Journal of Chromatography, 151 (1978) 339–345

CHROM. 10,518

CATION-EXCHANGE CHROMATOGRAPHY OF BISMUTH(III), CADMIUM(II), INDIUM(III) AND ZINC(II) IONS WITH HYDROCHLORIC ACID IN AQUEOUS ACETONE SOLUTION

KAZUYOSHI KAWAZU and HITOO KAKIYAMA
National Industrial Research Institute of Kyushu, Shuku-machi, Tosu 841 (Japan)
(First received August 2nd, 1977; revised manuscript received August 19th, 1977)

SUMMARY

Trace amounts of bismuth(III), indium(III), cadmium(II) and zinc(II) were separated from each other by stepwise elution chromatography and detected by continuous flow spectrometry. A macroreticular cation-exchange resin was used to achieve rapid separation in hydrochloric acid–acetone covering the acid and acetone concentration ranges 0.1–0.64 *M* and 18–80%, respectively.

INTRODUCTION

Aqueous acetone–hydrochloric acid solutions have frequently been used[1–10] to separate elements on cation-exchange resins because of the high complex-formation capability of the solutions and the low viscosity of acetone solvent. The rapid chromatographic separation of cadmium(II), zinc(II), iron(III), lead(II), copper(II), uranium(VI), cobalt(II), iron(II), manganese(II), vanadium(IV) and nickel(II) has been reported previously[10]. These metal ions were eluted by stepwise elution chromatography using aqueous acetone and aqueous acetone–dimethylformamide solutions of hydrochloric acid on the macroreticular cation-exchange resin, and detected continuously by the on-stream addition of a colour-forming reagent. Ion-exchange behaviour and the incidental detection of bismuth(III) and indium(III) together with the elements mentioned above were examined in detail in order to use the method effectively for the analysis of samples containing other, more metallic elements, as reported here.

Few studies on the mutual separation of bismuth(III), cadmium(II), indium(III) and zinc(II) have been reported. Fritz and Rettig[1] reported the separation of bismuth(III), cadmium(II), zinc(II) and other elements using aqueous acetone–hydrochloric acid eluents, but indium(III) and cadmium(II) were not separated from one another. Strelow *et al.*[7] separated cadmium(II), indium(III), zinc(II) and other elements using aqueous acetone–hydrochloric and/or hydrobromic acid eluents. Bismuth(III) was accompanied by cadmium(II) in their study. Willis and Fritz[11] reported the rapid chromatographic separation and the continuous spectrophotometric determination of mercury(II), bismuth(III), cadmium(II) and antimony(III) by the use of aqueous hydrobromic acid eluents, but they failed to separate indium(III), zinc(II) and antimony(III). We have now achieved the mutual separation of bismuth(III), cadmium(II), indium(III), zinc(II) and some other elements. The continuous spectrophotometry method described previously[10] was used to obtain elution curves.

EXPERIMENTAL

Equipment

Metering pumps from Japan Electron Optics Lab. Co. (JEOL, Tokyo, Japan) were used to force the eluent through a chromatographic column and the colour-forming reagent solution through a mixing chamber. These pumps can deliver liquid at outlet pressures up to 30 atm. The materials contacting the solutions were made of glass and polytrifluoroethylene(PTFE).

A reciprocating mini-pump of the single-piston type (Milton-Roy, St. Petersburg, Fla., U.S.A.) was used at outlet pressures up to 45 atm for the dynamic packing of the chromatographic column.

A sample-injection valve was obtained from Kyowaseimitsu Co. (Mitaka, Tokyo, Japan) and fitted with calibrated sample loops made of 1 mm I.D. PTFE tubing. The volume (0.2 ml) of a loop was calibrated according to the procedure described previously[9].

A chromatographic glass tube (5 mm I.D.) obtained from Kyowaseimitsu Co. was equipped with fixed outlet plungers.

A three-way polytrifluorochloroethylene (PTFCE) tap obtained from Kyowaseimitsu Co. was used as a mixing chamber.

PTFE tubing (1 mm I.D.) was used for the pipeline of the chromatographic system. In order to ensure the reaction of a colour-forming reagent with a metal ion in the effluent solution, a 150 cm long PTFE tube was used between the mixing chamber and the flow-through cell.

