

THIN-LAYER CHROMATOGRAPHY OF METAL IONS ON ION EXCHANGER LAYERS

金属イオンのイオン交換樹脂薄層クロマトグラフィ

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Introduction

Both ion exchange chromatography and thin layer chromatography are extensively employed methods in modern laboratory praxis. Recently many attempts are made towards a successful combination of these two methods. Impregnation with liquid ion exchangers and separations on ion-exchange papers were frequently carried out. Layers of solid ion exchangers were used by Cozzi and his group^{1),2)} and by Berger and his coworkers^{3),4),5)}. The present paper deals with the behavior of metal ions on layers with cation exchangers and chelate resins admixed to crystalline cellulose.

Experimental

The chelate resin (Diaion CR-10) which has the resin matrix of styrene-divinylbenzene copolymer and the exchange group of iminodiacetic acid was conditioned with a NaOH solution, thoroughly washed with water and converted into the H form with a HCl solution. This process was repeated. The resin was then dried, ground and sieved (150 mesh) and used for the preparation of the thin layers as described below.

For the cation exchange layers we used the two resins Amberlite CG-120 (strong cation exchanger) and Amberlite CG-50 Type 3 (weak cation exchanger) without further processing.

Thin layers

Layers with 2%, 5%, and 10% resin content were prepared the main component being crystallized cellulose (Avicel purchased from Asahi Kasei Co.). For the preparation of 5 plates (20×20cm)

15g of the solid (cellulose+resin) was suspended in 50 ml water, allowed to stand for 1 hr. and spread on the carefully cleaned glass plates. The layers were dried at room temperature for about 12 hours. After the sample application the layers were saturated in the eluent vapor for one hour and developed in a sandwich type chamber (Model TL-IS from the Yamato Kagaku Kikai Co.).

The eluent was allowed to ascend 10 cm.

Eluents

NH₄Cl-HCl buffer solutions were adjusted to pH 2, 3, 4, and 5, respectively keeping the ionic strength constant. The concentration was 0.1 M. Samples

The metal ions used were:

ZnSO₄·7 H₂O, MnSO₄·4-5 H₂O, CuCl₂·2 H₂O, Fe(NO₃)₃·9 H₂O, Co(NO₃)₂·6 H₂O, NiSO₄·7 H₂O, UO₂SO₄, Al(NO₃)₃·9 H₂O, CrCl₃·6 H₂O, Pb(NO₃)₂, HgCl₂, Bi(NO₃)₃·5 H₂O in 0.1 M HNO₃ and Cd acetate·2 H₂O.

Solutions of the metal salts in water were 0.01 M. 5 μl each were spotted on the plate with a micropipette. (Mikropipette Marburg from Eppendorf Geraetebau Hamburg)

Developing agent.

The layers were sprayed with a solution of 0.5 g 8-hydroxy-quinoline in 100 ml ethanol water mixture (60 ml ethanol: 40 ml water). The spots were detected under an UV lamp.

Results and Discussion

The *R_f* values of various metal ions are plotted against the pH of the buffer solution. Fig. 1 represents the results obtained on a layer of pure cellulose. Mn, Co, and Bi are not adsorbed at all independently of the pH. Fe is strongly adsorbed at pH 3.

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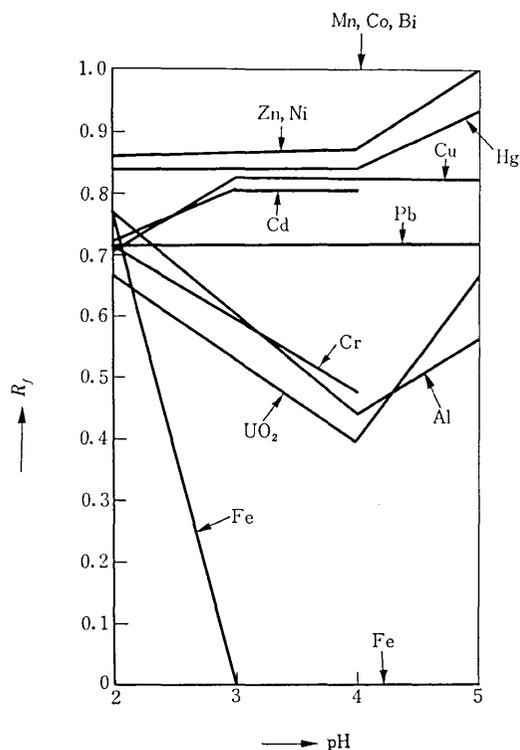


