

Inorganic ion exchangers for thin-layer chromatography

The purpose of this communication is to report some preliminary results obtained with several inorganic ion exchangers in thin-layer chromatography. Although TLC is now a well-established analytical method, there have been relatively few papers dealing with the separation of inorganic ions^{1,2}. The properties of inorganic ion exchangers have been reviewed by KRAUS *et al.*³ and AMPHLETT⁴. Recently, a paper relating the values of distribution constants *versus* pH for 60 metal ions has been published⁵. The unusual selectivities of these materials for various ions led us to believe that a variety of useful separations could be made.

Preparation and stability of plates

The materials chosen for study were zirconium phosphate (ZP) and hydrous zirconium oxide (HZO). Both are cation exchangers, but the latter exhibits anion exchange properties in acid media. Analytical grade ion exchange crystals—Bio-Rad ZP-1 (hydrogen form) and Bio-Rad HZO-1 (ammonium form) for TLC*—were used in these experiments. The material can be used without binder if the precaution is taken to place a layer of glass wool on the bottom of the developing jar to prevent sloughing off of the material. In this study, 3% corn starch was used as a binder. A slurry was prepared by mixing 20 ml of water with 20 g of the exchanger. This mixture was heated in a double boiler until a thick gel formed. A small amount of water was then added to form a slurry suitable for spreading on the plates. A plate thickness of 500 μ was used. The plates were dried at 40° for 30 min or overnight at room temperature. Both ZP and HZO formed extremely hard plates.

Separations on HZO

For most separations, the ammonium or cation form of the exchanger was found to be superior to the HCl (anion) form. The latter can readily be prepared by washing on a Buchner funnel with 1 M HCl followed by water to remove excess acid. Approximately 0.001 ml of 0.1 M solutions of Ni, Co(II), Pb, Fe(III), Ag, Hg, Cd and Cu were applied to one end of the TLC plate. Table I shows the R_F values obtained by elution of the ammonium form of HZO with several solvents.

TABLE I
 R_F VALUES OF METAL IONS ON THE AMMONIUM FORM OF HZO
(Development time: 10 cm in 10 min)

	Ni	Co	Pb	Fe	Ag	Hg	Cd	Cu
0.01 M HCl	1.0	1.0	0-0.1	0	0	0.1	0.75	0
0.1 M NH ₄ NO ₃	0.9	0.9	0	0	0	0.15	0.6	0
2.0 M NH ₄ NO ₃	0.5	0.5	0	0	0	0.9	0.3	0

The spots were detected by spraying with an ammoniacal solution of ammonium sulfide. It is interesting to note that a variation in HCl concentration from 0.001 to

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TABLE II
 R_F VALUES OF METAL IONS ON THE HCl FORM OF HZO
 (Development time: 10 cm in 45 min)

	Ni	Co	Pb	Fe	Ag	Hg	Cd	Cu
0.01 M HCl	0.9	0.9	0.5	0	0	0.1	0.9	0.9
0.1 M NH ₄ Cl	0.95	0.95	0.4	0	0	0.1	0.8	0.95

0.1 M results in little change in the R_F values. However, Table I indicates that a change in the NH₄NO₃ concentration does result in some changes in the R_F values.

Table II shows some of the results obtained with the HCl form of HZO. In these cases, mercury was the only ion which showed any variation of R_F values with changes in the eluent concentration and that only with NH₄Cl.

Separations on ZP

Table III lists the R_F values obtained on eluting the hydrogen form of ZP with 0.1 M HCl.

TABLE III
 R_F VALUES OF METAL IONS ON THE HYDROGEN FORM OF ZP
 (Development time: 10 cm in 50 min)

	Ni	Co	Pb	Fe	Ag	Hg	Cd	Cu
0.1 M HCl	0.65-0.95	0.3-0.6	0	0-0.1	0	0.85	0.4	0.1

It appears that many of the metal ions have a tendency to tail with the eluents used. However, with the exception of nickel and cobalt, the tailing is not serious. A very specific separation was obtained for mercury from the rest of the ions. This was performed on the ammonium form of ZP, obtained by neutralizing the slurry with NH₄OH before forming the plate, and eluting with 3 M NH₄Cl-NH₄OH solution.

In conclusion, inorganic ion exchangers can be adapted to the technique of thin-layer chromatography and several very specific separations have been demonstrated. Furthermore, it is expected that these materials should be especially applicable to the separation of alkali and alkaline earth ions owing to their vast differences in selectivities towards these ions.

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Received December 16th, 1963