Application of a Coagulated Mixture Prepared from Finely Divided Cation and Anion Exchange Resins to the Enrichment of Copper(II)

Masutaro ABE, Kunio OHZEKI, and Tomihito KAMBARA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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Mutual coagulation takes place, when a suspension of finely divided cation exchanger is added to that of anion exchanger. The resulting mixed resin is bulky and easily separated from the solution by filtration. A rapid and selective collection of a trace amount of copper(II) ion was carried out by the combined use of mixed resin and 8-quinolinol-5-sulfonic acid (H_2qs). The copper(II) collected on the mixed resin in the form of $[Cu(qs)_2]^{2-}$ was brought into solution from the resin with ethylenediaminetetraacetate, converted into copper(II)-diethyldithiocarbamate, extracted into methyl isobutyl ketone, and determined by atomic absorption spectrometry. The method was satisfactorily applied to the determination of a trace amount of copper(II) in well water.

Finely divided ion exchange resin particles can collect ions from solutions much more rapidly than beads of the conventional size, since the rate of ion exchange reaction is inversely proportional to the square of the radius of the resin particles.1) One of the characteristics of such a fine resin is coagulation caused by the addition of suspensions of oppositely charged resin particles.2) The use of the coagulated resin for rapid ion removal has been demonstrated by Pinfold and Karger.2)

We have examined the analytical utilization of the mixed resin of finely divided cation and anion exchangers. A rapid and selective concentration of a trace amount of copper(II) ion is reported.

Experimental

Reagents. A copper(II) standard solution was prepared from nitrate and standardized against EDTA. A 10^{-2} M (mol dm^{-3}) 8-quinolinol-5-sulfonate (Hqs^-) solution was prepared by dissolving the acid (H_2qs, Wako Pure Chemicals Inc.,), in an alkaline solution. The Dotite 4 NA (Dojindo Lab.) was dissolved to give ethylenediaminetetraacetic acid tetrasodium salt (Na_4edta) solution. Sodium diethyldithiocarbamate for atomic absorption spectrometry (Naddtc, Wako) was used in a 5 w/v% aqueous solution. Methyl isobutyl ketone (MIBK) and other reagents of guaranteed grade were used. Deionized-redistilled water was used.

Apparatus. A Hitachi 508 atomic absorption spectrometer with a Fe–Co–Ni–Cu–Cr–Mn multielement hollow cathode lamp was used for the determination of copper(II) in MIBK extract under the following conditions: wavelength 324.8 nm, lamp current 10 mA, slit width 0.18 mm, acetylene flow rate 1.5 l min^{-1} at 0.5 kg cm^{-2}, and air flow rate 13 l min^{-1} at 1.8 kg cm^{-2}. A Toyo KG 25 filter holder (Toyo Roshi Co., Ltd.) was used.

Ion Exchange Resin. Macroreticular type Amberlyst 15 and A-26 (both Rohm and Haas Co.) in RSO_3Na and $RN(CH_3)_3Cl$ forms, respectively, were used. The dry cation exchange resin was washed with ethanol until the washings became colorless, and then cleaned and recycled several times between hydrogen and sodium forms. The chloride form of the anion exchange resin was regulated as usual. The wet resin was crushed into a slurry which was then diluted to a suspension. The suspension was then filtered through a 3G3 glass filter to remove resin particles larger than 30 μm. The particle sizes of the resins in the resulting stock suspension were in the range 0.2—30 μm. The lower limit was confirmed by the fact that the resin particles in the suspension could not pass a millipore filter of 0.2 μm pore size.

The ion exchange capacity of the resin in the suspension was determined as follows. In the case of the cation exchanger, the solid particles in a known amount of the suspension were collected onto a millipore filter, and the sodium ion on the resin was eluted with hydrochloric acid solution and determined by atomic absorption spectrometry. For the anion exchange resin, the chloride ion on the resin was eluted with sodium nitrate solution and determined absorptiometrically by the mercury(II) thiocyanate method.3) The exchange capacities thus obtained were 0.031 meq ml^{-1} for the cation exchange resin suspension (CRS) and 0.030 meq ml^{-1} for the anion exchange resin suspension (ARS), respectively.