A Hitachi Model 124 spectrophotometer was used for the continuous detection of metal ions in the effluent solution. The sample compartment of the spectrophotometer was altered to accommodate a flow-through cell (Hitachi Model 034-0249). The light path of the cell was 4 mm long and the internal volume was *ca.* 90 μl. The materials contacting the solution were made of quartz and stainless steel.

Reagents

Resin. The macroreticular strongly acidic cation-exchange resin Amberlite 200 was obtained as beads in the sodium form from Rohm & Haas (Philadelphia, Pa., U.S.A.). The dried beads were fragmented in a ball-mill. The fraction of graded particles (25–30 μm in diameter) was obtained by continuous elutriation and purified by procedures described previously[12]. The capacity of the air-dried resin was 4.2 mequiv./g.

Metal solutions. Standard solutions were prepared by dissolving each metal compound of the reagent grade in the dilute acid solution. Bismuth nitrate, indium hydroxide, cadmium chloride and zinc chloride were used. Synthetic sample mixtures for the column separation were prepared by mixing an aliquot of each metal ion solution and deionized water.

Eluents. The eluents were solutions of aqueous acetone in dilute hydrochloric acid. Each eluent was prepared so that the concentrations of hydrochloric acid and organic solvent were expressed as a molarity and a percentage by volume, respectively.

Colour-forming reagent solution. 4-(2-Pyridylazo)-resorcinol (PAR) solution in ammonia was prepared according to the procedure described previously[9]. This solution was used for the determination of cadmium(II), indium(III), zinc(II) and other metal ions. Another solution of PAR in dilute sodium hydroxide was also prepared as the standard solution for the determination of bismuth(III). An aliquot of this solution was mixed with solutions of acetic acid and sodium acetate for use in the continuous determination of bismuth(III) in the effluent solution.

Procedure

A chromatographic tube was filled with a thick slurry of the resin fraction in acetone by the method of dynamic packing, as described previously[12].

The elution curves were obtained by continuous detection using flow spectrometry. The colour-forming reagent (PAR) reacted with bismuth(III) in aqueous acetone solution containing sodium chloride and acetate buffer (pH, 6.5). The bismuth(III)–PAR complex had its absorption maximum at 545 nm. The flow-rate and the sodium hydroxide concentration of the PAR solution were set so that the effluent stream from the mixing chamber would have a pH in the range 6–7. The continuous detection of cadmium(II), indium(III) and zinc(II) was carried out by the procedure described previously[9]. The wavelength was set at 525 nm for the simultaneous detection of these four ions.

RESULTS AND DISCUSSION

Distribution coefficients and separation factors

The distribution coefficients of the metal ions were determined by column chromatography. The effect of the acetone concentration on the distribution coefficients in 0.1, 0.32 and 0.64 *M* hydrochloric acid solutions is shown in Figs. 1–5. The effect of the column temperature was also examined. The distribution coefficients shown in Figs. 1, 3 and 4 were obtained at 40°. The distribution coefficients shown in Figs. 2 and 5 were obtained at ambient temperature (25–30°).

Good separation factors (> 3) for the bismuth(III)–cadmium(II) and cadmium(II)–zinc(II) pairs were obtained by using 75–82% concentrations of acetone in 0.1 *M* hydrochloric acid solutions at 40° and ambient temperature (see Figs. 1 and 2). Sharp and rapid separation of bismuth(III) and cadmium(II) was best in *ca.* 80% acetone, and of cadmium(II) and zinc(II) in *ca.* 83% acetone. However, the mutual separation of indium(III) and zinc(II) in the aqueous acetone–0.1 *M* hydrochloric acid media, was not achieved.

Good separation factors for the cadmium(II)–indium(III) and indium(III)–zinc(II) pairs were obtained using 60–70% acetone–0.32 *M* hydrochloric acid (see Fig. 3). The separation factor for the former pair was more than 2.5 and for the latter *ca.* 2.

