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APPLICATION OF A COULOMETRIC DETECTOR TO RAPID ION-EXCHANGE CHROMATOGRAPHY*

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SUMMARY

A flow coulometric detector was applied to a study of the rapid separation of heavy metal ions by cation-exchange chromatography using sodium tartrate solution as the eluent.

The effects of pH, composition and flow-rate of the eluent, degree of cross-linking and particle size of the ion-exchange resin, and column temperature on the retention time and column efficiency were investigated. The separation of a six-component mixture of metal ions (copper, zinc, nickel, lead, cobalt and cadmium) was completed within 2 min under optimum conditions.

INTRODUCTION

At present, the speed of separation by liquid chromatography is almost the same as that by gas chromatography, and several organic and biochemical substances can be separated by liquid chromatography within a few minutes[1]. However, the rapid separation and analysis of metal ions and inorganic anions has been less successful because no suitable detectors have been found for these substances. A light-absorption method based on colour-forming reactions was applied to the detection of metals by Seymour and other workers[2–5], and radiometric flow detectors were applied by Sisson *et al.*[6] and Huber and Van Urk-Schoen[7]. For the detection of ions, Gilbert and Dobbs[8] developed a membrane detector that responds to the small volume changes produced in an ion-exchange membrane. However, difficulties still remain in the use of photometric and radiometric detectors for general applications and in the use of the membrane detector when high sensitivity and good precision are required.

A flow coulometric detector for liquid chromatography has been developed[9]. It has been shown that the detector is suitable for the detection of substances such as metal ions, inorganic anions and organic acids. The present work is concerned

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with the application of a flow coulometric detector to the rapid ion-exchange chromatography of heavy metal ions.

EXPERIMENTAL

Liquid chromatograph

The experiments were carried out with a Hitachi Model 034 liquid chromatograph and a coulometric detector. A few parts of the apparatus shown in the earlier paper[9] were modified, *viz.*, a sample injection port for micro-syringe injection, a different type of electrolytic cell and a shorter and more slender conduit were used. PTFE tubes of length 40 cm and I.D. 0.5 mm were used for the conduits from the sample injection port to the detector.

Detector cell (electrolytic cell)

The construction of the cell is the same as that used in a Hitachi Model 630C coulometric monitor, and therefore it is different from that used by Johnson and co-workers[10,11] for the detection of copper(II), iron(III) and antimony(III). A cross-section of the cell is shown in Fig. 1. The cell consists of a porous, thin plate-like working electrode, a porous auxiliary electrode and a diaphragm (an ion-exchange membrane) between the electrodes. The thickness of the working electrode, which is made of carbon-cloth, is 0.6–1.0 mm. The solution (column effluent) penetrates into the electrode.

The auxiliary electrode is made from silver–silver iodide netting of about 40 mesh. As the auxiliary electrode is not polarized with a slow flow of electrolytic current, the potential of the auxiliary electrode is kept constant. The potential of the working electrode can therefore be set at a constant value only by applying a constant voltage between the working and auxiliary electrodes.

The response time of the cell was less than 1 sec and the electrolytic efficiency was greater than 99.5% for copper(II) ion at a flow-rate of 4 ml/min.

Preparation of columns

As all of the cation-exchange resins used were strongly acidic (sulphonated polystyrene resins of nominal 8, 10 and 12% divinylbenzene cross-linking; Hitachi

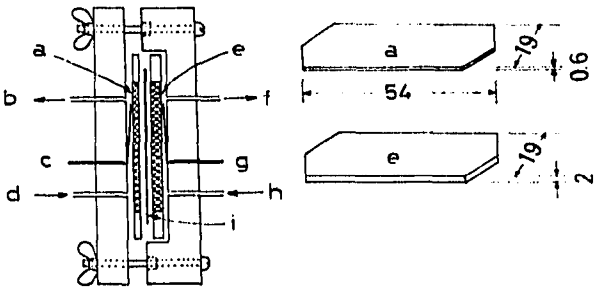


Fig. 1. Detector cell. a, Working electrode; b, sample solution outlet; c, working electrode lead; d, sample solution inlet; e, auxiliary electrode; f, electrolyte outlet; g, auxiliary electrode lead; h, electrolyte inlet; i, diaphragm (ion-exchange membrane).

