

CHROM. 4002

Inorganic micro-thin-layer chromatography

In previous papers¹⁻⁴ the results of our investigations on the mechanism of inorganic TLC on cellulose and the procedure for a complete scheme of analysis of metal ions are described. Recently we became acquainted with the excellent results of BRINKMAN, DE VRIES AND VAN DALEN⁵ using a micro-technique for reversed-phase TLC. An improved version of their apparatus is described in ref. 4.

The object of this work was to investigate the possibility of separating cations on cellulose layers, according to our own scheme, within a few minutes and with a length of run of 2-3 cm.

It should be emphasized that there are other solvent mixtures of various composition and several spray reagents which can give good separations (see refs. 1, 2, 4), but in this paper only the data necessary to obtain the results shown in the Figs. 1-8 are presented.

Experimental

Precoated cellulose plates without fluorescence indicator, Merck (No. 5716) are cut into small pieces. The size of a microscope slide is ideal. It is not advisable to use any other cellulose layer, because other layers are often too thin or too loose to get a sharp separation in a few minutes. Samples of the solution to be analyzed are spotted on the plates using a pointed paper strip, impregnated with the solution.

By this means it is possible to apply very small spots on the plate (diameter 1 mm). It is advisable to spot several different concentrations on the plate each time

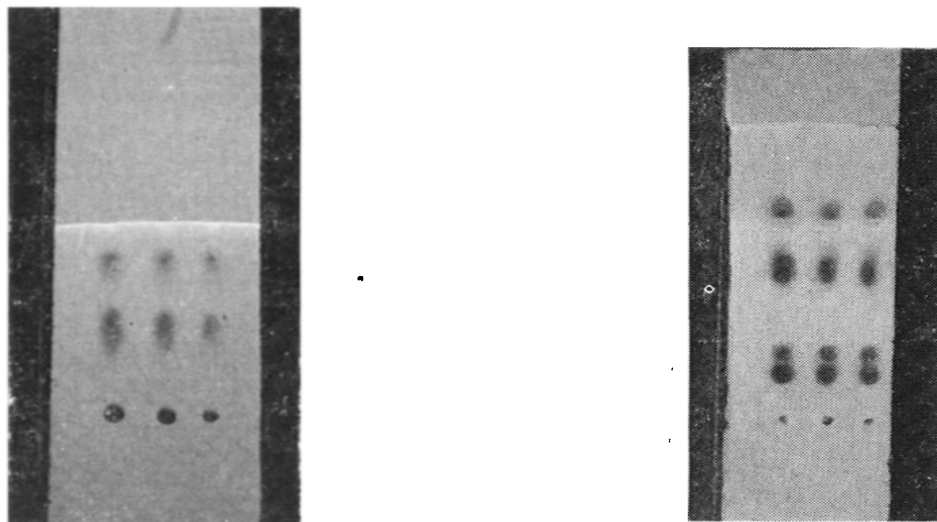


Fig. 1. Separation of Pb < Tl < Ag. Solvent mixture: ammonia (10% NH₃ in water). Detection: after development, the wet plate is held above a bottle containing a saturated ammonium sulphide solution or treated with H₂S gas. The solution applied to the plate may be a solution of the three cations or a suspension of the insoluble chlorides in water.

Fig. 2. Separation of Cu < Pb < Bi < Cd (invisible) < Hg. Solvent mixture: *n*-butyl alcohol, saturated with 3 N HCl. Detection: the plate is left wet, exposed to ammonia vapor and subsequently treated with H₂S (see Fig. 1). The Cd spot is yellow and therefore invisible on this picture.

