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Note

Retention of Cu^{2+} on glass beads coated with chelating agent

NOBORU OKUBO, TOSHIHIKO HANABUSA and MOTOICHI MIYAZAKI

Faculty of Pharmaceutical Sciences, Kanazawa University, Kanazawa (Japan)

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Recently, the study of the preconcentration of trace amounts of metals in environmental samples prior to their analysis has been extended¹⁻¹⁶.

A preliminary report on a promising method using glass beads coated with dibenzoylmethane (DBM) for the retention of micro-amounts of Cu^{2+} has appeared¹². In this communication, the method was further investigated by using some chelating agents such as 8-hydroxyquinoline (HQ), 2-thenoyltrifluoroacetone (TTA) and benzoyltrifluoroacetone (BFA).

EXPERIMENTAL

Apparatus and conditions

A glass chromatographic column (40 × 1.0 cm I.D.) was packed with glass beads coated with chelating agent. A Mitsumi SJ-1210 peristaltic pump (Mitsumi Scientific, Tokyo, Japan) was used for maintaining a constant flow-rate of eluate from the column. A Toyo fraction collector SF-160 K (Toyo Kagaku Sangyo, Tokyo, Japan) was used to collect the eluates. A Hitachi-Horiba M 7 meter (Hitachi, Tokyo, Japan) was used for measuring the pH of the sample solution and the eluates. The chelating agents HQ, TTA and BFA were of analytical grade and were obtained commercially. Acids, alkalis, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{-EDTA}$ of analytical grade were purchased from Wako (Tokyo, Japan). Organic solvents were of commercial reagent grade and were purified in the usual manner. Glass beads were prepared by Nihon Chromat Works (Tokyo, Japan) Water was purified by distilling twice deionized water in all-glass vessels. Apiezon L for precoating the glass beads was obtained from AEI (Manchester, Great Britain), and metal indicator and the reagents used for EDTA titration were of analytical grade.

The preconcentration system is the same one as previously reported¹² (Fig. 1), and the chelating agents used are listed in Table I.

Preparation of Cu^{2+} solution

A 1000 ppm Cu^{2+} solution was prepared by dissolving a known amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water and used as a stock solution. Solutions of 5, 10, and 30 ppm Cu^{2+} were made by diluting the stock solution with water just before use.

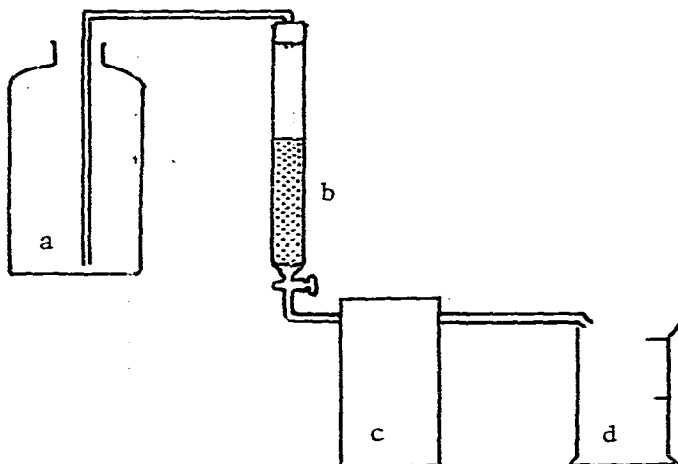


Fig. 1. Preconcentration system. a = Reservoir; -b = column containing glass beads coated with chelating agent; c = peristaltic pump; d = measuring cylinder.