Results and Discussion

Coagulation. The mutual coagulation of the finely divided cation and anion exchangers was examined first. A 5.0-ml portion of CRS was taken into a 50-ml stoppered measuring cylinder and varying amounts of ARS were added. After adjusting the total volume to 50 ml with water, the mixture was shaken vigorously for 5 min and allowed to stand for 5 min. The coagulated material thus obtained was removed by filtration with a 3G3 glass filter. The extent of coagulation was estimated from the turbidity of the resulting filtrate.

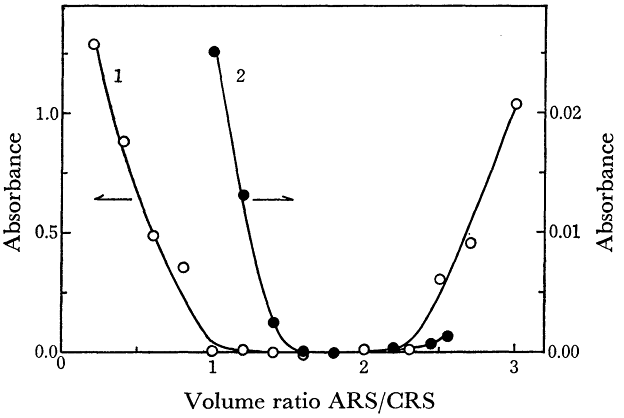

Fig. 1. Coagulation of cation and anion exchangers. Amounts of CRS involved in 50 ml of the mixtures: ●; 1.0 ml, ○; 5.0 ml.

As a measure of turbidity, the absorbance of the solution was determined in a 1-cm cell at an arbitrary wavelength of 500 nm against water. The results are shown in Fig. 1. The turbidity of the filtrate due to the remaining CRS decreased with increasing amount of ARS, almost complete coagulation being attained when 6—10 ml of ARS was added to 5.0-ml portion of CRS (curve 1, Fig. 1). With further addition of ARS, the solution became turbid due to excess ARS. The 1.0-ml portion of CRS was most satisfactorily deposited from the solution with addition of 1.6—1.8 ml of ARS (curve 2, Fig. 1).

Exchange Capacity of the Coagulated Resin. The number of ion exchange sites consumed for the association of 5.0 ml of CRS with 8.0 ml of ARS was estimated by determining the sodium and chloride ions expelled from both resins as a result of mutual coagulation. The proportions of the ion exchange sites taking part in the coagulation to the total ion exchange sites in CRS and ARS were found to be 3.7 and 5.3%, respectively. The exchange capacities of cation and anion exchangers decrease only a little by coagulation.

Effect of Concentration of Sodium Chloride on Coagulation. A 1.0-ml portion of CRS and 1.6 ml of ARS were added to 250 ml of a solution containing various amounts of sodium chloride. The mixture was shaken for 10 min. The resins coagulated on being left to stand for 10 min from a 0.1 M sodium chloride solution. With increasing concentration of sodium chloride, it took a longer time to obtain sufficient coagulation. No satisfactory coagulation was attained in the solution containing sodium chloride (0.5 M) even after long standing.

Adsorption of Copper(II). The adsorption of copper(II) ion onto the coagulated resin was investigated in the presence of calcium and chloride ions which are most commonly present in natural water. A 1.0-ml portion of CRS and 1.6 ml of ARS were taken into an eggplant type flask, and 5 μg of copper(II) and varying amounts of calcium chloride solution were then added. The mixture was diluted to *ca.* 40 ml with water and shaken for 30 min. The resulting coagulated resin was removed by filtration. The copper(II) in the filtrate was extracted as copper(II)–ddtc complex into MIBK and determined by atomic absorption spectrometry.