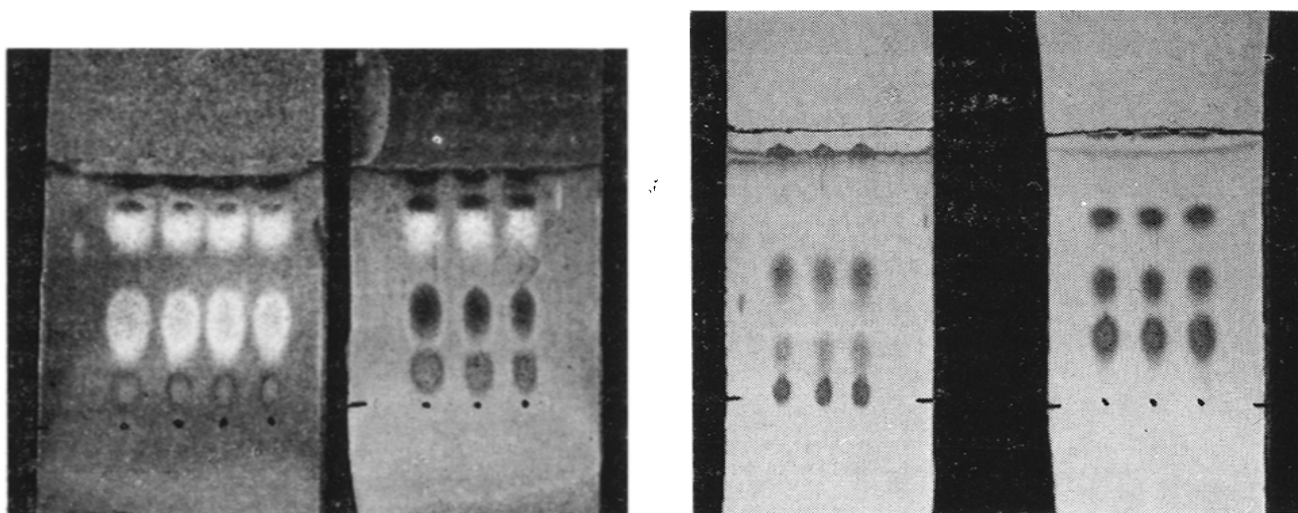


Fig. 3. Separation of Th < Al < Be < UO₂ < Fe (left); separation of Th < Cr(III) < Be < UO₂ < Fe (right). Solvent mixture: acetone-HCl ($d = 1.19$)-H₂O (40:20:15). Detection: (left) spray with 8-hydroxyquinoline (0.5% in 60% ethanol), expose to NH₃ vapor and view under U.V. light; (right) spray with quercetin (0.2% in ethanol) mixed with an equal volume of the 8-hydroxyquinoline reagent. After spraying with this mixture the plate is treated with NH₃ vapor and viewed under U.V. light. These two pictures show that there is little difference in the R_f values of Cr(III) and Al. After detection, however, the dark spot of Cr(III) and the fluorescent spot of Al are very specific.

Fig. 4. Separation of Ni < Mn < Co < Zn. Solvent mixture: (left) acetone-HCl ($d = 1.19$)-H₂O (90:5:5); (right) acetone-HCl ($d = 1.19$)-H₂O (45:20:10). Detection: spray with 1-(2-pyridylazo)-2-naphthol (= PAN)-solution (0.2% in methanol) and expose the plate to NH₃ vapor. The red spots of Zn are located between the first and second front.

