LETTERS TO THE EDITOR

A SIMPLE ION-EXCHANGE THIN LAYER CHROMATOGRAPHIC TECHNIQUE FOR THE DETERMINATION OF TRACES OF METALS

A simple method for quantitative determination of traces of metals was developed by means of the frontal chromatographic technique¹⁾ on ion-exchange thin layer. The main procedure consists of (1) preparation of an acidic bufferized sample solution, (2) preparation of the thin layer strip of cation-exchange cellulose powder of 4 mm in width and 200 mm in length on a glass plate, (3) development of the sample solution ascendingly on the thin layer which is supported vertically with its bottom in the sample solution, (4) coloration of the metallic ion on the thin layer and (5) measurement of the length of the colored part of the cellulose strip. The amount of the metallic ion in the sample can be estimated from the length of the colored part of the strip. This report is concerned with the sensitivity of the analysis of Cd ion by the method described here in relation with the various analysing conditions such as the volume and pH of the sample solution, the size of the thin layer strip and the kinds and the concentration of ion-exchange groups of the cellulose. Cellulose papers were also used in some experiments as well as thin layers for Cd ion analysis. Besides, the method for coloring the metal retained on the thin layer was investigated.

The main experimental results were as follows.

The effect of the kinds of the ion-exchange groups of the cellulose

The cellulose with no ion-exchange groups was able to develop Cd ion on it from neutral aqueous solution, when Cd ion was selectively adsorbed on the cellulose from the solvent and the distance of the Cd development on the chromatogram expanded with the increasing amount of the ion. But, this chromatographic layer was unable to adsorb the metallic ion from acidic solutions such as 0.1N and 1N HNO₃ solution, and Walpole's buffer solution (pH=4.0)²⁾.

Various ion-exchange cellulose was examined in the form of paper for the development of Cd ion from neutral and acidic solutions. CM-paper (carboxymethyl group, 0.30 meq/g), ECTEOLA-paper (not a definite but various kinds of groups, 0.10 meq/g) and DEAE-paper (dimethylaminoethyl group, 0.36 meq/g) were applied to Cd ion development. The cation exchanging CM-paper most strongly adsorbed Cd ion from both of neutral and acidic solutions, the anion exchanging ECTEOLA- and DEAE- paper moderately adsorbed the ion from neutral solution but not from acidic solutions. Cellulose with no exchanging capacity adsorbed the ion from only neutral solution most weakly in comparison with the cellulose derivatives. The experimental results of Cd ion development from neutral solutions are presented

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Fig. 1. Development of cadmium ion in 50 μl of neutral solution on filter papers.

The abscissa shows the amount of Cd ion in the sample (μg) and the ordinate shows the distance of Cd ion development (mm) on the papers.

The size of the papers: 4 mm in width

200 mm in length

—○—○—○— on Toyo Roshi No. 51 (non ion-exchange paper)

—●—●—●— on ECTEOLA-paper

—△—△—△— on DEAE-paper

—○—○—○— on CM-paper

in Fig. 1 by these various cellulose papers.

In the cases when metallic ion is not selectively adsorbed on the chromatographic layer, the ion is transferred and condensed to the frontal part of the solvent development on the layer. In such cases, we could not find any regular relation between the amount of Cd ion in the sample and the length of the part of the thin layer where the ion was retained. From these results, only CM-cellulose was able to develop Cd ion from acidic solutions and the distance of the development of the metal on this layer was linearly related to the amount of the ion in the sample.

The effect of the concentration of the ion-exchange group of the cellulose

Next, the concentration of the carboxymethyl group of the cellulose in the form of thin layer was varied by mixing CM-TLC-cellulose with cellulose powder to be the final exchanging capacity of 0.015, 0.03, 0.06, 0.15 and 0.3 meq/g. When Cd ion solution of 100 μl (Walpole's buffer solution, pH=4.0) was developed on these

series of thin layers, Cd ion was moved to some distance adversely related to the concentrations of the carboxymethyl group in the thin layer. The results of these experiments are presented in Fig. 2. From these results, a simple quantitative determination of Cd ion in the sample solution can be realized by measuring the length of the metallic ion developed on the layer, at various sensitivity by applying thin layer strips of various cation-exchange capacity. Using CM-TLC-cellulose thin layer examined here, Cd ion up to the amount of 300 μg in 100 μl solution can be quantitatively determined.

Fig 2. Development of cadmium ion in 100 μl of Walpole's buffer solution (pH=4.0) on CM-TLC-cellulose thin layer with various exchanging capacity.

The abscissa shows the amount of Cd ion in the sample (μg) and the ordinate shows the distance of Cd ion development (mm) on the thin layer.

The size of the thin layers: 4 mm in width

200 mm in length

Concentration of CM group in cellulose (meq/g):

① 0.015 ② 0.03 ③ 0.06 ④ 0.15 ⑤ 0.3

The effects of the other factors of the procedure on the analysing sensitivity

The width of the thin layer affects the developing distance of the metallic ion. On the thin layer with 2 mm of width, Cd ion of a definite amount extends longer than on that with 4 mm of width. But, the capillary condensation at the both peripheries of the thin layer caused the more rapid diffusion of the sample solution than that at the central part of the layer, therefore, the frontal line of the Cd ion

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development became vague on the narrow thin layer. The width of 4 mm was adequate for the analysis of 100 μ l solution on thin layer.

The amount of the sample solution was also effecting. The smaller amount of the solution such as 20 μ l was instantly developed on the thin layer, 50 μ l solution needed 10 minutes and 100 μ l solution did 30 minutes to be developed on the thin layer of 4 mm in width. But the metallic ion of a definite amount developed to longer distance when the larger amount of the solvent was used, that is, 10 μ g of Cd ion in 100 μ l solution showed 76 mm development and the same amount of Cd in 50 μ l did only 58 mm development. When 20 μ l of the solution was developed, the metallic ion reached only the shorter distance. So that, larger size of the sample solution is more favorable for highly sensitive analysis of the metal if the longer time developing is permitted.

To produce the color of the metal retained on the thin layer, diphenylcarbazide solution³⁾ (0.8% ethanol solution) was sprayed on the thin layer after the solution was completely developed and the solvent was vaporized. After spraying the reagent, the thin layer was again dried, then it was put in ammonia vapor. Stable color was produced at the part where metal was bound on the layer. The color background of the thin layer was slight, and the frontal line of the metal band was clear against the cellulose background even when as little as 1 μ g of Cd was developed from 100 μ l solution.

By the best conditioned method described above, 1 to 300 μ g of Cd ion in 100 μ l solution could be quantitatively determined. The advantages of this method are that the procedure is simple, can be carried out without any electric equipments and that acidic sample solution can be analysed.⁴⁾

Cellulose papers with and without exchanging capacity were proved to be applied to this technique as well as thin layers except one drawback that the regulation of the ion-exchange capacity in the papers was more technically complicated. The elevation of the sensitivity of this technique is further investigated.

(The detailed informations about this investigation are to be published in Japanese on *Kogyo-Kagaku-Zasshi* (J. Chem. Soc. Japan, Ind. Chem. Sec.) **74**, No. 3 (1971).

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