Fig. 1 R_f -values of metal ions on the layers containing pure cellulose (Avicel)

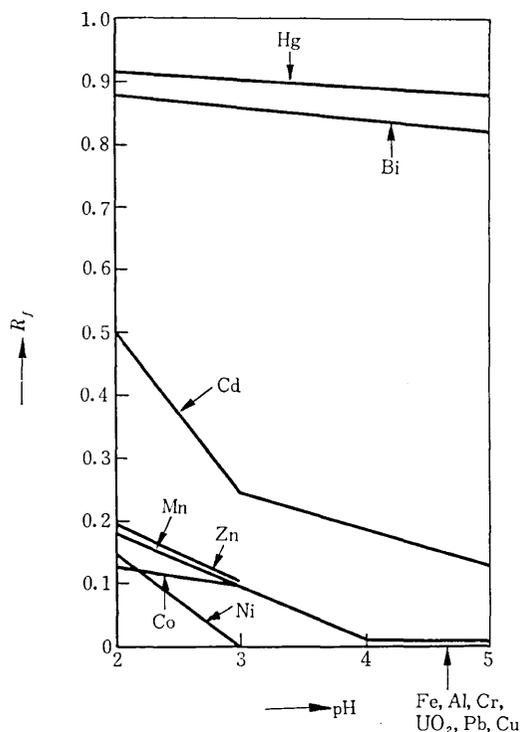


Fig. 2 R_f -values of metal ions on the layers containing a strong cation exchange resin (2%)

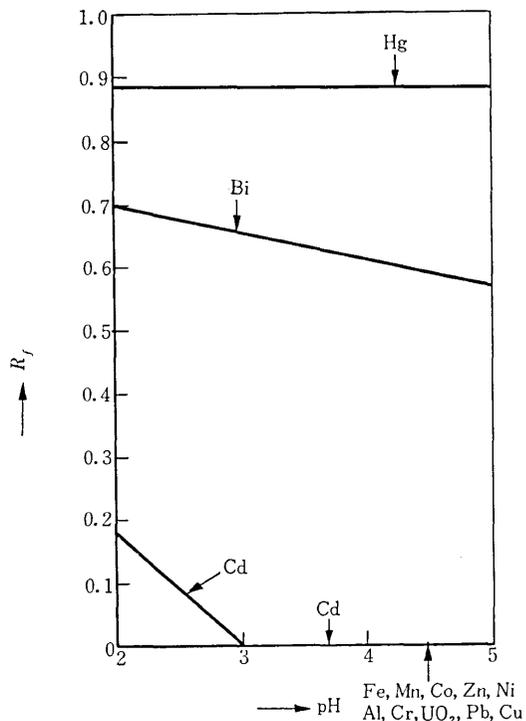


Fig. 3 R_f -values of metal ions on the layers containing a strong cation exchange resin (5%)

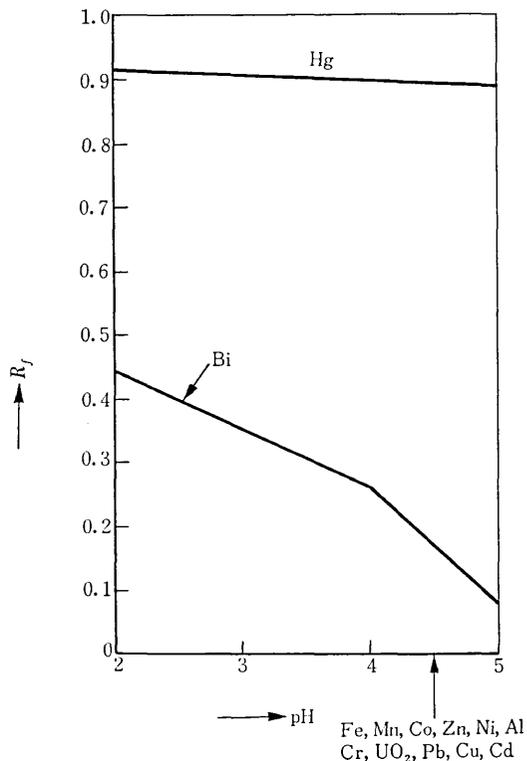


Fig. 4 R_f -values of metal ions on the layers containing a strong cation exchange resin (10%)