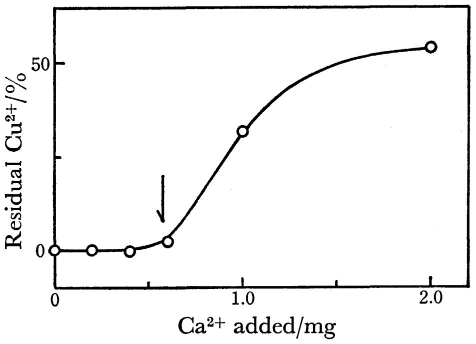

Fig. 2. Recovery of 5.0 μg of copper(II) from 40 ml of solutions containing varying amounts of calcium chloride onto the coagulated resin prepared from 1.0 ml of CRS and 1.6 ml of ARS. Arrow indicates the amount of calcium ion corresponding to the exchange capacity of CRS.

As shown in Fig. 2, copper(II) was quantitatively collected onto the mixed resin until the exchange capacity of the cation exchanger in the mixed resin was satisfied by the calcium ion. Thereafter, the amount of non-fixed copper(II) in the solution increased with increasing amount of calcium ion.

Choice of Chelating Agent. The utilization of complexation in ion exchange analysis was described by Ringbom.[4] Recently, the use of ion exchange resins in combination with chelating agents, such as 8-quinolinol-5-sulfonic acid[5] and a sulfonic acid derivative of dithizone[6] has been reported. In order to enhance the selectivity of the mixed resin for copper(II), ethylenediamine (en) and Hqs$^-$ were examined as chelating agents. The former combined with copper(II) to form the complex cation while the latter formed the complex anion. Both complexes could be more strongly fixed onto the resin than simple ions. In the presence of 3 μmol of en, 15 μg of copper(II) were quantitatively collected from a solution containing 2 mg of calcium ion onto the coagulated resin prepared from 1.0 ml of CRS and 1.6 ml of ARS under the optimal conditions. The effect of en is obvious. However, better results were obtained by use of Hqs$^-$.

Effect of Hqs$^-$. In the presence of 2 μmol of Hqs$^-$, 5 μg of copper(II) were collected from 40 ml of a calcium chloride solution containing 20 mg of calcium ion onto the coagulated resin prepared from 1.0 ml of CRS and 1.6 ml of ARS (curve 1, Fig. 3).By combination of 2.5 ml of CRS and 4.0 ml of ARS, copper(II) was effectively collected onto the mixed resin in the presence of 50 mg of calcium ion (curve 2, Fig. 3).

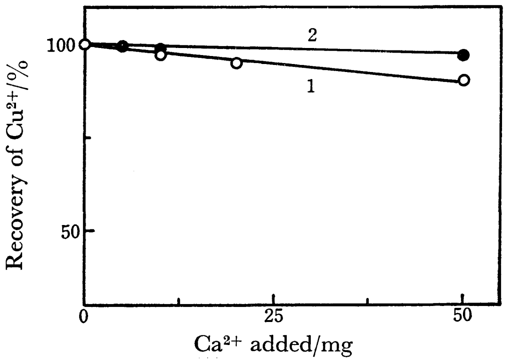

Fig. 3. Recovery of 5.0 μg of copper(II) from 40 ml of solutions containing varying amounts of calcium chloride in the presence of 2 μmol of Hqs$^-$ onto the mixed resin: ○; 1.0 ml of CRS and 1.6 ml of ARS, and ●; 2.5 ml of CRS and 4.0 ml of ARS.

