CHROM. 4904

Chromatography of metal ions on thin layers of polytetrafluoroethylene with di-(2-ethylhexyl)orthophosphoric acid*

The development of polytetrafluoroethylene layers for thin-layer chromatography (TLC) has already been described[1]. The chromatography of some readily available radioisotopes of metal ions with the commonly used liquid cation exchanger di-(2-ethylhexyl)orthophosphoric acid (HDEHP) was selected to demonstrate the performance of the layers. The liquid ion exchanger HDEHP has been used extensively in the reversed-phase partition chromatography of inorganic substances[2]. For reversed-phase TLC, it has been used with layers of silica gel[3–5], polyvinyl chloride[5], and Corvic (vinyl chloride–vinyl acetate co-polymer)[6] to separate inorganic substances. On HDEHP-impregnated paper, some alkaloids and heterocyclic bases have been separated[7]. Also, HDEHP has been used as the mobile phase in the TLC of the rare-earth elements on layers of Silica Gel H (ref. 8). The chemistry and mechanism of extractions with HDEHP have been studied extensively[9–16].

In this work, the radioisotopes of some 31 metal ions and of chloride ion were chromatographed on thin layers of 100% polytetrafluoroethylene. The polytetrafluoroethylene was layered onto Mylar film from a slurry in methyl isobutyl ketone that contained nitric acid and a wetting agent. The chromatograms were developed with a methyl isobutyl ketone solution of HDEHP. The positions of the metal ions on the chromatograms were detected by autoradiography. The autoradiograms show the migration of numerous of the metal ions and indicate the suitability of the polytetrafluoroethylene layers for the separations.

Materials

The following materials were used: *Particulate polytetrafluoroethylene*, Fluoroglide 200 TWO218, from Chemplast, Inc., 150 Dey Road, Wayne, N.J. 07470. *Mylar polyester film*, 0.0075 in. thick × 48 in. long, from Kensington Scientific Corp., P.O. Box 531, Berkeley, Calif. 94701. *Radioisotopes* were obtained from the ORNL Isotopes Division. The radioisotopes were in acid solution, usually nitric acid. When dilution of the original solution was required, nitric acid was used. *Di-(2-ethylhexyl)orthophosphoric acid (HDEHP)*, >99% pure, was obtained from J. R. STOKELY, ORNL Analytical Chemistry Division, who obtained HDEHP from the Union Carbide Corporation and then purified it according to the procedure of SCHMITT AND BLAKE[16]. *Fluorochemical wetting agent FX-173*, from the Atlanta Branch, Industrial Chemical Division, 3M Company, 5925 Peachtree Industrial Blvd., Chamblee, Ga. *Methyl isobutyl ketone*, b.p. 114–116°, reagent grade, from Matheson, Coleman and Bell, Norwood, Ohio, was used without further purification. *Nitric acid*, C.P. reagent grade, from Allied Chemical, Morristown, N.J. *Special 1-μl pipet.* For spotting the solutions of the radioisotopes onto the chromatofilm, special expendable micropipets were used. They were made as follows. A Drummond "Microcaps" type 1-μl pipet was positioned with Silastic 731RTV adhesive/sealant (Dow Corning Corp., Midland, Mich.) in the end of a 4-in.-long × 1/4-in.-O.D. glass tube. The other end of this tube was attached

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to a short length of rubber tubing connected to the top half of a medicine dropper into which a 4-μl micropipet was held by rubber tubing. This pipet control sufficiently restricted the expulsion pressure so that the contents of the 1-μl pipet was deposited onto the chromatofilm without splattering of the radioisotope solution.

Procedures

Preparation of the polytetrafluoroethylene slurry

The slurry was prepared by dissolving 0.2 g of FX-173 in 72 ml of methyl isobutyl ketone, adding 0.8 ml of concentrated nitric acid, and then adding to the solution 24 g of Fluoroglide 200 TW0218. The mixture was shaken for about 30 sec on an orbital sander. This amount of slurry was sufficient to layer a 20 × 20 cm area of Mylar film to microscope-slide thickness.

Preparation of chromatofilms

Eight strips of 1 × 8 in. Mylar film (0.0075 in. thick) were placed side by side on a glass plate and were held to the plate by a thin film of acetone. The long sides of the outer strips were edged with microscope slides aligned end-to-end. The slurry was then poured onto the film strips and was spread manually by rolling a heavy glass rod back and forth along the microscope slides. The chromatofilms were dried for 1 h at the face of a laboratory hood, with the hood window lowered. When almost dry, they were marked with a stylus at the 3-cm (origin) and 13-cm (solvent-front) positions.

Preparation of chromatograms

Spotting. With an expendable micropipet, a 1-μl portion of a radioisotope solution was spotted at the origin on each of the chromatostrips. The spot was allowed to dry in air until the area it covered became opaque.