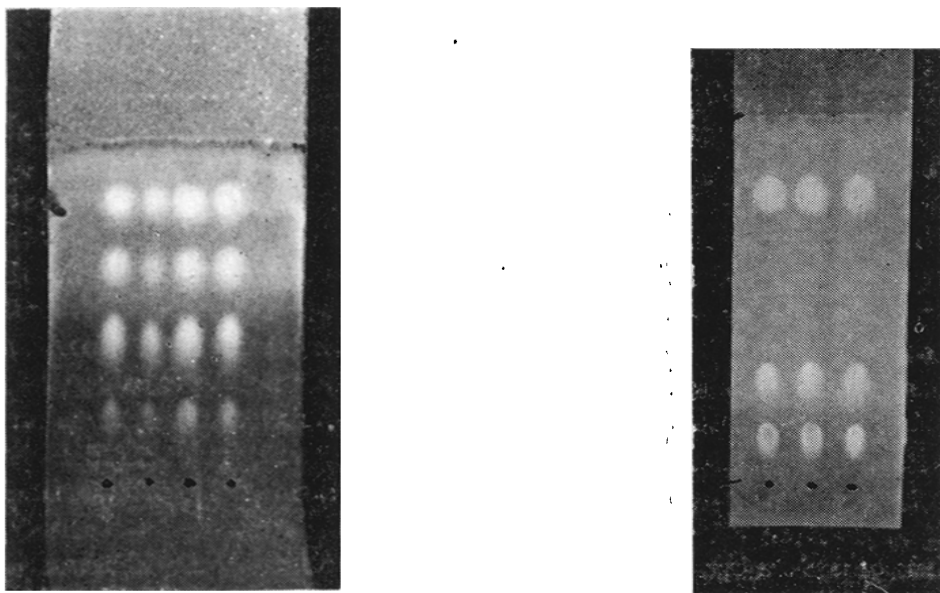


Fig. 5. Separation of Ba < Sr < Ca < Mg. Solvent mixture: methanol-HCl ($d = 1.19$)-H₂O (8:1:1). Detection: spray with a mixture of 8-hydroxyquinoline and kojic acid (0.1% and 0.5%, respectively, in 60% ethanol) and expose the plate to NH₃ vapor. View under U.V. light. For the separation of Be from the other alkaline earth cations other solvent mixtures are recommended e.g. acetone-10 N HCl-H₂O (6:3:2) (cf. ref. 4).

Fig. 6. Separation of K < Na < Li. Solvent mixture: methanol-HCl ($d = 1.19$)-H₂O (8:1:1). Detection: spray with zinc uranyl acetate (saturated solution in 1N acetic acid). The spots are visible in U.V. light. This reagent is only sensitive for Na.

and to run a standard mixture of cations on the same chromatogram. After application of the sample solution, containing for instance 1 mg of the cation in 1 ml, the plate is air dried and developed in a small bottle without equilibration. In 5–10 min the solvent

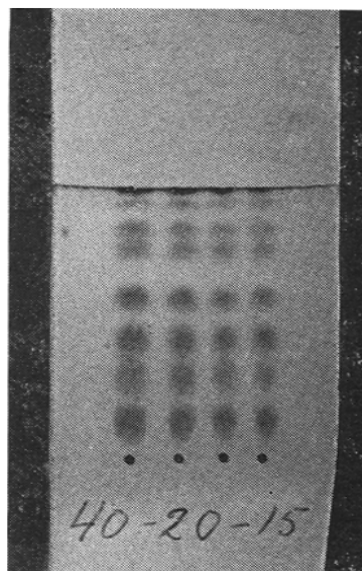
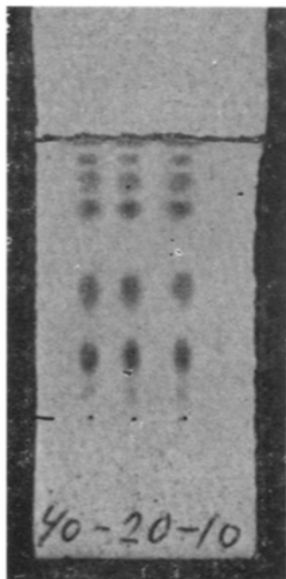


Fig. 7. Separation of $\text{Th} < \text{Ni} < \text{Mn} < \text{Co} < \text{Cu} < \text{UO}_2 < \text{Fe}$. Demonstration of a separation of cations from several groups in one chromatogram. Solvent mixture: acetone–HCl ($d = 1.19$)– H_2O (40 : 20 : 10). Detection: same reagent as in Fig. 4, *viz.* PAN.

Fig. 8. Same separation as in Fig. 7. Solvent mixture: acetone–HCl ($d = 1.19$)– H_2O (40 : 20 : 15). Detection: 8-hydroxyquinoline (*cf.* Fig. 3).

mixture covers a distance of 2–3 cm. The plate is air dried or dried with warm air and subsequently treated with ammonia vapor, because a neutral pH on the plate favors the visualization in most cases. After spraying with the reagent the plate is treated again with ammonia vapor. Sometimes the spots are only visible in U.V. light (365 nm). The separations obtained are represented in the Figs. 1–8 in actual size.

R.C. Hospital, Sittard
(The Netherlands)

F. W. H. M. MERKUS

- 1 F. W. H. M. MERKUS, *Thesis*, Amsterdam, 1966.
- 2 F. W. H. M. MERKUS, *Pharm. Weekblad*, 103 (1968) 1037.
- 3 F. W. H. M. MERKUS, *Vth International Symposium, Chromatography-Electrophoresis, Brussels*, Presses Académiques Européennes, Brussels, 1969, in press.
- 4 F. W. H. M. MERKUS, to be published.
- 5 U. A. TH. BRINKMAN, G. DE VRIES and E. VAN DALEN, *J. Chromatog.*, 25 (1966) 447.

Received February 13th, 1969