The separation of metal ions by solubilization thin-layer chromatography

Separations of inorganic ions by thin-layer chromatography have already been reported by many workers. There are, however, only two papers published dealing with the separation of inorganic ions on the basis of the difference of solubility in the developing solvents of the salts which are formed by the ions in question with a precipitant in the thin-layer. MUTO[1] separated halogen ions and phosphate ions by using a silica gel layer impregnated with silver nitrate as a precipitant and developing with water-saturated isobutanol + 40 % ammonium acetate (4:1). NAGAI AND MOROKUMA[2] separated copper, iron(III), nickel and cobalt by using silica gel plates containing oxine (8-quinolinol) as a stationary phase and 15 % acetic acid saturated with isobutanol as a developer. No research concerning the separation of cations on thin-layers containing an inorganic compound as a precipitant has been reported.

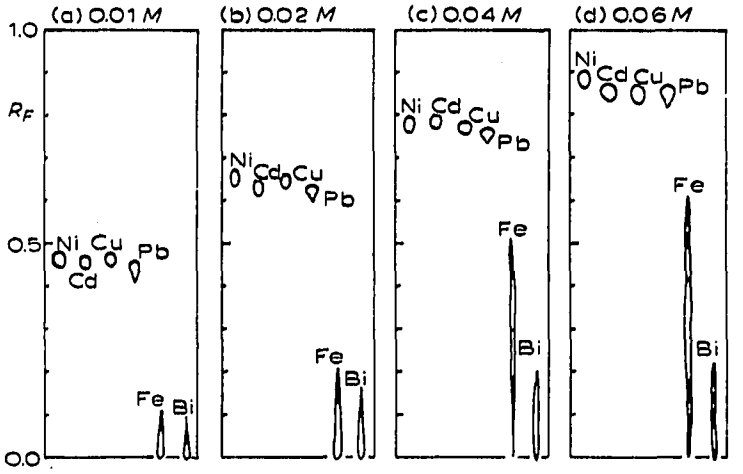

Fig. 1. The change of R_F values with the concentration of HNO_3.

The results in this work are an initial evaluation of disodium hydrogen arsenate as a reagent for solubilization thin-layer chromatography of metal ions. Using thin-layer plates prepared from a silica gel paste in 0.01 *M* disodium hydrogen arsenate solution instead of water, iron(III) and bismuth were separated from copper, lead,

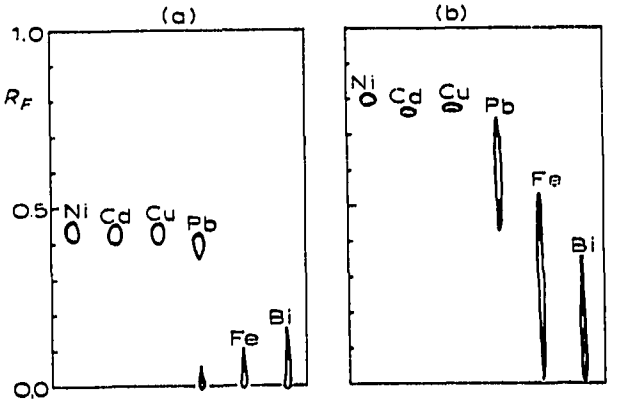

Fig. 2. The behaviour of metal ions in a HNO_3–methanol system. (a) 0.1 *M* HNO_3–methanol (1:9 v/v); (b) 0.5 *M* HNO_3–methanol (1:9 v/v).

cadmium and nickel by developing with 0.02 *M* or 0.04 *M* nitric acid, and lead was separated from copper, nickel and cadmium with a mixture of ethanol–0.5 *M* nitric acid (9:1).

Experimental

Sample solutions. A test solution of each ion, except bismuth, was made as an 0.1 *M* aqueous solution of the nitrate. The 0.1 *M* solution of bismuth was prepared by dissolving an appropriate amount of bismuth nitrate in 3 *M* nitric acid.