Development. Each chromatofilm was developed in a sparge-gas bottle (chromatographic chamber) that contained 5 ml of 0.5 *M* HDEHP in methylisobutyl ketone. The bottle was covered with plastic film during the development. The chromatofilms were developed to a distance 10 cm from the origin; the duration of the development was about 1 h.

Drying. The chromatograms were removed from the chambers, dried in air at the face of the hood until they were opaque, and wrapped in clear 1/4-mil-thick Mylar film.

Preparation of autoradiograms

The chromatograms were autoradiographed by placing them face down in contact with Eastman Medical No-screen X-ray film. The assembly was then confined in a dark box[17] for two to three days. After being thus exposed, the X-ray film was developed as specified by the manufacturer.

Results and discussion

The autoradiograms are shown in Figs. 1–4. They indicate the innumerable separations that are possible with the particular system and conditions chosen. Since the extractability of metal ions by HDEHP is known to be highly pH dependent, it is to be expected that a slight change in the acidity of the layer will cause a change in

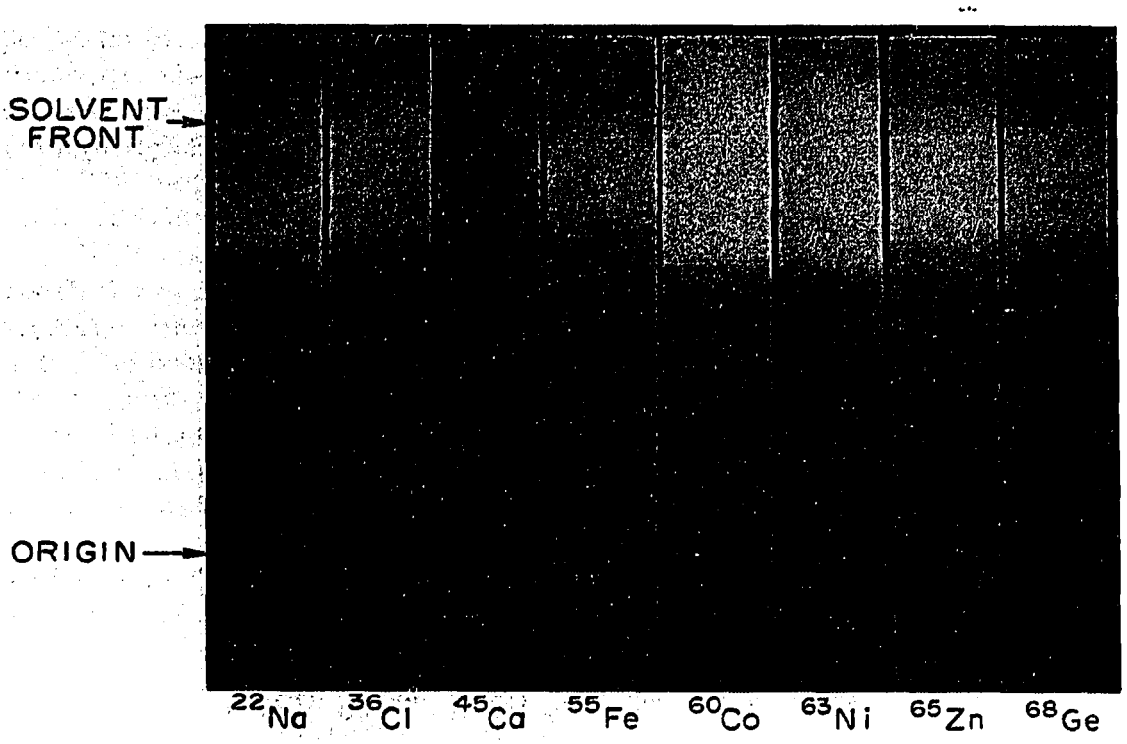

Fig. 1. Autoradiograms of chromatograms of ions of ^{22}Na, ^{36}Cl, ^{45}Ca, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{65}Zn, and ^{68}Ge on Fluoroglide 200 TWO218 layers.