Custom ion-exchange resins No. 2611 and 2613, and CK 10 and 12 resins of Mitsubishi Chemical Industries), they were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. The water-jacketted glass columns were filled with these resins.

Column operation and detection of metal ions

The eluent (sodium tartrate solution) is pumped into a separation column through a sample injection port. The column effluent is mixed with buffered mercury(II) diethylenetriaminepentaacetate (DTPA) solution before it flows into the detector cell and the solution pumped into the cell then flows out through the outlet of the cell. Through another inlet to the cell, 0.5 *M* potassium iodide solution is pumped into the auxiliary electrode in order to keep the potential constant.

The principle of the detection is based on constant-potential coulometry. All constituents of the effluent are almost completely electrolyzed before the effluent flows out from the cell. The electric charge that arises by the electrochemical reaction is measured with a laboratory potentiometric recorder. The electrochemical reaction for the detection is as follows[12]:

$$M^{2+} + \text{Hg-DTPA}^{3-} + 2e \rightarrow \text{M-DTPA}^{3-} + \text{Hg} \qquad (1)$$

where M^{2+} is a divalent metal ion. The potential applied to the working electrode is sufficient to effect reaction 1 essentially completely but the reaction 2 to only a negligible extent:

$$\text{Hg-DTPA}^{3-} + 2e \rightarrow \text{DTPA}^{5-} + \text{Hg} \qquad (2)$$

Many metal ions that form stable complexes with DTPA become detectable with little influence by dissolved oxygen. This method was applied to studies of the elution behaviour of rare earth elements on ion-exchange columns by Yamabe and coworkers[13-15].

RESULTS AND DISCUSSION

Separation with resins of various degrees of cross-linking

The effect of the degree of cross-linking on the retention times of heavy

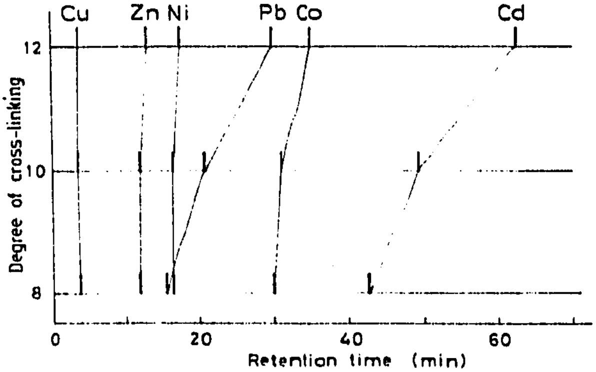


Fig. 2. Effect of degree of cross-linking on retention time. Resins: sulphonated polystyrene ion-exchange resin of nominal 8, 10 and 12% cross-linking. Column: 110 mm × 9 mm I.D., room temperature. Eluent: 0.2 *M* sodium tartrate, pH 3.8; flow-rate, 1.5 ml/min.

