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Note

Retention of Cu^{2+} on dibenzoylmethane-coated glass beads

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The pre-concentration of a metal from aqueous solutions is considered to be essential prior to its determination when its concentration is very low and does not permit direct analysis. Many methods for the concentration of trace metals have been reported, including the utilization of an ion-exchange resin[1], chelating resin[2], polyamine–polyurea resin[3], chelating agent-impregnated cellulose powder[4], polystyrene beads[5], oxine-immobilized silica gel[6,7], porous glass beads[8,9], the natural carbohydrate polymer chitosan[10], and soybean protein[11].

However, there have been few attempts to use a chelating agent on a suitable support directly in a simple and convenient form for this purpose. This study was undertaken in order to investigate this aspect and to examine on-column chelate formation for collecting metals by using a chelating agent-coated glass beads as a chromatographic support.

Taking Cu^{2+} as the metal ion, it was passed through a column packed with 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM)-coated glass beads, with which it reacted to form a copper chelate which was retained. DBM was adopted for chelation with Cu^{2+} as it has strong chelating ability with many heavy metal ions[12] and gives characteristic colours, and both DBM and the chelates formed have very low solubilities to water. Glass beads were used as the support for DBM, as they are chemically stable and inert to common chemicals, have relatively uniform particle sizes (spherical) and are commercially obtainable at moderate cost.

The method reported here was found to be effective for the quantitative retention of Cu^{2+} and is simple and convenient.

EXPERIMENTAL

Apparatus and conditions

A glass chromatographic column (40 × 1.0 cm I.D.) was packed with DBM-coated glass beads. A Mitsumi SJ-1210 peristaltic pump (Mitsumi Scientific, Tokyo, Japan) was used for maintaining a constant flow-rate of eluate from the column throughout the chromatography. A Toyo SF-160 K fraction collector (Toyo Kagaku Sangyo, Tokyo, Japan) was used to collect the eluates. A Hitachi-Horiba M7 pH meter (Hitachi, Tokyo, Japan) was used for measuring the pH of the sample solution and the eluates.

DBM was of analytical-reagent grade, purchased from Tokyo Kasei Kogyo

(Tokyo, Japan), and was used without further purification. $CuSO_4 \cdot 5H_2O$ and EDTA·2Na of analytical-reagent grade were obtained from Wako (Tokyo, Japan). Glass beads of different particle sizes were purchased from Applied Science Labs. (State College, Pa., U.S.A.) and Nihon Chromat Works (Tokyo, Japan). Water was obtained by redistilling deionized water in all-glass vessels, and all organic solvents used were of analytical-reagent grade. Apiezon L (AEI, Manchester, Great Britain) was used to pre-coat the glass beads as a liquid phase before coating with DBM. Metal indicators and the reagents for EDTA titration were of analytical-reagent grade.

Preparation of Cu^{2+} solution

A 1000 ppm Cu^{2+} solution was prepared by dissolving a known amount of $CuSO_4 \cdot 5H_2O$ in water and used as a stock solution. Cu^{2+} solutions of concentration 5, 10, 15 and 30 ppm were made by diluting the stock solution with water just before use.

Preparation of DBM-coated glass beads column

Glass beads (500 ml) of four different particle sizes (40–60, 60–80, 80–100 and 100–120 mesh) were treated overnight with 1 l of hydrochloric acid (1:1) in order to remove metal contaminants such as Fe^{3+} and Al^{3+} by the method of Seiler and Seiler[13], washed with water and methanol and finally air dried. The purified glass beads were immersed in a solution of Apiezon L in chloroform (0.1% of Apiezon L relative to the weight of the glass beads was dissolved in chloroform) and evaporated *in vacuo* so as to coat a film of Apiezon L on the surface of the glass beads. Then, a known amount of the Apiezon L pre-coated glass beads was immersed in DBM–acetone solution (for example, 3% of DBM relative to the weight of the pre-coated glass beads), and evaporated *in vacuo* in order to remove the solvent. The DBM-coated glass beads were air dried and a known amount (about 10 g) was packed to a height of 10 cm in the column. Purified glass beads (uncoated) were laid on top of the DBM-coated glass beads to a height of 1 cm and then the column was washed with water until the eluate became clear.