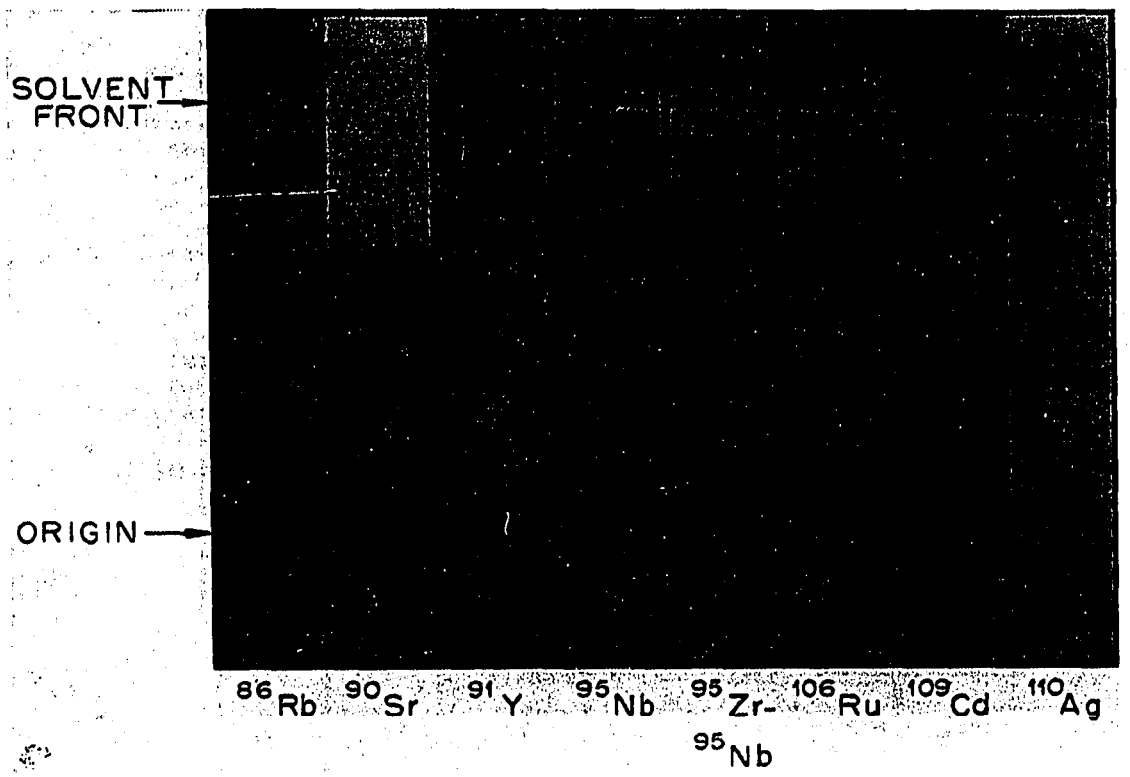

Fig. 2. Autoradiograms of chromatograms of ions of ^{86}Rb, ^{90}Sr, ^{91}Y, ^{95}Nb, ^{95}Zr-^{95}Nb, ^{106}Ru, ^{109}Cd, and ^{110}Ag on Fluoroglide 200 TWO218 layers.

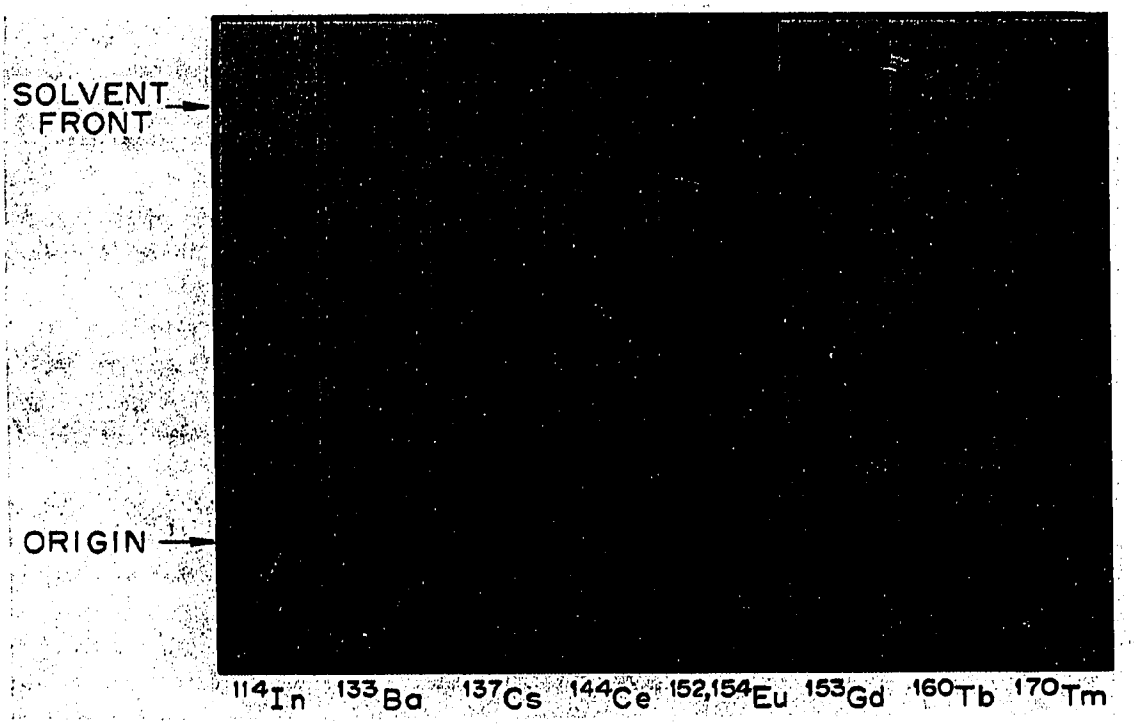

Fig. 3. Autoradiograms of chromatograms of ions of ^{114}In, ^{133}Ba, ^{137}Cs, ^{144}Ce, $^{152,154}Eu$, ^{153}Gd, ^{160}Tb, and ^{170}Tm on Fluoroglide 200 TWO218 layers.