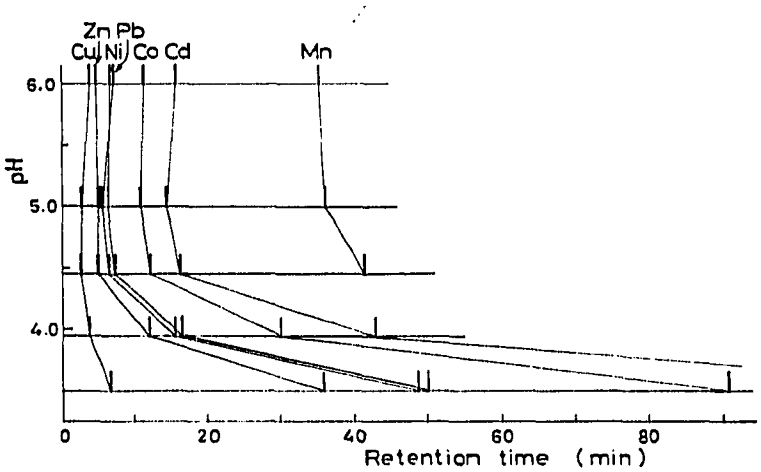
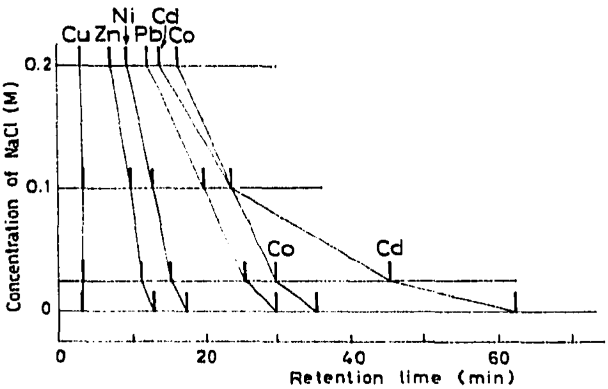


Fig. 3. Effect of eluent pH on retention time. Resin: Hitachi Custom ion-exchange resin No. 2613. Column: 100 mm × 9 mm I.D., room temperature. Eluent: 0.2 *M* sodium tartrate; flow-rate, 1.5 ml/min.

metal ions was examined. The results are shown in Fig. 2. The retention times of lead and cadmium increased more than those of the other ions with the resins of higher degrees of cross-linking. As shown in Fig. 2, the resins with more than 10% cross-linking are suitable for the separation of nickel from lead.



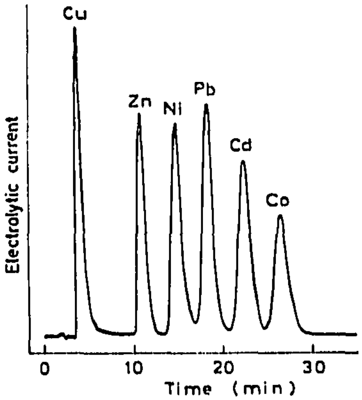


Fig. 4. Effect of sodium chloride added to eluent on retention time. Resin: ion-exchange resin, 12% cross-linking. Column: 110 mm × 9 mm I.D., room temperature. Eluent: 0.2 *M* sodium tartrate–*xM* NaCl, pH 3.8; flow-rate, 1.5 ml/min.

Fig. 5. Typical chromatogram for heavy metal ions. Sample size: $5 \cdot 10^{-7}$ mole. Resin: Hitachi Custom ion-exchange resin No. 2611. Column: 90 mm × 9 mm I.D., room temperature. Eluent: 0.2 *M* sodium tartrate–0.12 *M* NaCl, pH 3.63; flow-rate, 1.5 ml/min. Detection potential: 0.22 V *vs.* Ag–AgI.

Effect of pH

The retention time of metal ions was influenced by the pH of the eluent (Fig. 3). The retention time of metal ions decreased with increasing pH when the pH of the eluent was less than 4.5. It is thought that this effect is caused by a decrease in the dissociation of tartaric acid below pH 4.5.

Addition of sodium chloride to the eluent

The behaviour of metal ions on elution when sodium chloride was added to the eluent was examined (Fig. 4). The retention time of each ion is reduced by the addition of sodium chloride, especially the retention time of cadmium.

The behaviour of the mercury(II) ion was also examined. It was found that the effect for mercury is more pronounced than that for cadmium. It is thought that this effect arises from the difference in the formation constants of the chloro-complexes.

