

CHROM. 7953

Note

Thin-layer chromatography of a number of metal ions on DEAE-cellulose in acidic sulphate media

TSUNEO SHIMIZU, MICHIKO KATSUNO and NORIKO IIZUKA

Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Gunma (Japan)

(Received September 16th, 1974)

Brinkman *et al.*¹ attempted to cover all studies on inorganic thin-layer chromatography (TLC) published up to end of 1972. Oguma and Kuroda² systematically investigated the TLC behaviour of 46 metals on DEAE-cellulose in binary solvent mixtures of organic solvents and sulphuric acid. The behaviour of indium(III), iron(III), lanthanum(III), uranium(VI) and rhenium(VII) on DEAE-cellulose and aminoethylcellulose papers in sulphuric acid was described by Lederer and Ossicini³. Gasco and Gatti⁴ studied the TLC behaviour of copper(II), nickel(II), zinc(II), chromium(III), chromium(VI) and iron(III) on the mixture of CM- and DEAE-celluloses (1:1, w/w) in 0.4 *M* ammonium sulphate medium.

We have previously reported the TLC behaviour of the trivalent rare earths, hafnium(IV), thorium(IV), zirconium(IV) and uranium(VI) on DEAE-cellulose in sulphuric acid-ammonium sulphate media of varying concentrations, and effected the separation of these metal ions by either a one-way or a two-way technique⁵. This work has been extended in order to obtain general information on the TLC of metals in aqueous acidic ammonium sulphate media.

EXPERIMENTAL

Test solutions

For most metals, stock solutions containing *ca.* 2 mg/ml of the metal in 0.05 *M* sulphuric acid were prepared from the sulphate, oxide or metal. For indium(III), hafnium(IV), titanium(IV) and zirconium(IV), the stock solutions were 1.5 *M* with respect to sulphuric acid. For silver(I) and bismuth(III), 0.1 and 3 *M* nitric acid solutions, respectively, were prepared from the nitrates. Stock solutions were adjusted to 0.05 *M* hydrochloric acid for barium(II), calcium(II), mercury(II) and strontium(II), 1 *M* for gold(III) and platinum(IV), 2 *M* for ruthenium(III) and 6 *M* for tin(II), antimony(III) and arsenic(III). Ammonium and sodium salts of selenium(IV), tellurium(IV), molybdenum(VI), tungsten(VI) and rhenium(VII) were simply dissolved in deionized water. For preparing niobium(V) and tantalum(V) stock solutions, the oxides were fused with potassium hydrogen sulphate and the resulting melts were dissolved in the calculated volume of saturated ammonium tartrate solution to give metal concentrations of 0.5 mg/ml.

Preparation of plates

A cellulose anion exchanger, DEAE-cellulose (for TLC, Serva, Heidelberg, G.F.R.), was used as adsorbent. A portion of DEAE-cellulose (*ca.* 12 g), pre-treated with 0.5 *M* sodium hydroxide solution to convert it into the free amine form and subsequently washed with deionized water, was slurried with 80 ml of 0.025 *M* sulphuric acid–2.0 *M* ammonium sulphate solution and stirred mechanically for 1 h. The DEAE-cellulose was then washed three times with deionized water, each wash solution subsequently being removed by centrifugation. The DEAE-cellulose thus treated was slurried with 35 ml of water and spread to a thickness of 250 μm on five glass plates (200 \times 200 \times 3 mm). The plates were allowed to dry at 40° for 3 h after air-drying for 24 h and stored in a desiccator over saturated potassium bromide solution.

Application and detection

A sample or test solution, usually 1 μl , was spotted with a micropipette at a distance of 15 mm from one edge of the plate. The plate was dried in air for 30 min and then immediately developed up to 170 mm from the spot by the ascending technique. All of the developments were carried out at room temperature. The solvent system investigated was sulphuric acid–ammonium sulphate solution of varying concentrations; the concentration of free sulphuric acid, however, was usually kept constant at 0.025 *M*.

After development, the plate was dried under an infrared lamp, and the positions of metals were detected as described by Oguma and Kuroda², except for hafnium(IV) and zirconium(IV), which were detected by spraying with 0.1% aqueous xylenol orange solution.

The R_F values reported are the average of triplicate determinations and are given for the leading and trailing edges of the spots in the separation of multi-component mixtures.

