Inductively Coupled Plasma Atomic Emission Spectrometric Determination of Copper by Suction-Flow On-Line Liquid-Liquid Extraction of Its Macrocyclic Dioxotetramine Chelate

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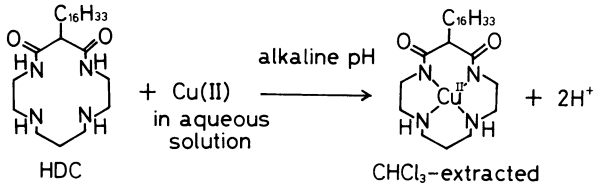
Synopsis. The flow manifold described permits suction-flow liquid-liquid extraction of copper(II) in a discrete aqueous sample as its macrocyclic dioxotetramine (6-hexadecyl-1,4,8,11-tetraazacyclotetradecane-5,7-dione, HDC) chelate into chloroform. The organic extract is successively fed into the inductively coupled plasma by a peristaltic pump. The detection limit is 1.5 ng cm^{-3} copper(II) and the relative standard deviation is 2.2% (n=10) for 100 ng cm^{-3} copper(II).

The chemical properties of macrocyclic polyamines have received much attention in recent years.[1] However their applications to chemical analysis have been limited.[2] Kimura et al.[3] recently synthesized HDC and found that it selectively encloses copper(II) with simultaneous deprotonation of two amides as a neutral 1:1 complex in alkaline pH and is potentially useful for the separation of copper(II) by solvent extraction.



This paper demonstrates an analytical application of HDC as a chelating agent for copper(II) to an on-line liquid-liquid extraction for the inductively coupled plasma atomic emission spectrometry (ICPAES) of copper. The limiting factors for the extraction and the ICPAES were investigated to obtain the maximum sensitivity of copper, and the technique was applied to the analysis of some biological samples.

Experimental

Apparatus and Reagents. A Kyoto Koken Model UOP-1S ICP atomic emission spectrometer was used. The flow system comprised a Teflon suction cup,[4] a 6-channel variable-speed peristaltic pump (Tokyo Rikakikai Model MP-3), T-joints, a segmentor, a Teflon extraction coil (1 mm i.d., 2 m long) and a phase separator (4 mm i.d., 40 mm horizontal long, 60 mm vertical long). The phase separator was made up of a T-piece glass fitting into which a Teflon fiber string was inserted at one of the bends.[5] As for the pump tubing, Acidflex (Technicon Corp.) for chloroform and Tygon (Norton Co.) for aqueous solutions were used. The inner diameters of the tubing for sample, HDC, buffer, and chloroform were 2.4, 1.6, 1.6, and 1.6 mm, respectively. The other parts of the flow system were made of 1-mm i.d. Teflon tubing. The assembly is shown in Fig. 1.

HDC was prepared by refluxing dimethyl hexadecylmalonate and 3,7-diazanonane-1,9-diamine in methanol (25% yield, mp 113°C from methanol-benzene).[3] A solution of the chelating agent [5.0×10^{-4} M (1 M=1 mol dm^{-3})] was prepared by dissolving HDC in dilute hydrochloric acid and diluting with water. A 1000 μg cm^{-3} copper(II) standard stock solution was prepared by dissolving 0.500 g of copper metal (99.999%) in dilute hydrochloric acid diluting to 500 cm^3 with water. Solutions of suitable concentrations were prepared by dilution. A 1000 μg cm^{-3} nickel(II) solution was prepared by dissolving 0.500 g of nickel metal

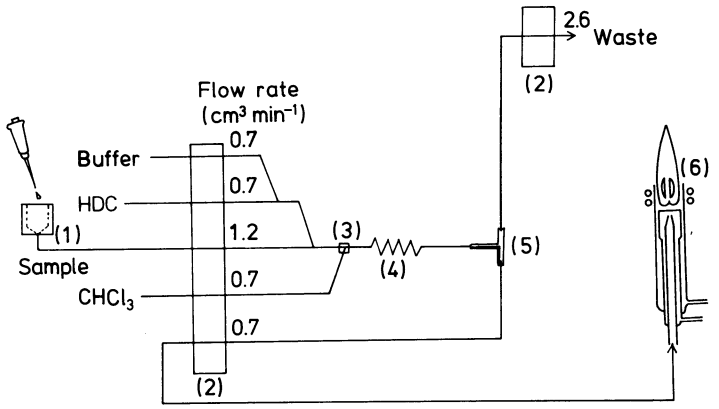


Fig. 1. Flow diagram for extraction of copper(II) with HDC into chloroform. (1) Teflon suction cup, (2) peristaltic pump, (3) segmentor, (4) extraction coil, (5) phase separator, (6) ICP.

(99.999%) in dilute hydrochloric acid and diluting to 500 cm^3 with water. A borate buffer solution (1 M, pH 9) was prepared by mixing boric acid and sodium hydroxide. Chloroform was used without further purification.