Good separation factors (more than 3) for the indium(III)–zinc(II) or cadmium(II)–zinc(II) pairs were obtained using 50% acetone–0.64 *M* hydrochloric acid at 40° and ambient temperature (see Figs. 4 and 5). More effective separation of

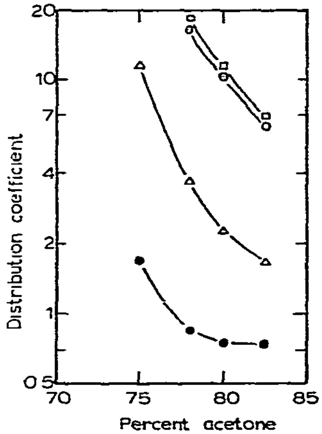


Fig. 1. Distribution coefficients as a function of the acetone concentration in 0.1 *M* hydrochloric acid solution at 40°. Flow-rate of eluent, 20 cm/min; ●, bismuth (III); ○, indium (III); △, cadmium (II); □, zinc (II).

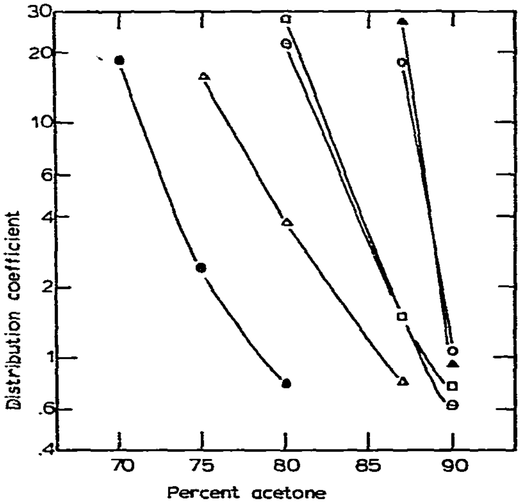


Fig. 2. Distribution coefficients as a function of the acetone concentration in 0.1 *M* hydrochloric acid solution at the ambient temperature. Flow-rate of eluent, 20 cm/min; ▲, iron (III); ○, gallium (III); symbols for other metal ions as in Fig. 1.

indium(III) and cadmium(II) was achieved at ambient temperature than at 40°, with a separation factor of more than 2.5 with 18% acetone–0.64 *M* hydrochloric acid.

The distribution coefficient of bismuth(III) in these aqueous acetone–hydrochloric acid media was smaller than that of any other metal ion examined. It was easy to separate bismuth(III) from other metal ions. The distribution coefficients in aqueous acetone–0.32 and –0.64 *M* hydrochloric acid solutions were so small (less than 0.5) that the bismuth(III) peak overlapped the blank noise, so 0.1 *M* hydrochloric acid solution was used to delay the elution of bismuth(III) (the distribution coefficient was more than 0.7).

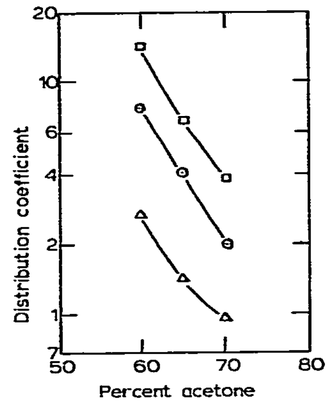
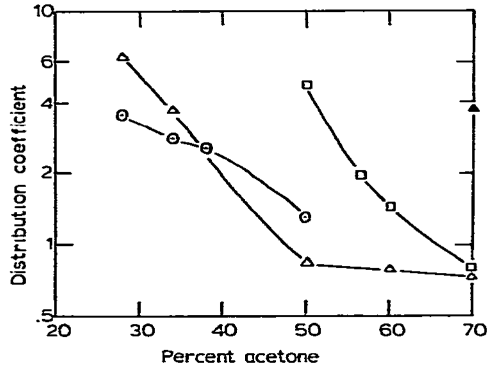


Fig. 3. Distribution coefficients as a function of the acetone concentration in 0.32 *M* hydrochloric acid solution at 40°. Flow-rate of eluent, 11 cm/min; symbols for metal ions as in Fig. 1.



