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Ion-Exchange Paper Chromatography of Metal Ions with Mixed Aqueous-Organic Solvents Containing Mineral Acid and a Selective Extractant

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Summary

Mixed solvents containing an organic extractant provide selective separations of metal ions on cation- and anion-exchange papers. The separations of scandium, hafnium plus zirconium, nickel, and thorium from complex mixtures are demonstrated. Various separations in dithizone and dimethylsulfoxide media are also reported. Results are often the same as those achieved on columns of resin with the same mobile phase.

Earlier studies of metal ion separations on papers impregnated with strong-acid and strong-base polystyrene ion-exchange resins were made using solvents composed of aqueous complexing agents and buffers (*1–5*) and then with aqueous-organic solvents containing a mineral acid (*6–9*). This work is now extended to include mixed solvents containing mineral acid, an organic solvent, and a selective organic extractant. Many of the particular solvents chosen were suggested by column ion-exchange results reported in a recent series of papers by Korkisch and Orlandini. Numerous useful separations are reported, and it is shown that results on ion-exchange papers are often, but not always, the same as those achieved with column systems employing the same mobile phase and a similar resin.

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EXPERIMENTAL

Amberlite SA-2 sulfonic acid cation-exchange paper (Na^+ form) and SB-2 quaternary ammonium anion-exchange paper (Cl^- form) were obtained from the H. Reeve Angel Co., Clifton, N. J. Different batches of each type of paper were tested and gave identical results. The SA-2 paper was converted to the H^+ form by soaking overnight in a 4% solution of perchloric acid, equilibrating for four 30-min periods with distilled water, and air drying. Some runs were made on Whatman No. 1 cellulose paper to prove that the resin in the ion-exchange paper was primarily responsible for the separations obtained.

Individual test solutions (0.050 *M*) of most metals were prepared by dissolving reagent-grade nitrates or chlorides in water. In some cases, other procedures of sample preparation were employed, some of which have been previously described (*10*). Scandium nitrate and rare earth oxides were dissolved in 0.05–2 *M* HNO_3 as required; $HfOCl_2 \cdot 8H_2O$ was dissolved in 1 *M* HCl. Certain mixtures, which were 0.050 *M* in each metal, were also tested in parallel with the individual ions.

Initial zones were applied to the origins (1 in. up from the bottom of the paper and 1 in. apart) with wooden applicator sticks which produced spots of 6–10 μl of solute. This was sufficient for the detection of all metals except potassium, which required application of 30 μl.

Development was usually by the ascending "dry-start" method in round, glass Shandon Unikit tanks which were equilibrated with 50 ml of solvent for at least 15 min before each run. The spotted paper sheets (20 × 25 cm) were clipped into the form of a cylinder, placed in the equilibrated tank, and developed for a distance of about 15 cm. Development times ranged from 30 min [e.g., for HCl–tetrahydrofuran (THF)–0.10 *M* trioctylphosphine oxide (TOPO)] to 115 min [for dimethylsulfoxide (DMSO)-containing solvents].

To obviate the effects of solvent demixing (i.e., to insure that the initial spots were in contact with the bulk eluent) and to obtain conditions more closely simulating those in a column, a "wet-start" descending development technique was employed with some solvents: the solvent front is allowed to migrate 5–10 cm past the origin or to drip off the end of the paper; the initial spots are then placed on the paper as it hangs in the tank, or the paper is removed from the tank, spotted, and returned if this can be accomplished before any appreciable drying occurs.

Detection tests for the elements were carried out by spraying the air-dried chromatogram with the following spray reagents:

(a) Dark ammonium sulfide. Detects Fe(III), Co(II), Ag(I), Cu(II), Bi(III), Pb(II), Cd(II), Sb(III), Hg(II), Au(III), and Ni(II).

(b) 1–2% alcoholic solution of alizarin. Place the paper in an NH_3 atmosphere for 5 min, spray with the reagent followed by 1.0 *N* acetic acid (*10*). Detects Sc(III) (red-violet), rare earths, Zr(IV), Hf(IV), Th(IV), Mo(VI) (blue-violet), and Ti(IV) (orange-pink).

(c) 8-Hydroxyquinoline (0.5 g in 60 ml of absolute alcohol) followed by dilute NH_3 and inspection under UV light. Detects Mn(II), Cr(III) absorption, and Mg(II), Zn(II) (fluorescence).

(d) Cobalt-lead acetate solution. 11.4 g cobalt acetate monohydrate + 16.2 g lead acetate monohydrate + 20 g $NaNO_2$ + 2 ml glacial acetic acid in 150 ml of H_2O, mixed with 25% methanol. Detects K(I) as a dark brown zone.

(e) 1% aq potassium ferrocyanide. Detects U(VI) as a brown zone.

RESULTS AND DISCUSSION

R_F values are reported below for the leading and trailing edges of the developed zones.