Recommended Procedure for Copper Determination. A sample solution ([Cu(II)]$\lesssim$500 ng cm^{-3}) in which nickel(II) had been added in the concentration of 30 μg cm^{-3}, usually 2 cm^3, was added to the suction cup from a Pipetman P-5000 (Gilson International). As shown in Fig. 1, the sample was sucked into the mixture of the HDC and the buffer solutions, and with chloroform in the segmentor. The segmented solution was carried into the extraction coil and the phase separator. The organic extract was introduced by the peristaltic pump into the nebulizer of the ICP spectrometer. The transient Cu I 324.754-nm emission signal at an observation height of 13 mm above load coil was recorded on a strip-chart recorder, and the peak height was measured. The optimum argon gas flow rates for the ICP were 12 dm^3 min^{-1} of plasma gas, 1.0 dm^3 min^{-1} of auxiliary gas and 0.325 dm^3 min^{-1} of nebulizer gas.

Results and Discussion

The effect of pH on the extraction was investigated, keeping the other variables in the recommended procedure constant. The HDC-copper(II) complex was confirmed to be quantitatively extracted into chloroform in the pH 8—14; a pH 9 borate buffer solution (1 M) was used throughout. Under the conditions, the pH of the sample solution had to be above ca. 0.8 to obtain a maximum and constant intensity.

It is interesting to note that the extraction rate of copper(II) was much accelerated by addition of nickel(II). When a 1-mm i.d. and 2-m long Teflon extraction coil was used and nickel(II) was absent in the aqueous phase, the recovery of copper(II) was no more than about 50%. However, in the presence of nickel(II) of more than 60-fold amounts of copper(II), the extraction of copper(II) was confirmed to be complete even with the same length of the extraction coil. The behavior of nickel(II) is not understood as yet and awaits further investigation.

The volume of sample taken in the suction cup was varied by using the volume-adjustable pipet. Figure 2 shows some typical signals obtained with different volumes of a 100 ng cm^{-3} copper(II) solution at a time constant for the electronic circuit of 10 s. Variation of the time constant had no appreciable effect on the sensitivity provided that it was in the range 3—10 s. However, the signal became noisy at the smaller time constant. The best reproducibility was obtained at 10 s. The peak height was proportional to the volume added up to about 3 cm^3 and thereafter was constant. A 2-cm^3 sample plug showed ca. 80% of the plateau intensity. This volume seems to be a good compromise between high sensitivity and the practical requirements of high sampling rate and low reagent consumption.

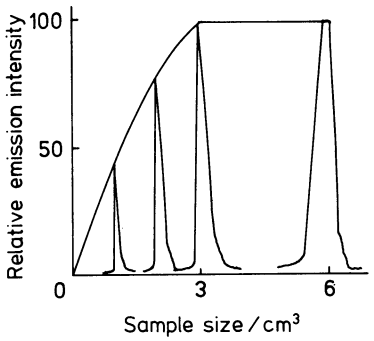


Fig. 2. Recorder tracings obtained with various sample volumes. Copper(II): 100 ng cm^{-3}.

Table 1. Determination of Copper in Human Organs[a)]

Sample	Copper found/μg g^{-1}	
	Present method	GF-AAS[b)]
Liver 3374	9.3±0.2	9.7±0.2
Liver 3355	4.8±0.1	4.7±0.1
Liver 3308	4.2±0.2	4.5±0.2
Pancreas 3355	1.2±0.0	1.3±0.1
Kidney 3354	4.0±0.1	3.8±0.3

a) Wet base. b) Mean±av. dev., 2 results.

Under the recommended procedure, a linear calibration graph was obtained for up to 500 ng cm^{-3} copper(II). The detection limit (S/N=3) was 1.5 ng cm^{-3} copper. The detection limit is about 11-fold better than that obtained by direct aspiration of the aqueous solution. The improvement is attributed not only to the preconcentration of copper by extraction, but also to the enhancement effect of chloroform.[6)] The relative standard deviation for 10 replicate measurements was 2.2% for 100 ng cm^{-3} copper(II) and the sample throughput was 25 h^{-1}.

The interferences of large amounts of alkali and alkaline earth metal salts could be avoided by the extraction. Most other metal ions such as cobalt(II), nickel(II), zinc(II), cadmium(II), tin(II), antimony(III), mercury(II), lead(II), and bismuth(III) did not interfere with the determination of copper when present in 200-fold amounts of 100 ng cm^{-3} copper(II). Interferences were encountered only with aluminum(III), chromium(III), and ion(III); the maximum permissible amounts within 10% error of these species were 91-, 45-, and 32-fold, respectively. The interferences may arise from metal hydrolysis during the extraction process of copper(II) under the alkaline condition.

The reliability of the present method was examined by comparing the analytical results of some human organ samples with those obtained by the graphite-furnace atomic absorption spectrometry (GF-AAS) combined with dithizone-carbon tetrachloride batch-extraction.[7)] The samples were prepared by digesting in Teflon beakers with nitric acid and perchloric acid on a hot plate. As Table 1 shows, the data are in good agreement with each other.

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