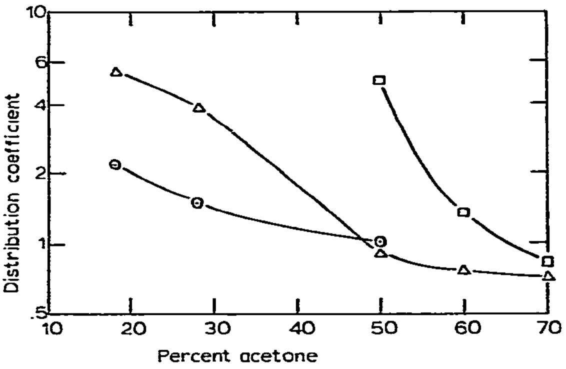


Fig. 4. Distribution coefficients as a function of the acetone concentration in 0.64 *M* hydrochloric acid solution at 40°. Flow-rate of eluent, 11 cm/min; symbols for metal ions as in Figs. 1 and 2.

Fig. 5. Distribution coefficients as a function of the acetone concentration in 0.64 *M* hydrochloric acid solution at the ambient temperature. Flow-rate of eluent, 19 cm/min; symbols for metal ions as in Fig. 1.

Chromatographic separations

Bismuth(III), indium(III), cadmium(II) and zinc(II) were separated at ambient temperature by stepwise elution chromatography, as shown in Fig. 6. Bismuth(III), indium(III) and cadmium(II) were eluted with 18% acetone–0.64 *M* hydrochloric acid solution. Zinc(II) was eluted with 60% acetone–0.64 *M* hydrochloric acid solution. Iron(III), gallium(III), lead(II) and many other elements were retained by the column resin. The bismuth(III) peak overlapped the blank noise.

Results of the stepwise elution chromatography of bismuth(III), cadmium(II), indium(III) and zinc(II) at 40° are shown in Fig. 7. Bismuth(III) and cadmium(II) were separated using 78% acetone–0.1 *M* hydrochloric acid solution. Indium(III) and zinc(II) were separated using 50% acetone–0.64 *M* hydrochloric acid solution. Similar separation was achieved at ambient temperature. Iron(III), gallium(III),

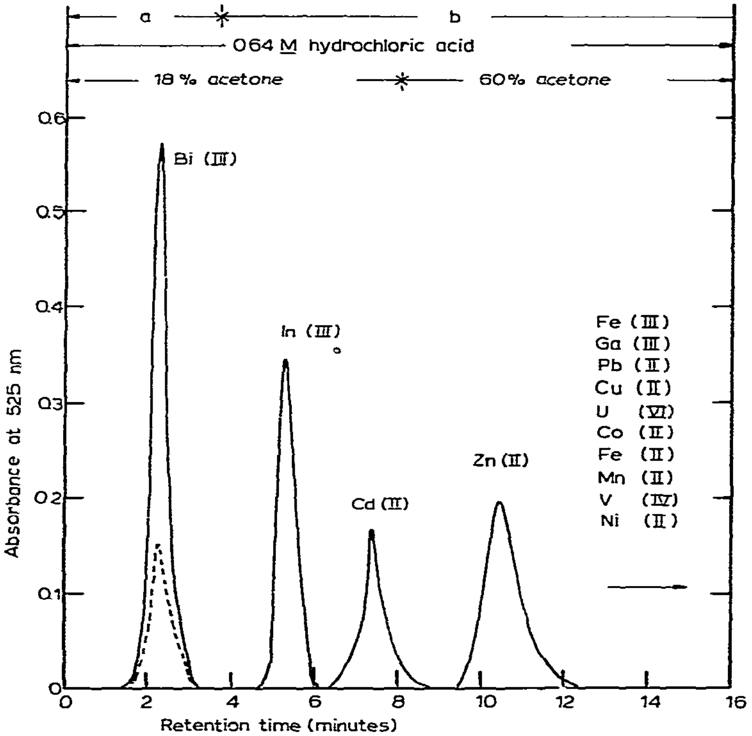


Fig. 6. Separation of bismuth (III), indium (III), cadmium (II) and zinc (II). Column, 130 × 5 mm I.D.; flow-rate, 19 cm/min; column inlet pressure, 8–14 atm; colour-forming reagent solution, 0.02% PAR in (a) 0.4 *M* sodium acetate–0.04 *M* acetic acid–0.64 *M* sodium hydroxide, (b) 0.75 *M* ammonia; amount of metal (10^{-8} mole): bismuth (III), 1; indium (III), 5; cadmium (II), 4; zinc (II), 4; broken line, blank noise.

