The Preconcentration and Separation of a Trace Amount of Copper(II) in Water as Its Silica-Immobilized Salicylaldimine Chelate by Means of Column Chromatography

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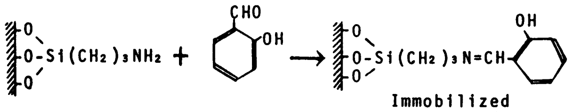
Synopsis. The behavior of a trace amount of copper(II) in solid-liquid extraction and back extraction has been examined with silica-immobilized salicylaldimine; the results have also been applied to the preconcentration and separation of a trace amount of copper(II) in water as its silica-immobilized salicylaldimine chelate by means of column chromatography.

Extraction chromatography has been applied to the concentration and separation of a trace amount of cobalt(II) in sea water as its 1-nitroso-2-naphtholate.[1] However, this technique has a weak point—the loss of 1-nitroso-2-naphthol from the stationary phase during the chromatographic process; this may decrease the usefulness of the column for the preconcentration of a trace amount of cobalt(II) in sea water. It has been generally known that salicylaldimine specifically reacts with copper(II) among transition metals to form a green chelate. After preliminary experiments on the solid-liquid extraction behavior of metals like copper(II), iron(III), nickel(II), palladium(II), cobalt(II), manganese(II), and zinc(II) with silica-immobilized salicylaldimine, it was found that copper(II) and iron(III) especially have high reactivities in a weakly acidic solution.

In this investigation, the behavior of a trace amount of copper(II) in solid-liquid extraction and back extraction with silica-immobilized salicylaldimine of a bidentate Schiff base has been examined in detail; the results have also been applied to the preconcentration and separation of a trace amount of copper(II) in water as its silica-immobilized salicylaldimine chelate by means of column chromatography. Some silica-immobilized salicylaldimines have already been prepared by the reaction of salicylaldehyde on silylated silica gel, and microgram amounts of iron(III), cobalt(II), nickel(II), copper(II), lead(II), vanadium(V), chromium(VI), and zinc(II) have also been collected with silica-immobilized salicylaldimine from weakly acidic and neutral solutions by means of solid-liquid extraction for subsequent X-ray fluorescence analysis.[2]

Experimental

The "aminopropyl silica gel" was prepared by a slight modification of the method of Aue and Hastings.[3] Silica-immobilized salicylaldimine was prepared as follows: A 50 g portion of aminopropyl silica gel was added to 100 cm^3 of 5% salicylaldehyde in acetone, after which the mixture was stirred in a sealed flask for 2 h at about 50 °C. The product thus obtained was washed with acetone and dried under a vacuum at room temperature. The color of the product was brown. The solid-liquid extraction of copper(II) in water was carried out with silica-immobilized salicylaldimine as follows: A 0.1—2 g portion of the silica-immobilized salicylaldimine and 10 cm^3 of a 1—1000 ppm copper(II) solution adjusted to pH 1—7 with 0.1M HCl (1M=1 mol dm^{-3}), 0.1M CH_3COOH 0.1M CH_3COONa, and 0.1M NaOH were



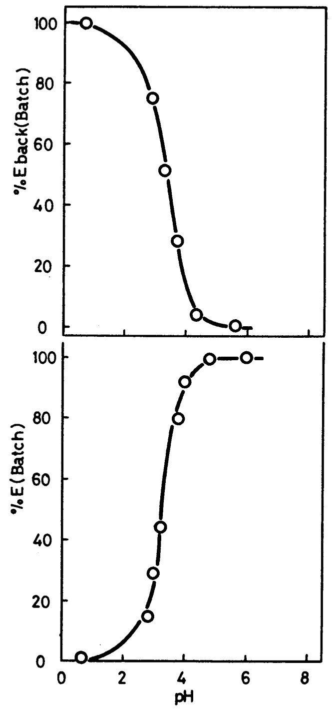


Fig. 1. Effect of pH on the extraction and the back extraction of copper(II) with silica-immobilized salicylaldimine.
Silica-immobilized salicylaldimine: 1.0 g, Cu(II): 100 μg, Aqueous solution: 10 cm^3, Shaking time: 30 min.

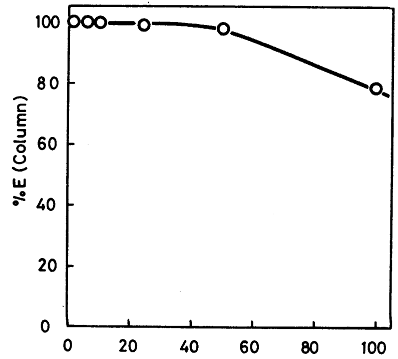


Fig. 2. Effect of flow rate on the preconcentration of copper(II) with silica-immobilized salicylaldimine column.
Silica-immobilized salicylaldimine: 1.0 g, Cu(II): 100 μg, pH 5.0.