TABLE I
CHELATING AGENTS USED FOR COATING GLASS BEADS

Chelating agent	Name	Formula	M.p. ($^{\circ}\text{C}$)
Dibenzoylmethane (DBM)	1,3-diphenylpropane-1,3-dione	$\text{C}_{15}\text{H}_{12}\text{O}_2$	80
Oxine (HQ)	8-hydroxyquinoline	$\text{C}_9\text{H}_7\text{NO}$	76
Thenoyltrifluoroacetone (TTA)	4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione	$\text{C}_8\text{H}_5\text{F}_3\text{O}_2\text{S}$	44-46
Benzoyltrifluoroacetone (BFA)	4,4,4-trifluoro-1-phenylbutane-1,3-dione	$\text{C}_{10}\text{H}_7\text{F}_3\text{O}_2$	39-41

Preparation of a column with glass beads coated with chelating agent

The Apiezon L-precoated glass beads were coated with 3% HQ, TTA, and BFA, respectively, and the coated glass beads were packed into a glass column. The procedure is summarized in Fig. 2.

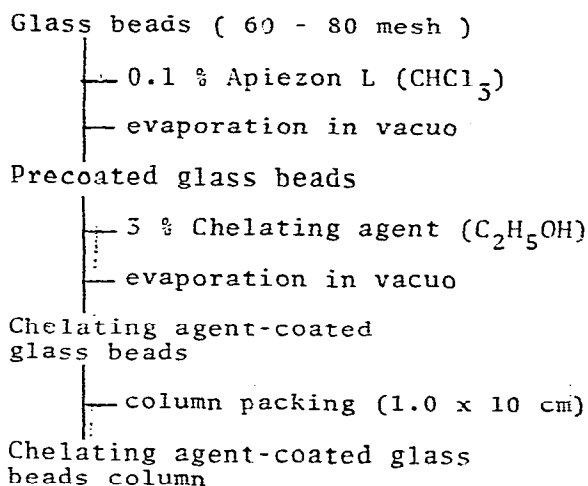


Fig. 2. Preparation of a column containing glass beads coated with chelating agent.

Elution profiles

The elution profiles for the retention of Cu^{2+} were obtained from the TTA and BFA columns. To the top of the column, 1.5 l of 10 ppm Cu^{2+} solution was applied, and the flow-rate of the eluate was maintained at 5 ml/min by using a peristaltic pump.

Each 50-ml fraction of the eluates which had not reacted with the chelating agent on the glass beads and, therefore, was not retained in the column, was determined by titrating the eluate with 0.005 M EDTA solution at pH 4.5 using pyrocatechol violet as a metal indicator. The coating of the glass beads with HQ was found insufficient to perform the retention study of Cu^{2+} owing to its relatively high solubility in water, and its poor adhesiveness on the surface of the Apiezon L-precoated glass beads. As seen in Fig. 3, the retention profile of the TTA-coated glass beads column showed that TTA hardly retained Cu^{2+} at all and is apparently unsuitable for the preconcentration of Cu^{2+} , probably owing to the relatively high solubility of TTA in water and hence a significant loss of TTA from the column during the elution procedure. The retention of Cu^{2+} on BFA-coated glass beads was found to be quantitative until the total eluates amounted to 0.5 l in volume, when the Cu^{2+} solution had a concentration below 10 ppm (Fig. 4).

The elution pattern of the BFA system was similar to that of DBM system which had been reported previously at low concentration of Cu^{2+} .