Typical example of separation under optimum conditions

An example of a chromatogram for heavy metal ions is shown in Fig. 5. The conditions for the optimum separation were obtained by varying the capacity factor and the separation factor[16] based on the data stated above. It took about 30 min to separate six components (copper, zinc, nickel, lead, cadmium and cobalt). It seemed possible to separate them more rapidly by changing the column parameters and operating conditions so as to improve the column efficiency. Conditions for more rapid separation were therefore sought.

Effect of flow-velocity of the eluent on column efficiency

In general, a long and narrow-bore column is used with an eluent flow of high pressure and high velocity in order to attain a rapid separation[16,17]. The situation is different, however, when a conventional ion-exchange resin that is sulphonated into the

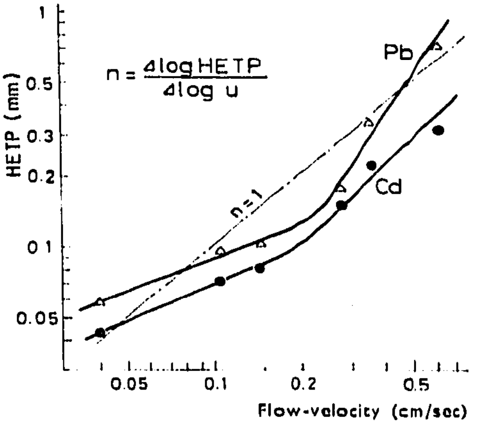


Fig. 6. Effect of flow-velocity of eluent on column efficiency. Sample size: $5 \cdot 10^{-8}$ mole. Resin: Hitachi Custom ion-exchange resin No. 2611. Column: 60 mm × 6 mm I.D., 50°. Eluent: 0.25 *M* sodium tartrate–0.019 *M* NaCl, pH 3.7.

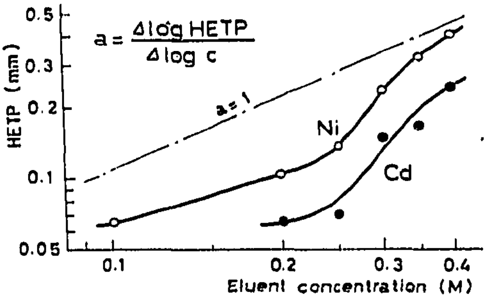


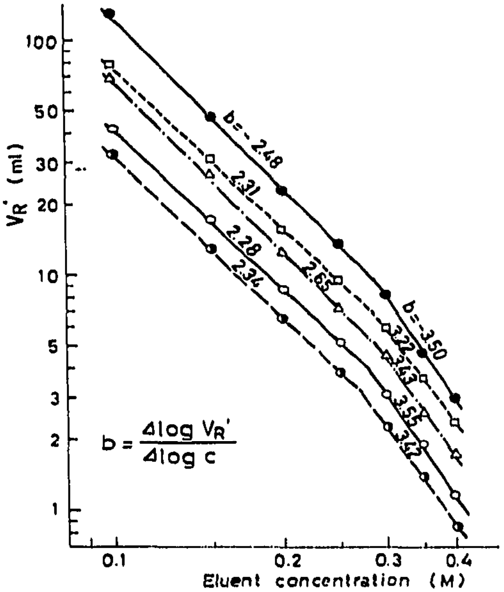
Fig. 7. Effect of eluent concentration on column efficiency. Conditions as in Fig. 6. Eluent: sodium tartrate-NaCl (mole ratio = 4:0.3), pH 3.7; flow-rate, 1.61 ml/min.

bulk is used. Fig. 6 shows the changes in column efficiency (height equivalent to a theoretical plate, HETP) obtained in the separation of lead and cadmium at various linear flow-velocities, u. As shown in Fig. 6, the slope of the log HETP *versus* log u plots is greater than unity at a flow-velocity of more than 0.2 cm/sec. This indicates that a higher flow-velocity of the eluent does not always ensure a higher speed of separation.