Table 1. Recovery of Copper(II) in an Aqueous Solution of pH 5.0 with a Silica-Immobilized Salicylaldimine Column

Cu(II) spike/µg	Solution volume/cm^3	Silica-immobilized salicylaldimine/g	Cu(II) recovery/%
100	10	1.0	100±2
100	100	1.0	97±2
10	500	1.0	100±2
10	1000	1.0	62±2
10	1000	2.0	100±2

Table 2. Content of Copper(II) in Distilled Water and Tap Water of Kanazawa University

Sample	Solution volume/cm^3	Cu(II) collected/µg	Cu(II) collected/ppb
Distilled water	500	12.0, 13.5, 12.5	25.3±2.2
	1000	23.2, 23.7, 27.0, 24.0	24.5±1.5
	2000	46.6, 52.8	24.9
Tap water	2000	1.0, 1.4, 1.2	0.6±1

placed into a 30-cm^3 centrifuged tube, and the mixtures were shaken for 1—30 min. The capacity of the silica-immobilized salicylaldimine was determined by adding 0.1 g silica-immobilized salicylaldimine to 10 cm^3 of a 100 ppm copper(II) solution adjusted to pH 5.2, after which the mixtures were shaken for 30 min. The concentration of copper(II) in water was determined by the atomic-absorption method. The chromatographic column was prepared as follows: A 1.0—2.0 g portion of silica-immobilized salicylaldimine was added to a 0.1M acetate buffer solution of pH 5.0—6.0, and the mixtures were poured into a chromatographic glass tube (1 cm in inner diameter and 30 cm in length) with a fritted glass filter. The top of the column was covered with a small amount of glass fiber.

Results and Discussion

Silica-immobilized salicylaldimine was stable in the region of pH 3.5—7.0, and it reacted rapidly with copper(II) in water to form a green chelate.

When the behavior of a trace amount of copper(II) in solid-liquid extraction and back extraction has been studied with 1.0 g of silica-immobilized salicylaldimine, the quantitative extraction of 100 µg copper (II) is attained at pH 5.0—7.0 in about 1 min shaking (Fig. 1). Copper extracted as the silica-immobilized salicylaldimine chelate was easily back-extracted with an aqueous solution of 0.1—1M hydrochloric acid. On the basis of the experimental results described above, the chromatographic behavior of a trace amount of copper(II) in water was studied by means of 1.0 g of silica-immobilized salicylaldimine in a glass column at the flow rate of 0.8—200 cm^3 min^{-1} under suction. The column capacity of silica-immobilized salicylaldimine with copper(II) was 0.10 mmol g^{-1} at pH 5.2. A 10—1000 cm^3 portion of 10—100 µg copper(II) in water adjusted at pH 5.0—6.0 was passed through the column. It was found that the quantitative preconcentration of 0.01—10 ppm copper(II) was accomplished at the flow rate of 0.8—24 cm^3 min^{-1} (Fig. 2). The results of the recovery (Table 1) of copper(II) in water adjusted at pH 5 with silica-immobilized salicylaldimine indicated that the preconcentration of trace amounts of copper(II) in water was quantitatively accomplished by using 1—2 g of silica-immobilized salicylaldimine. Foreign ions added, up to 100 µg of nickel(II), cobalt(II), manganese(II) and zinc(II) each, and 1000 µg of iron(III), did not interfere with the preconcentration of 10 µg copper in a 500 cm^3 solution. Copper(II), probably held on silica-immobilized salicylaldimine by the 1:1 metal-chelate formation, as is seen in the case of metal-ion chelation chromatography on silica-immobilized 8-quinolinol,[4] was easily eluted with 10 cm^3 of 1.0M hydrochloric acid within 1 min under increased pressure with air in order to prevent both the tailing of copper(II) and the hydrolysis of the silica-immobilized salicylaldimine during the process. About 70% of the collection ability of copper(II) with this reagent was lost when it was placed in contact with 1.0M hydrochloric acid for 30 min; however, there is no problem in concentrating traces of copper(II) for at least a few times by the procedure described above. The copper(II) was determined by the atomic-absorption method. The content of copper(II) in distilled water and tap water at Kanazawa University was determined by the preconcentration method described above. The results (Table 2) revealed that the concentration of copper(II) in distilled water prepared by means of an electric distillation apparatus constructed with copper plate (YAMATO WS-5) was about 25 ppb, while that of copper(II) in tap water was 0.6±1 ppb, which is compatible with the value of 0.5 ppb obtained with the column of 2-mercaptobenzothiazole supported on silica gel.[5]

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