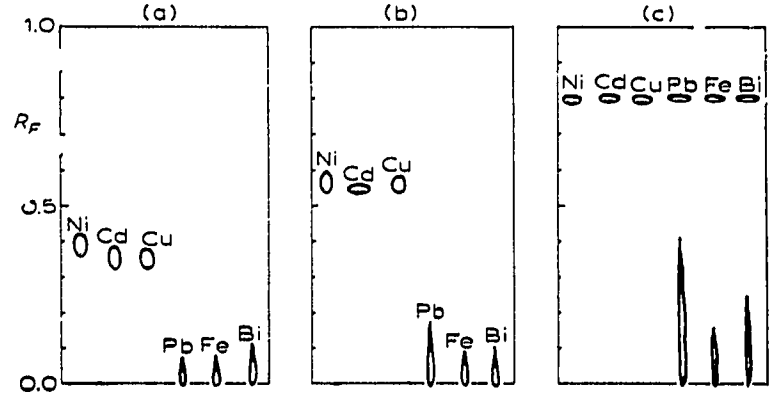

Fig. 3. The behaviour of metal ions in a HNO_3–ethanol system. (a) 0.1 *M* HNO_3–ethanol (1:9 v/v); (b) 0.5 *M* HNO_3–ethanol (1:9 v/v); (c) 1.0 *M* HNO_3–ethanol (1:9 v/v).

Preparation of the silica gel layer. Commercially available silica gel for thin-layer chromatography was purified by the method proposed by SEILER[3]. 3.8 g of purified silica gel and 0.2 g of soluble starch were slurried with 9 ml of 0.01 *M* disodium hydrogen arsenate solution and spread on a 20 cm × 10 cm glass plate with an applicator, at a thickness of 250 μ. The plate was then dried in air overnight.

Procedure. About 1 μl of each stock solution was spotted on the plate at a distance of 2.5 cm from one side with a glass capillary and dried in air for 20 min. Development was then carried out by the ascending technique at room temperature until the solvent front rose to 12 cm. Then the plate was dried in air and the spots of cadmium, iron, bismuth, copper and lead were visualized by spraying with colour-

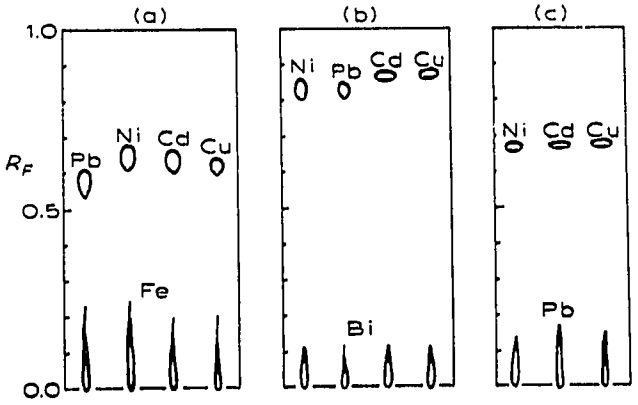

Fig. 4. Separations of selected mixtures. Developer: (a) 0.02 *M* HNO_3; (b) 0.04 *M* HNO_3; (c) 0.5 *M* HNO_3–ethanol (1:9 v/v).

less ammonium sulphide solution and nickel by spraying 1 % dimethyl glyoxime solution in 95 % ethanol. First, the development of each ion was tested separately with each developer and then some selected mixtures were developed.

Results and discussion

The behaviour of each ion in various developers is shown in Figs. 1–3. As is seen from Fig. 1, copper, cadmium, nickel and lead give similar results in nitric acid medium. The R_F values for these elements increase with increasing concentration of nitric acid. Both arsenates of iron and bismuth are slightly soluble in nitric acid of lower concentration, so that they are retained at or near the origin. The solubility of iron arsenate increases in 0.04 ~ 0.06 *M* nitric acid and iron travels to about R_F 0.53 ~ 0.60. The R_F values for bismuth, on the other hand, are not so much affected by the concentration of nitric acid.

Addition of methanol or ethanol to nitric acid results in a decrease of the solubilities of all the arsenates of the metals tested. By developing with ethanol–0.5 *M* nitric acid (9:1), lead is retained near the origin together with iron and bismuth, while nickel, cadmium and copper travel to about R_F 0.55. Thus, the addition of ethanol to nitric acid seems very effective for the separation of lead from nickel, cadmium and copper.

In Fig. 4, results are illustrated for separations of mixtures of some of these ions.

The time required for the solvent front to ascend to a height of 12 cm is ~220 min with nitric acid alone, ~ 30 min with methanol–nitric acid (9:1) and 45 min with ethanol–nitric acid (9:1).

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