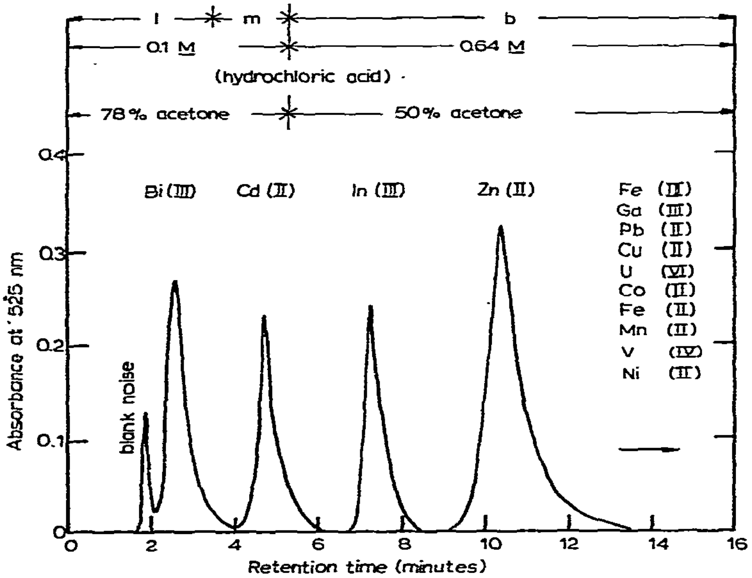


Fig. 7. Separation of bismuth (III), cadmium (II), indium (III) and zinc (II). Column, 130 × 5 mm I.D.; flow-rate, 20 cm/min; column inlet pressure, 8–14 atm; colour-forming reagent solution, 0.02% PAR in (l) 0.2 *M* sodium acetate–0.02 *M* acetic acid–0.1 *M* sodium hydroxide, (m) 0.16 *M* ammonia, (b) 0.75 *M* ammonia; amount of metal (10^{-8} mole): bismuth (III), 6; cadmium (II), 2; indium (III), 4;

lead(II) and many other elements were retained by the column resin. The chromatographic separation of these elements has been reported previously[10].

The distribution coefficients of mercury(II), tin(IV), germanium(IV), arsenic(III, V), antimony(III), gold(III), palladium(II) and platinum(II) in aqueous or aqueous acetone-hydrochloric acid media were as small as that of bismuth(III)[6]. Bismuth(III) may be accompanied by most of these metal ions in the present chromatographic scheme. The separation of some of these metal ions would be achieved by the aqueous or aqueous acetone-hydrochloric acid eluent if the acid concentration were kept high (0.2–0.5 *M*) in order to prevent the hydrolysis of metal ions such as tin(IV) and antimony(III).

REFERENCES

1 J. S. Fritz and T. A. Rettig, *Anal. Chem.*, 34 (1962) 1562.
2 J. S. Fritz and J. E. Abbink, *Anal. Chem.*, 37 (1965) 1274.
3 J. Korkisch, *Separ. Sci.*, 1 (1966) 159.
4 J. Korkisch and H. Gross, *Separ. Sci.*, 2 (1967) 169.
5 S. F. Peterson, F. Tera and G. H. Morrison, *J. Radioanal. Chem.*, 2 (1969) 115.
6 F. W. E. Strelow, A. H. Victor, C. R. van Zyl and C. Eloff, *Anal. Chem.*, 43 (1971) 870.
7 F. W. E. Strelow, C. H. S. W. Weinert and T. N. van der Walt, *Talanta*, 21 (1974) 1183.
8 K. Kawazu and J. S. Fritz, *J. Chromatogr.*, 77 (1973) 397.
9 K. Kawazu, M. Shibata and H. Kakiyama, *J. Chromatogr.*, 115 (1975) 543.
10 K. Kawazu, *J. Chromatogr.*, 137 (1977) 381.
11 R. B. Willis and J. S. Fritz, *Talanta*, 21 (1974) 347.
12 K. Kawazu, *J. Chromatogr.*, 120 (1976) 171.