Previous experiments showed that the Apiezon L pre-coating was more effective in holding DBM on the glass beads than was direct coating with DBM without Apiezon L.

Retention of Cu^{2+}

Cu^{2+} solution was delivered continuously to the top of the column at a constant flow-rate by using a peristaltic pump, and 50-ml portions of the eluate were collected. The elution of Cu^{2+} solution was continued until the total volume of the eluate collected was 1–1.5 l. The amount of Cu^{2+} in the eluate which had not reacted with DBM 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 indicator. Standardization of the EDTA solution was carried out in the usual way and all experiments were performed at room temperature.

RESULTS

Loss of DBM from the column

Elution of water was carried out at a flow-rate of 5 ml/min in order to measure the loss of DBM from the 3% DBM-coated glass beads (60–80 mesh) column during chromatography. The DBM found in 1.5 l of the eluate amounted to only about 2% of its total amount on the glass beads in the column. Therefore, the amount of DBM in any portion of eluate taken for titration would be very small, and its influence on the EDTA titrations was observed to be virtually negligible.

The DBM in the eluate could possibly be recovered and re-used as the reagent for the retention study.

A change in pH of the Cu^{2+} solution occurred during elution; the pH of a 10 ppm Cu^{2+} solution gradually decreased from 5.3 to 4.0. This result showed that chelate formation between Cu^{2+} and DBM had clearly occurred according to the equations $Cu^{2+} + DBM = CuDBM + H^+$ and $CuDBM + DBM = Cu(DBM)_2 + H^+$, the release of the proton from DBM increasing the hydrogen ion concentration of the eluate.

Flow-rate

Flow-rates of the eluates from the column of 1.6, 3.3, 5.0 and 10.0 ml/min were used and were maintained at these levels by using the peristaltic pump during chromatography. With 3% DBM-coated glass beads (60–80 mesh), a 10 ppm Cu^{2+} solution was fed to the column and 50-ml portions of the eluate were collected. As expected, better retention of Cu^{2+} on the column was observed at slower elution flow-rates. The results are shown in Fig. 1.

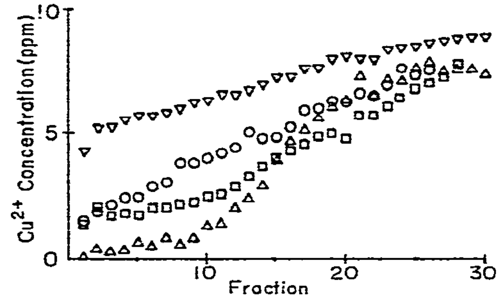

Fig. 1. Effect of different flow-rates. Initial Cu^{2+} concentration: 10 ppm. Column: 3% DBM-coated glass beads (60–80 mesh). Flow-rate: △, 1.6; □, 3.3; ○, 5.0; ▽, 10.0 ml/min.

Particle size of glass beads

Particle sizes of the glass beads of 40–60, 60–80, 80–100 and 100–120 mesh were compared with regard to their ability to retain Cu^{2+}. The finer glass beads showed a greater retention of Cu^{2+} on the glass beads. The results are shown in Fig. 2.

However, the finer the glass beads, the greater was the resistance to elution, and adjustment of peristaltic pump was needed in order to keep the flow-rate constant. Considering from the data, the particle sizes of glass beads seem to be rather a matter of choice.