Effect of eluent concentration

In general, the higher the concentration of the eluent, the more rapid is the elution, and the effect of an increase in concentration on the speed of separation was investigated.

At first, the relationship between log HETP and log concentration (log c) was



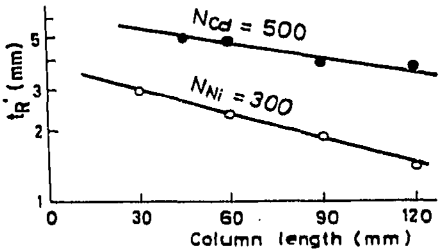


Fig. 8. Effect of eluent concentration on apparent retention volume. Conditions as in Fig. 7.

ig. 9. Relationship between apparent retention time and column length at constant theoretical plate umbers. Conditions as in Figure 7.

examined (Fig. 7). It can be seen that the slope of the graphs is greater than unity in a certain range of concentration. In Fig. 8, the logarithm of the apparent retention volume, V_R', is plotted against log c. It can be seen that the slope ($-b$) in Fig. 8 is greater than that (a) in Fig. 7. These results indicate that there is a possibility of achieving more rapid separations by using a higher eluent concentration and a longer column.

The relationship between the apparent retention time, t_R', and the length of the column, L, was obtained at a constant theoretical plate number, N, and flow-rate, F. Fig. 9 shows the result calculated from the data in Figs. 7 and 8 according to the following equations:

$$L = N \cdot \mathrm{HETP} \tag{3}$$

and

$$t_R' = \frac{V_R'}{F} \tag{4}$$

Fig. 9 apparently shows that the use of a longer column and an eluent of higher concentration is very effective in shortening the separation time.

Effect of column temperature

The effect of the column temperature on column efficiency was also investigated (Fig. 10). The resolution of the chromatogram is improved by increasing the temperature.

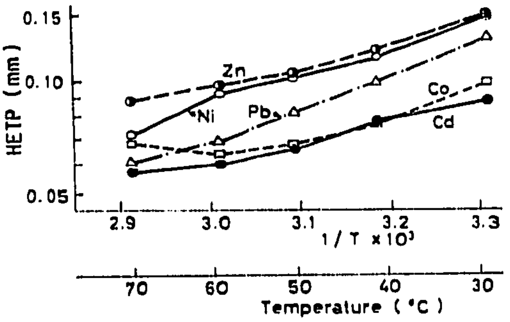


Fig. 10. Effect of column temperature on HETP. Conditions as in Fig. 6; flow-rate, 1 ml/min..

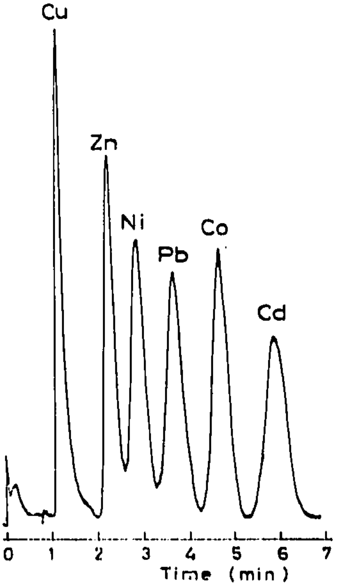


Fig. 11. Rapid separation of heavy metal ions with resin of fixed particle size. Sample size: $5 \cdot 10^{-8}$ mole. Resin: Hitachi Custom ion-exchange resin No. 2611, 15.5 ± 2 μm. Column: 60 mm × 6 mm I.D., 50°. Eluent: 0.4 M sodium tartrate–0.02 M NaCl, pH 3.63; flow-rate, 1 ml/min; pressure, 5 kg/cm^2.