Adsorption of the Chelate. The recovery of copper(II) increased with increasing concentration of Hqs$^-$ until the mole ratio of the reagent to copper content reached 2: 1, and thereafter, copper(II) was quantitatively collected as shown in Fig. 4. The results indicate that the copper(II) was fixed onto the resin in the form of $[Cu(qs)_2]^{2-}$. The recovery of copper(II) was retarded when the amount of the chelating agent increased beyond the exchange capacity of the anion exchanger in the coagulated resin. This is attributable to competition between anions of copper(II)–qs complex and the

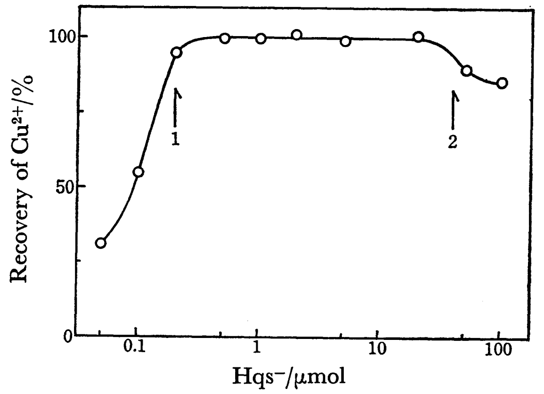

Fig. 4. Effect of the amount of Hqs^- on the recovery of 5.0 μg of copper(II) from 40 ml solutions containing 20 mg of calcium ion onto the coagulated resin prepared from 1.0 ml of CRS and 1.6 ml of ARS. Arrow 1 indicates the point where mole ratio of copper(II) to Hqs^- reached to 1 to 2, and arrow 2 shows the amount of Hqs^- corresponding to the exchange capacity of ARS in the mixed resin.

excess chelating agent for anion exchange sites in the mixed resin. Even if a molecular adsorption of the complex onto the resin matrix might exist,[7] it seems to be much less effective than the ion exchange.

Effect of pH. As shown in Fig. 5, copper(II) was quantitatively collected onto the mixed resin from the solution over the pH range 4—12. The optimal pH range confirmed was much wider than that of 3.5—6.0 observed in the liquid-liquid ion-association extraction system in which an ion-pair of $[Cu(qs)_2]^{2-}$ with quaternary ammonium cation, zephiramine, was extracted into chloroform.[8]

Shaking and Standing Times. A 5-μg portion of copper(II) in 250 ml of a sample solution containing 1.0 ml of CRS, 1.6 ml of ARS, and 2 μmol of Hqs^- was well fixed onto the anion exchanger when the mixture was shaken for more than 5 min. The appreciable coagulation of the resins occurred on standing for 10 min. The resulting mixed resin was easily separated by filtration.

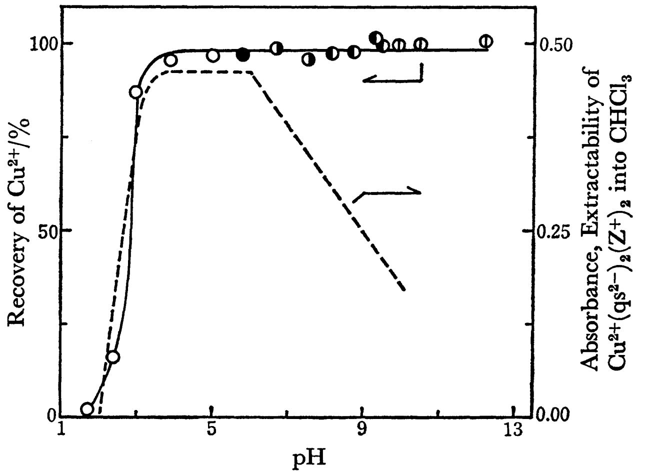

Fig. 5. Effect of pH on the recovery of 5.0 μg of copper(II) from 40 ml of solutions containing 20 mg of calcium ion and 2 μmol of Hqs^- onto the coagulated resin prepared from 1.0 ml of CRS and 1.6 ml of ARS. Dashed line indicates the results obtained in ion-association extraction system.