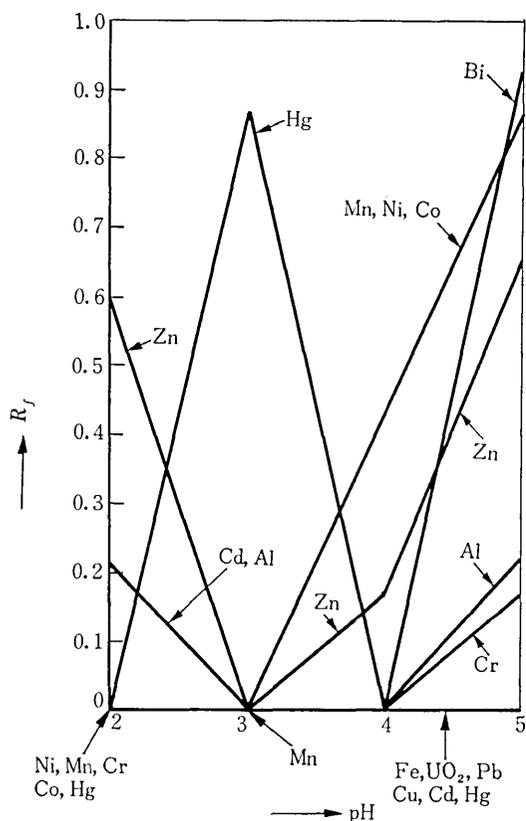


Fig. 5 R_f -values of metal ions on the layers containing a weak cation exchange resin (2%)

The best separability is given at pH=5.

Results obtained on plates containing a strong cation exchange resins are shown in Figs. 2, 3 and 4. Only 2% resin content causes strong adsorption (low R_f values of many ions mainly at pH 4 and above). Hg and Bi have high R_f values independent of the pH, Cd is somewhat adsorbed. Increasing the resin content (Figs. 3 and 4) has no influence on the adsorption of Hg. The adsorption of Bi increases steadily with increasing resin content (Figs. 2, 3 and 4). All the other ions are strongly adsorbed on both the layers with 5% and the layers with 10% resin content, even Cd shows the $R_f=0$ independently of the pH. (With the exception of Cd at pH=2 on the layer with 5% resin: with 10% resin content Cd also has the $R_f=0$ even at lower pH values). The strong adsorption of most common metal ions on the thin layer plates containing a strong cation exchange

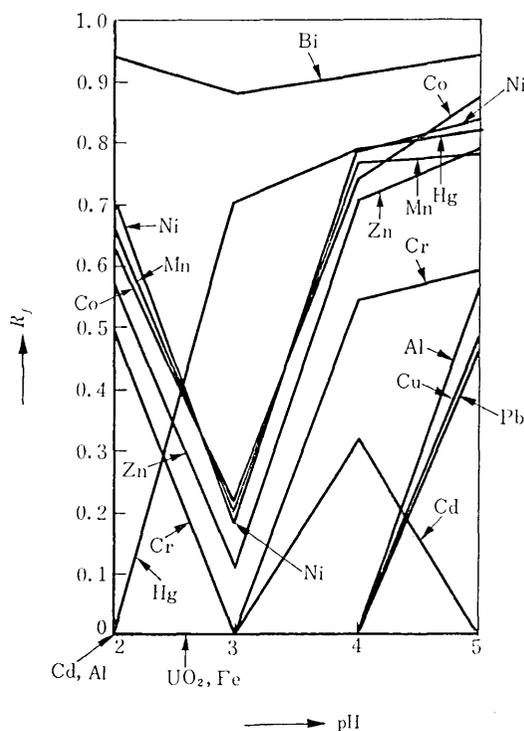


Fig. 6 R_f -values of metal ions on the layers containing a weak cation exchange resin (5%)