Amount of DBM used for coating glass beads

The results obtained with 1.5% and 3% (w/w) DBM-coated glass beads were

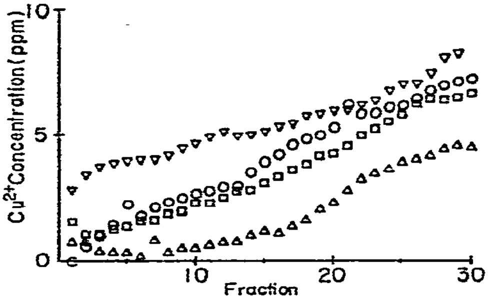

Fig. 2. Effect of glass beads of different particle sizes. Initial Cu^{2+} concentration: 10 ppm. Column: 3% DBM-coated glass beads. Flow-rate: 5 ml/min. Particle size: ▽, 40–60; ○, 60–80; □, 80–100; △, 100–120 mesh.

compared. Very similar results were obtained, but 3% DBM gave a slightly higher retention of Cu^{2+} from fraction 1 to fraction 30. A much greater retention was observed with 3% DBM in the initial stages of the elution (until fraction 8) than with 1.5% DBM. The results are shown in Fig. 3.

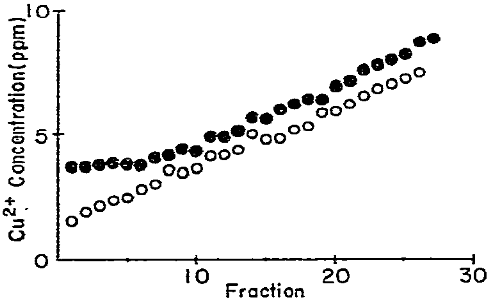

Fig. 3. Effect of amount of DBM coated on glass beads. Initial Cu^{2+} concentration: 10 ppm. Column: DBM-coated glass beads (60–80 mesh). Amount of DBM: ●, 1.5%; ○, 3%. Flow-rate: 5 ml/min.

Retention of Cu^{2+} from the solutions with various Cu^{2+} concentrations

Cu^{2+} solutions of 5, 15 and 30 ppm concentration were submitted to the retention study, and the results are shown in Fig. 4.

By using the 3% DBM-coated glass beads column, complete retention of Cu^{2+} was obtained with the 5 ppm Cu^{2+} solution at a flow-rate of 5 ml/min until the volume of eluate was 1.5 l. With both 15 and 30 ppm Cu^{2+} solutions, the retention of Cu^{2+} clearly decreased and showed a tendency for the eluate to become saturated at a level of about 7 ppm of Cu^{2+} below the initial Cu^{2+} concentration. This tendency was observed most clearly with the 30 ppm Cu^{2+} solution. These results indicate that the 3% DBM-coated glass beads had a Cu^{2+} retention capacity of about 7 ppm in the steady state of the elution under the conditions used, so that complete retention of Cu^{2+} from a 5 ppm Cu^{2+} solution would be assured with this Cu^{2+} retention capacity of the column.

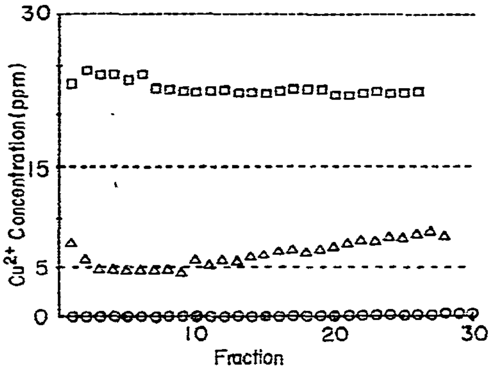

Fig. 4. Retention of Cu^{2+} from Cu^{2+} solutions of different concentrations. Column: 3% DBM-coated glass beads (60–80 mesh). Flow-rate: 5 ml/min. Cu^{2+} concentration: ○, 5; △, 15; □, 30 ppm.

CONCLUSION

There have been very few attempts to collect metals as chelates directly on chromatographic columns. The retention of metals with a chelating agent-coated glass beads column has been shown to be a possible convenient means for the pre-concentration of metals. The method reported here could be used to collect trace metals from aqueous samples such as environmental materials, and should serve as an effective pre-treatment prior to subsequent analyses for metals.

Further studies on the application of the method are being carried out, and the results will be published elsewhere.

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