Buffer systems: ○; NaOAc-HCl, ●; unbuffered, ◑; γ-collidine-HCl, ◐; NH_3-NH_4Cl, ⦶; Borax-NaOH.

Elution of Copper(II) Fixed on the Resin. Of the eluting agents studied, EDTA tetrasodium salt solution was the most satisfactory. Copper(II) fixed on the resin was quantitatively eluted with 20 ml of 0.1—0.2 M of EDTA tetrasodium salt solutions at an eluting rate of 1.0—2.0 ml min^{-1}.

Extraction of Copper(II) from the Eluate. The copper(II)–edta complex in the eluate was converted into the copper(II)–ddtc complex and extracted into MIBK. The organic extract was sprayed into the flame of an atomic absorption spectrometer, resulting in the sensitivity for copper by *ca.* 4 times that obtained by spraying an aqueous solution.[9]

Established Procedure. A 50—500-ml sample solution containing 0.5—5 μg of copper(II) is taken into a separatory funnel. The pH of solution is adjusted to 4—12 with sodium hydroxide solution. Then 2 ml of a 1.0×10^{-3} M Hqs^- solution, 1.0 ml of CRS and 1.6 ml of ARS are added. After shaking for 10 min, the mixture is allowed to stand for several minutes until the coagulated resin settles. The mixed resin is separated by filtration with suction from the solution onto a filter paper (Toyo Roshi No. 2). The copper(II) species on the resin are then eluted with 20 ml of a 0.2 M EDTA tetrasodium salt solution into another separatory funnel. Five ml of 5% Naddtc solution is added and the resulting copper(II)–ddtc complex is extracted into 5.0 ml of MIBK, and the organic extract is then subjected to atomic absorption spectrometry.

Blank Value. Several blank tests were carried out according to the established procedure using 250-ml portions of deionized-redistilled water. The recorder response corresponding to *ca.* 0.2 μg of copper was found.

Effect of Foreign Ions. The concentration procedure was tested with a synthetic sample solution, the components of which are given in Table 1. The effects of iron(III) and aluminum(III) were also examined by adding various amounts to 250-ml portions of the

TABLE 1. EFFECT OF VARIOUS IONS ON THE RECOVERY OF COPPER(II)

	Composition (μg ml^{-1})	Cu^{2+} found (μg)	Recovery[a] (%)
A:	Na^+ 33, K^+ 7.8, Ca^{2+} 10,	5.1	102
	Mg^{2+} 2.4, Cl^- 57, HCO_3^- 36,	5.1	102
	SO_4^{2-} 9.6, SiO_2 7.5	4.9	98
B[b): A+Fe^{3+}	0.08	5.3	106
	0.4	5.1	102
	2.0	5.1	102
C[c]: A+Al^{3+}	0.08	4.8	96
	0.4	4.8	96
	2.0	4.8	96

a) Cu^{2+} 5.0 μg, Sample 250 ml. b) Fe^{3+} added as ammonium iron(III) sulfate. c) Al^{3+} added as aluminum(III) potassium sulfate.

synthetic sample solution. Recovery of copper(II) was not affected by each addition up to 0.5 mg.

It was also found that good recovery of 5 μg of copper(II) contained in 50—500 ml of the sample solution (composition A, Table 1) can be made.

Analysis. The above developed method was applied to the determination of copper(II) in well water taken from our University campus. The standard addition method was employed using 250-ml portions of sample solution. The blank test was carried out using a 250-ml portion of deionized-redistilled water. The linear least-squares regression equation for recorder response of atomic absorption spectrometry, y cm, as a function of added amount of copper(II), x μg, is

$$y = 2.69\,x + 2.50,$$

where y is corrected for the blank value. The F-factor for regression analysis is 4918, highly significant to $F(1, 3: 0.01) = 34.1$. The 95% confidence limits are 3.72 ± 0.063 ng ml^{-1}, the value for the coefficient of variation being 5.3%.

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