Rapid separation with resin of fixed particle size

Based on the preceding data, parameters for rapid separations with a given apparatus were selected, *viz.*, a column of length 60 mm and I.D. 6 mm with an eluent of pH 3.7 consisting of 0.4 *M* sodium tartrate and 0.02 *M* sodium chloride. The chromatogram obtained under these conditions is shown in Fig. 11. The separation of six metal ions was completed within 7 min. In this example, an ion-exchange resin with a particle size distribution of 15.5 ± 2 μm was used.

High-speed separation with resin of smaller particle size

It is well known that a higher resolution is obtained with a resin of a smaller particle size. A resin with a size distribution of 8–11 μm was used in the separation column and the chromatogram obtained is shown in Fig. 12. It can clearly be seen that the resolution is considerably improved.

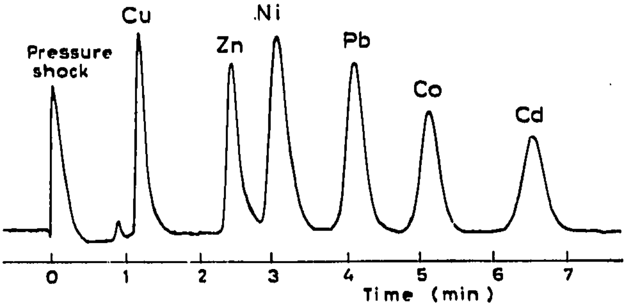


Fig. 12. Chromatogram obtained using a resin of smaller particle size. Sample size: $1 \cdot 10^{-7}$ mole. Resin: 10% cross-linked cation-exchange resin, 8–11 μm. Column: 90 mm × 6 mm I.D., 50°. Eluent: 0.4 *M* sodium tartrate-0.03 *M* NaCl, pH 3.65; flow-rate, 1.22 ml/min; pressure, 18 kg/cm².

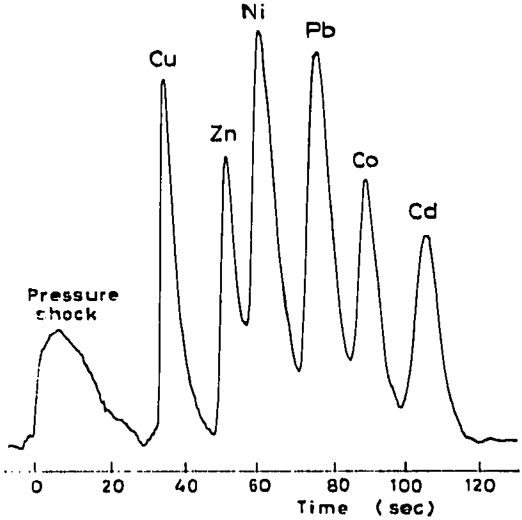


Fig. 13. High-speed separation of heavy metal ions. Sample size: $3 \cdot 10^{-8}$ mole. Resin: as in Fig. 12, 5–8 μm. Column: 40 mm × 6 mm I.D., 60°. Eluent: 0.5 *M* sodium tartrate-0.038 *M* NaCl-a few ppm sodium hexametaphosphate, pH 3.7; flow-rate, 0.82 ml/min; pressure, 13 kg/cm².

Fig. 13 shows a chromatogram obtained with a resin of particle size 5–8 μm. The six heavy metal ions (copper, zinc, nickel, lead, cobalt and cadmium) are separated within only 120 sec. The chromatogram shown in Fig. 13 was obtained at an inlet column pressure of 13 kg/cm^2, and the number of theoretical plates for cadmium is calculated to be 1 140. The number of plates per second is calculated to be 10.8 and the number of plates per atmosphere to be 87.7 for cadmium. This means that a separation of higher speed was successfully achieved with the coventional resin at lower pressures compared with pellicular type packings[18].

CONCLUSION

It is apparent that the response of the coulometric detector is sufficiently rapid and the detector is very useful for high-speed liquid chromatography.

In order to separate metal ions at high resolution and high speed using conventional ion-exchange resins, it is effective to increase the concentration of eluent and to use a longer column. It is also effective to use a resin of a small particle size.

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