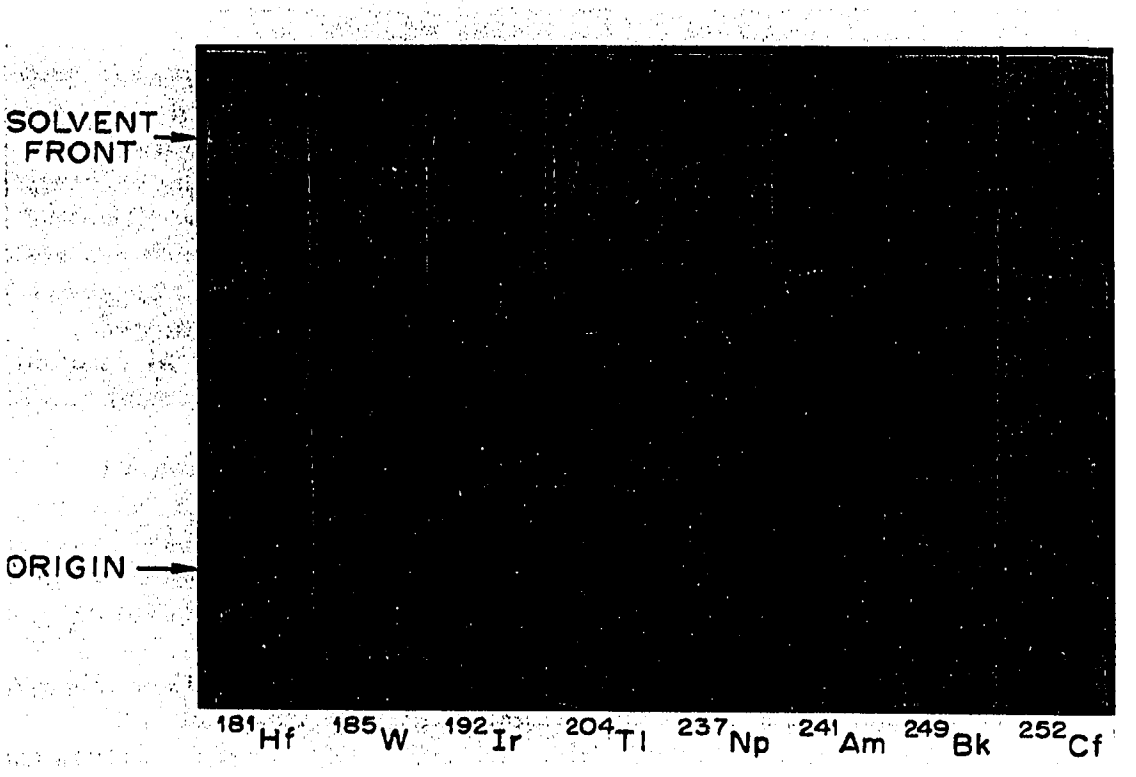

Fig. 4. Autoradiograms of chromatograms of ions of ^{181}Hf, ^{185}W, ^{192}Ir, ^{204}Tl, ^{237}Np, ^{241}Am, ^{249}Bk, and ^{252}Cf on Fluoroglide 200 TWO218 layers.

the positions of the ions. Also, if the HDEHP is located in the layer instead of in the developer, the order of migration of the resolved components can be reversed. This reversal was demonstrated experimentally with ^{55}Fe and ^{63}Ni. The polytetrafluoroethylene layers were thus shown to be suitable for either normal or reversed-phase TLC.

The results are in general agreement with those DANEELS *et al.*[8] obtained on a silica gel layer, which they also developed with HDEHP in the mobile phase.

This work provides experimental evidence that layers of 100% polytetrafluoroethylene (no binder present) can be used for satisfactory TLC separations. Although the experiments were done with HDEHP as the liquid ion exchanger, the layers should be equally useful with numerous other ion exchangers, extractants, and chelating agents. When a fluorochemical wetting agent is included in the TLC system, reversed-phase TLC is possible. By means of the polytetrafluoroethylene layers, it should be possible to scale down those column chromatographic separations of both inorganic and organic compounds in which the support is polytetrafluoroethylene.

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