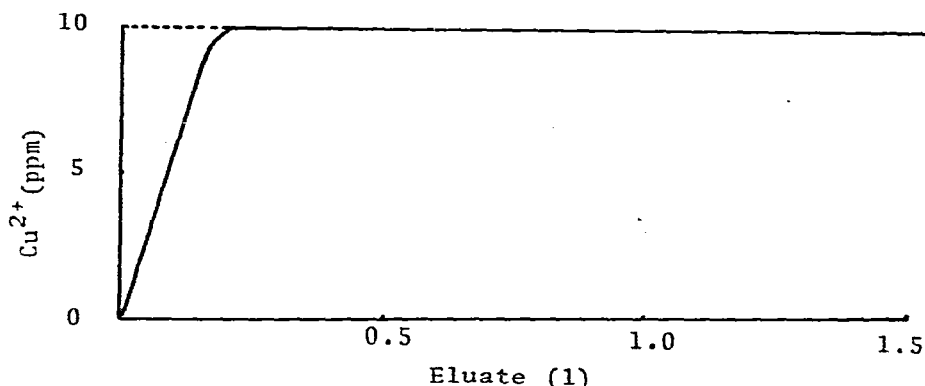


Fig. 3. Retention profile of Cu^{2+} by TTA-coated glass beads column. Column, 3% TTA-coated glass beads (60–80 mesh); flow-rate, 5 ml/min; Cu^{2+} concentration, 10 ppm.

Dissolution of the retained copper chelate on the glass beads column

The dissolution of the retained copper, which was present as the copper chelate on glass beads coated with chelating agent, was examined by using various organic solvents on the DBM and BFA glass beads.

It was shown that the dissolution of CuDBM chelate on the glass beads from the column was not easy with benzene, ethyl acetate, chloroform or methyl isobutyl ketone (MIBK), and generally needed a large amount of the solvent, whereas the dissolution of CuBFA chelate from the column was found to proceed more readily and required a relatively small amount of the solvent. Therefore, the dissolution of CuBFA chelate from the column was investigated more thoroughly.

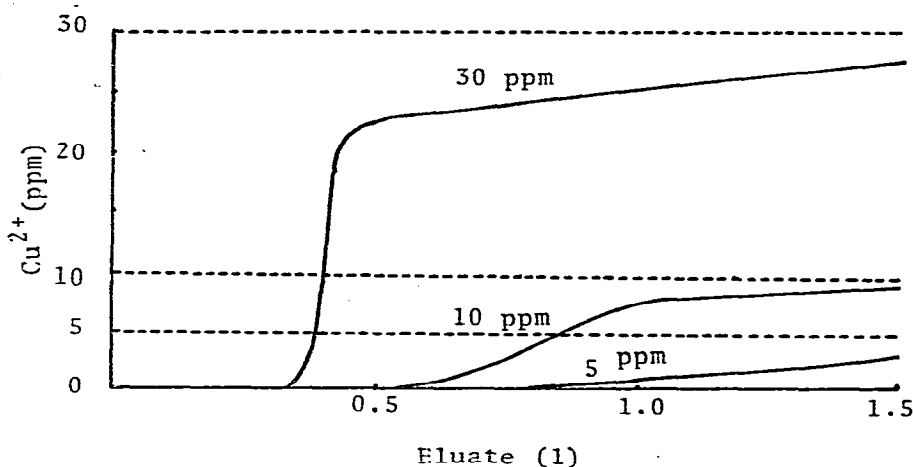


Fig. 4. Retention profile of Cu^{2+} by BFA-coated glass beads column. Column, 3% BFA-coated glass beads (60–80 mesh); flow-rate, 5 ml/min; Cu^{2+} concentrations, 5, 10 and 30 ppm.

Extraction of Cu^{2+} from the CuBFA chelate solution

To determine the proper conditions to extract Cu^{2+} from the CuBFA chelate solution, four solvent systems at various pH were used with a CuBFA chelate that was synthesized in the author's laboratory. The results are shown in Table II.

A 5-ml volume of CuBFA chelate solution, which contained 8 ppm Cu, was mixed with 5 ml of hydrochloric acid solution and Cu^{2+} was back-extracted into the acid solution twice and shaken for 2 min on a mechanical shaker. The two aqueous phases were combined and Cu^{2+} in the solution was determined by EDTA titration. Table II shows that quantitative extraction of Cu^{2+} from the CuBFA chelate solutions is attained at pH 0.8 with benzene, ethyl acetate and MIBK.