RESULTS AND DISCUSSION

R_F values for 57 metals chromatographed on DEAE-cellulose layers in acid ammonium sulphate solution are illustrated in Fig. 1 as a function of the sulphate concentration in the range 0.01–2.0 *M*. The concentration of free sulphuric acid was kept constant at 0.025 *M*. It can be seen that the R_F values for metals that precipitate as sulphate [barium(II), lead(II) and strontium(II)] or form strongly anionic complexes [hafnium(IV), zirconium(IV) and molybdenum(VI)] are generally low, the spots remaining near or at the start. The R_F values of antimony(III) and tungsten(VI) are also low, probably because of hydrolysis. Gold(III) and platinum(IV) are strongly adsorbed on DEAE-cellulose, probably by ion exchange of the chloro-complexes resulting from their stock solutions. In contrast, silver(I), beryllium(II), cadmium(II), calcium(II), cobalt(II), copper(II), magnesium(II), manganese(II), nickel(II), zinc(II), aluminium(III), chromium(III), iron(III) and tellurium(IV) are not adsorbed to any great extent. The other metals, including thallium(I), tin(II), indium(III), gallium(III), ruthenium(III), scandium(III), the trivalent rare earths, germanium(IV), tellurium(IV), titanium(IV), thorium(IV), vanadium(IV), uranium(VI) and rhenium(VII), which exhibit more or less adsorption on strongly basic anion-exchange resins in

sulphuric acid at concentrations less than 0.05 *M* (refs. 6 and 7), are separated chromatographically on the DEAE-cellulose plate. Generally, most metals behave in the acidic sulphate media in a similar manner to aqueous sulphuric acid media². However, scandium(III), thorium(IV) and uranium(VI) show more pronounced adsorption on DEAE-cellulose in the acidic ammonium sulphate solutions than those in aqueous acidic solutions, in accordance with the observations on a strongly basic anion-exchange resin⁸. The R_F values of bismuth(III), gallium(III), indium(III), ruthenium(III) and rhenium(IV) in the sulphate media are also lower than those in the acid only. The behaviour of many ions on DEAE-cellulose can be explained in a manner suggested by Lederer and Moscatelli⁹.

Inspection of the R_F values for metals chromatographed on DEAE-cellulose in the acidic sulphate media will permit separations of analytical interest to be conducted effectively. The spots of metals developed with the sulphate solution are generally much sharper than those with the aqueous acidic solution². At a sulphate concentration of 0.05 *M*, the R_F values for most of the metals tested have a minimum and the difference in adsorption among the metals is large enough to permit good separations. Results of typical multicomponent separations with 0.025 *M* sulphuric acid–0.05 *M* ammonium sulphate medium are:

Cu(96–88)–As(86–82)–As(42–32)–Pb(1–0);
Ni(100–95)–Y(93–76)–Sc(73–65)–Hf(22–0);
Mg(100–93)–Gd(90–79)–Th(73–39)–Ta(4–0);
Fe(100–92)–As(88–81)–As(43–32)–Pt(6–2);
Co(100–93)–Ti(77–68)–U(36–15)–Zr(10–0);
Be(100–94)–V(77–67)–U(35–15)–Nb(4–0);
Ca(100–93)–Er(90–80)–Th(73–40)–U(37–15)–Ba(2–0);
Al(97–90)–La(88–79)–Th(72–39)–U(36–14)–Sr(2–0);
Al(98–92)–Y(90–74)–Sc(71–63)–U(34–13)–Zr(11–0);
Zn(100–95)–Ag(92–84)–Hg(49–38)–U(35–14)–Ru(12–2);
Mn(100–94)–As(87–82)–V(78–66)–As(45–34)–Sb(12–0);
Te(93–86)–Se(62–59)–Se(38–31)–Re(19–11)–Mo(3–0);
Te(93–85)–Se(61–57)–Se(39–32)–Re(19–11)–W(4–0);
Cr(100–95)–Tl(91–84)–Ga(76–61)–Hg(48–36)–Ru(8–0);
Cd(100–93)–Tl(90–82)–In(82–69)–Hg(48–39)–Re(19–13)–Mo(4–0);
Zn(100–94)–Cu(92–84)–In(82–71)–Hg(51–39)–Re(19–11)–Au(5–1).

The values in parentheses indicate the range of the R_F values ($\times 100$).

ACKNOWLEDGEMENT

We are greatly indebted to Prof. R. Kuroda, University of Chiba, for many helpful discussions and suggestions during this study.

REFERENCES

- 1 U. A. Th. Brinkman, G. de Vries and R. Kuroda, *J. Chromatogr.*, 85 (1973) 187.
- 2 K. Oguma and R. Kuroda, *J. Chromatogr.*, 61 (1971) 307.
- 3 M. Lederer and L. Ossicini, *J. Chromatogr.*, 15 (1964) 514.

- 4 M. R. Gasco and G. Gatti, *Ing. Chim. (Milan)*, 17 (1968) 27.
- 5 T. Shimizu and A. Muto, *J. Chromatogr.*, 88 (1974) 351.
- 6 L. Danielsson, *Acta Chem. Scand.*, 19 (1965) 670.
- 7 F. W. E. Strelow and C. T. C. Bothma, *Anal. Chem.*, 39 (1967) 595.
- 8 H. Hamaguchi, A. Ohuchi, T. Shimizu, N. Onuma and R. Kuroda, *Anal. Chem.*, 36 (1964) 2304.
- 9 M. Lederer and V. Moscatelli, *J. Chromatogr.*, 13 (1964) 194.