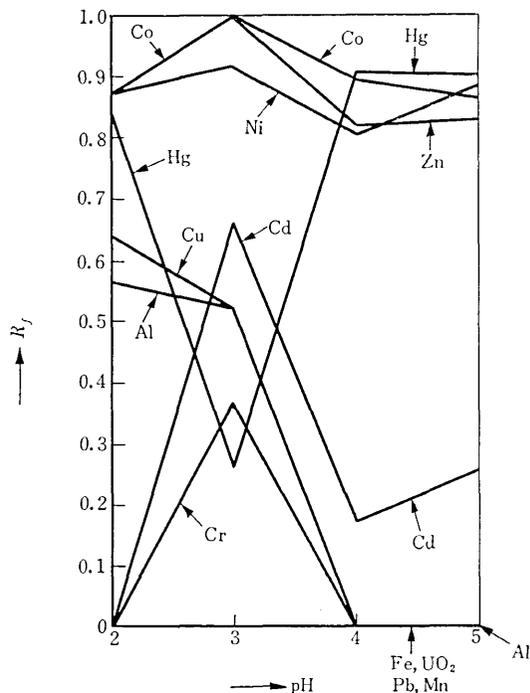


Fig. 7 R_f -values of metal ions on the layers containing a weak cation exchange resin (10%)

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resin is not surprising. Mercury forms complexes with chloride anions in the solution which are not adsorbed. Interesting is the influence of the resin content on the adsorbability of bismuth. Though the formation of polymer bismuth chloride complexes is well known, it is adsorbed on the layers with the strong cation exchanger content and in spite of the large capacity of the exchanger the percentage of the resin in the layer has a considerable influence on the adsorption of bismuth. This is interpreted as the influence of the resin content in the layer on the adsorption capacity for larger size particles rather than an ionic phenomenon. This feature or also the high R_f value of mercury against the $R_f=0$ for most common metals may well be used for specific separation tasks., e. g. for specific determination of mercury in waste waters which has gained some importance with the rise of the pollution problem, mercury being one of the most common poisons.

The use of thin layer plates with increasing content of a weak cation exchange resin (Figs. 5, 6, and 7) gives much more complex results. In this case, the R_f values are much more influenced by the pH. pH 3 seems to be about the pK of the acidic groups of the exchanger. Below the pH=3 the resin behaves as a simple organic polymer, above pH=3 the carboxylic groups are ionized, in effect which greatly influences the R_f values of the metallic ions as can be seen from the figures.

Here as well as on the plates with the strong cation exchange resin content and also with the chelate resin content the plates with 10% resin in

the layer pose some problems in the identification of the ions. This content must actually be considered as the critical resin concentration beyond which the spraying with oxine solution cannot be employed any more.

On the layers with chelate resin admixed to the cellulose the identification becomes most difficult. The ions are either strongly adsorbed ($R_f=0$) independent of the pH and the resin content in the layer (Fe, Cu, UO_2) or not at all (e. g. Zn, Mn; $R_f=1$). Al is adsorbed at pH values above 3. Bi is not affected by the pH and found at R_f values between 0.8 and 0.6 depending on the resin content in the layer similarly to its behavior on the layers with cation exchange resins content.

The specific feature of the layers with chelate resin content giving nearly exclusively $R_f=0$ or $R_f=1$ for all the metal ions studied except Bi might become very useful for specific separation problems. However, this phenomenon must be investigated more closely using a different identification technique.

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References

- 1) D. Cozzi, P. G. Desideri and L. Lepri, *J. Chromatog.* **35**, 396 (1968)
- 2) L. Lepri, P. G. Desideri, V. Coas and D. Cozzi, *ibid.*, **47**, 442 (1970)
- 3) J. A. Berger, G. Meyniel et J. Petit, *Compt. Rend.* **255**, 1116 (1962)
- 4) J. A. Berger, G. Meyniel, J. Petit et P. Blanquet, *Bull. Soc. Chim. France* **1963**, 2662
- 5) J. A. Berger, G. Meyniel et J. Petit, *J. Chromatog.* **29**, 190 (1967)