TABLE II

RECOVERIES OF Cu^{2+} ON ACIDIC BACK-EXTRACTION FROM THE $\text{Cu}(\text{BFA})_2$ CHELATE SOLUTION AT VARIOUS pH

Organic solvent	Extraction (%)			
	pH 2.9	pH 2.3	pH 1.5	pH 0.8
Benzene	91	96	99	100
Ethyl acetate	24	47	99	100
MIBK	45	57	82	100
CHCl_3	67	72	72	69

Recovery test of Cu^{2+} from the BFA glass beads column

The recovery test of Cu^{2+} from the BFA glass beads column was carried using 0.5 l of 5 ppm Cu^{2+} solution. After the elution, the column was air-dried and treated with 10 ml of benzene to dissolve the CuBFA chelate. A 1-ml volume of the benzene solution was diluted five-fold with benzene and the resulting solution was mixed with 5 ml of 0.16 N HCl (pH 0.8) to back-extract Cu^{2+} twice from the solution. The hydrochloric acid phases were combined and subjected to EDTA titration for the determination of Cu^{2+} . The procedure and the results are given in Fig. 5 and Table I.I.

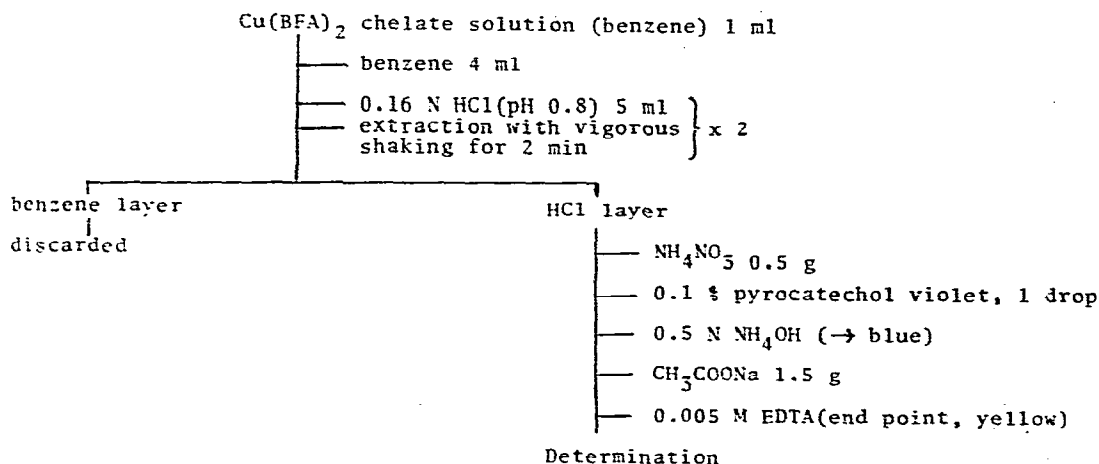


Fig. 5. Procedure for determination of Cu²⁺ (back-extraction method).

TABLE III

RECOVERIES OF Cu²⁺ AT LOW CONCENTRATION USING A BFA-COATED GLASS BEADS COLUMN

Column No.	Taken Cu ²⁺ (mg)	Recovered Cu (mg)	Recovery (%)
1	2.50	2.48	99
	2.50	2.48	99
			} mean 99
2	2.50	2.45	98
	2.50	2.45	98
			} mean 98
3	2.50	2.68	107
	2.50	2.70	108
			} mean 108

Using three separately prepared BFA glass beads columns and eluates amounting to 0.5 l from 5 ppm Cu²⁺ solution, the recovery of Cu²⁺ from the original solution was within the range 98–108% (average 103%).

CONCLUSION

Retention of Cu²⁺ on a coated glass beads column was effected by using benzoyltrifluoroacetone (BFA) as a chelating agent for coating. Complete dissolution of the retained CuBFA chelate from the surface of the glass beads was achieved using an organic solvent such as benzene. The resulting benzene solution was treated with diluted hydrochloric acid to back-extract Cu²⁺ for determination. Thus the BFA glass beads column system appears to be a promising one for the preconcentration of micro-amounts of Cu²⁺ in aqueous samples, such as environmental materials.

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