 1.08 ppb from 10 repeated measurements and the relative standard deviation was 2.3%. The content was also confirmed by adding known amounts of copper to the sea water; good recovery of these amounts was achieved. Some experiments were performed on different volumes (100, 500, 1000 cm^3) of a sample solution containing 0.75 μg of copper ions; these absorbances of copper agreed, within the experimental error allowed, with that obtained by use of a sample volume of 250 cm^3. The proposed method is therefore applicable to the determination of copper ions in water samples over a wide concentration range. That is, the content of a deionized water used in this laboratory was determined to be 0.12 ppb by using a 1000 cm^3 sample volume instead of 250 cm^3 as in the standard procedure.

In addition, it is possible to increase the apparent sensitivity for the determination of copper by changing the volume (5.0 cm^3) of resin-suspension or the volume (10 μdm^3) injected into the atomizer. The procedure is relatively simple to use, and few chemicals are required. The proposed technique may be applied not only to the determination of copper, but also to that of other metals at ppb levels.

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