Separation of Scandium from the Rare Earths. An effective separation of scandium from the rare earths is achieved by ascending development on hydrogen-form SA-2 paper with 5% 6 *M* HCl, 95% THF, and 0.50 *M* TOPO. Scandium migrates with R_F limits of 0.70–0.48 while the rare earths remain at or near the origin. Development with this solvent on Whatman No. 1 paper causes all ions to move with the solvent front (R_F, 1.0), indicating that the ions are attracted to the resin in the ion-exchange paper. Development on SA-2 paper with 5% 6 *M* HCl, 95% THF leaves all the ions at the origin, showing clearly that selective extraction of scandium by TOPO provides the separation obtained.

TOPO is more effective for this separation than the other organic phosphorous compounds tested, namely bis(2-ethyl-hexyl) orthophosphoric acid (HDEHP) and tri-*n*-butyl phosphate (TBP). If the solvent contains 0.5 *M* TBP, scandium remains very close to the origin and is poorly separated from the rare earths. With 0.5 *M* HDEHP, scandium has $R_F = 1.0$ but some of the rare earths (e.g., Yb) streak from the origin to the solvent front. If the solvent contains concentrations of TOPO below 0.5 *M*, scandium is separated from the rare earths but forms a more elongated, streaking zone. This is in contrast to results on a column of Dowex 50, with which the optimum solvent for this separation contained 0.1 *M* TOPO (*11*).

The SA-2 paper caused obvious frontal development (demixing) of these (and later) four component (HCl, THF, H_2O, organic phosphorus compound) solvents. The R_F value of the H^+ front was determined for solvents containing 0.5 *M* of each phosphorous compound by measuring the pH along the paper and was found to be approximately 0.9 for TOPO, 0.7 for TBP, and 0.4 for HDEHP. Despite this, a good separation of Sc from the rare earths was obtained by conventional dry-start ascending development as described above.

Separation of Hafnium and Zirconium from Various Ions. Solvents composed of 5% 12 *M* HNO_3, 95% methanol, and different concentrations of TOPO were tested for the ascending separation of Zr and Hf from rare earths, alkali metals, alkaline earth metals, Ti, Fe, Co, Mn, and Zn on SA-2 paper. When 0.20 *M* TOPO was employed, Hf and Zr had R_F values of 0.60–0.70 and were separated from all other ions that remained at or near the origin. The only other ions that moved at all were Ti, Sc, and some of the rare earths (e.g., Yb), the fronts of whose zones had R_F values of about 0.20. On Whatman No. 1 paper, all ions moved with the solvent front, and on SA-2 with 5% 12 *M* HNO_3, 95% methanol, all were at the origin. Again, the selective separation obtained is clearly due to the combined mechanisms of ion exchange and solvent extraction (CIESE) (*12*).

The slight elution of Ti, Sc, and Yb in addition to Zr and Hf occurs with solvents containing 0.1 *M* as well as 0.2 *M* TOPO. This is unexpected considering the relatively high distribution coefficients of these metal ions but was also found for Sc on columns of Dowex 50 (*12*). With 0.1 *M* TOPO these ions were eluted less, but Hf and Zr formed more elongated, streaking zones (R_F, 0.30–0.65).

Frontal development of the solvents was again evident. The R_F of the H^+ front was about 0.8 in most runs. Descending development of a mixture spotted after a 10-cm premigration of solvent also provided a good separation of Zr and Hf from the other ions. The leading edges of the Ti, Yb, and Sc zones had R_F values of about 0.20 relative to Zr and Hf which were taken as R_F 1.0.

Tri-*n*-butylphosphine oxide (TBPO) was tested as a substitute for TOPO and the separation was equally good. With ascending development, Hf and Zr moved farther (R_F, 1.0–0.88), Sc (0.05–0.0), and Yb (0.10–0.0) less far, but Ti was coeluted in a streaking zone to a much greater extent (0.44–0.0).

Separation of Nickel from Various Ions. In an as yet unpublished study (*13*), Wahlgren et al. achieved a highly specific separation of nickel by a two-step elution on a column of Dowex 50 cation exchange resin. When the column is washed with 10% 6 *M* HCl, 90% acetone, nickel, alkali metals, alkaline earth metals, rare earths, and other elements are strongly retained while elements that form anionic chloride complexes (e.g., Fe, Co, Mn, Cu, Zn, Cd, Hg, Pb) are eluted. Nickel is then selectively eluted from the adsorbed elements with 10% 6 *M* HCl, 90% acetone, and 0.25 *M* dimethylgloxime.

Very similar results were obtained on hydrogen-form SA-2 paper. Development with 10% 6 *M* HCl, 90% acetone gave the following R_F values for the ions that moved:

U	0.90–0.83	Co	0.70–0.58
Mn	0.37–0.27	Cu	0.39–0.19
Zn	0.33–0.21	Bi	0.67–0.28
Mo	0.96–0.90	Cd	0.91–0.83
Fe	0.99–0.94		

Nickel and the other ions tested (Th, Zr, Hf, Ce, Yb, K, Mg) remained at the origin. When these were developed with the same solvent containing 0.25 *M* dimethylgloxime, nickel moved with R_F 0.64–0.50.

Nickel was specifically separated from a representative mixture of these ions by developing with 10% 6 *M* HCl, 10% acetone, and cutting off the area of paper known to contain the migrating ions. The remainder of the paper was then developed with the solvent containing dimethylgloxime to move the nickel from the origin. Two-dimensional development with these solvents also gives this nickel separation.

Separation of Thorium from Rare Earths, Scandium, and Various Other Metals. Elution with 5% 12 *M* HNO_3, 95% methanol, and 0.1 *M* TOPO served to separate thorium from rare earths and other elements including scandium on a column of strong-acid cation-exchange resin (*14*). If the concentration of TOPO was raised to 0.25 *M* TOPO, this solvent provided the ascending separation of Th from Fe, Co, Ni, Cu, Ce, rare earths, and Sc. Th migrated with R_F 0.35–0.21, while the other ions had R_F values <0.15. Some rare earths and Ti streaked from the origin and overlapped the trailing edge of the Th zone. A slight trace of Th was also left at the origin.

Development with 5% 12 *M* HNO_3, 95% methanol on SA-2 paper gave R_F values below 0.03 for all ions including Th. With 0.10 *M* TOPO added to the solvent, Th formed a streaking zone from the origin to R_F 0.30. At TOPO concentrations >0.25 *M*, the rare earths and Sc badly contaminated the Th zone.

Cation-Exchange Separations with Dithizone as the Extractant. Attempts to achieve cation-exchange separations similar to those reported (*15*) in columns of Dowex 50 with 5% 1 *M* HNO_3, 95% THF and also this solvent containing 0.01 *M* dithizone were not especially successful using SA-2 paper. It was reported that numerous elements (U, Th, Fe, Co, Zn, Cd, Ag, Cu, Bi, Pb, rare earths, alkali and alkaline earth metals) are sorbed on Dowex 50 from 5% 1 *M* HNO_3, 95% THF, but that Hg and Sb are not retained and can be separated from the sorbed elements.

On SA-2 paper, only Sb migrates from the origin with this solvent while all the other elements plus mercury are retained at the origin. The sorption of mercury was not due to the cellulose in the paper because it migrated with the solvent front on Whatman No. 1 paper. Hg did not move from the origin when developed by the wet start descending technique. The reason for the anomalous behavior of Hg cannot be explained at this time.

In the column experiment (*15*), the sorbed elements can be fractionated by eluting Ag, Cu, and Bi with 5% 1 *M* HNO_3, 95% THF containing 0.01 *M* dithizone. On SA-2 paper, these elements plus Hg form long, streaking zones, the leading edges of which are at the solvent front. Many other elements (Pb, Fe, Co, Cd, Sc, Yb, Th, Mg, Zn, U, K) do not move and are separated from Ag, Cu, Bi, and Hg.

In general, we found that streaking could be reduced by increasing the concentration of extractant. This was not feasible in this system because the addition of even 0.01 *M* dithizone turns the solvent mixture a very dark green. Chromatograms dried after development changed from dark green to grey-brown so that the colored metal dithizonates could be located in many cases and spray reagents could be used with difficulty when necessary. With higher concentrations of dithizone, zone detection was very difficult.

Anion-Exchange Separations of Various Metal Ions with Solvents Containing DMSO. Many separations were achieved on SB-2 chloride-form anion-exchange papers by development with solvents composed of HCl-methanol–DMSO as suggested by Fritz and Gillette (*16*). Examples of the separations we performed include:

(a) Pb (R_F 0.08–0.01) separated from Zr (0.96–0.61), Mo (0.88–0.63), and Ni (0.98–0.86) with 50% DMSO–methanol–0.6 *M* HCl (i.e., 47.5 ml DMSO, 47.5 ml methanol, 5 ml 12 *M* HCl). Development of the mixture on Whatman No. 1 paper gave no separation (R_F of Pb was 1.0–0.91), again indicating the importance of the CIESE effect.

(b) Co (1.0–0.84) from Bi (0.03–0.0) and Pb (0.15–0.05) with DMSO–80% H_2O–0.6 *M* HCl.

(c) Ni (0.98–0.84) from Pb (0.09–0.02), Co (0.46–0.0), and Bi (0.08–0.0) with 50% DMSO–methanol–0.6 *M* HCl.

(d) Zr (1.0–0.86) from Mo (0.44–0.12) with 20% DMSO–methanol–4.85 *M* HCl.

(e) Cu (0.94–0.90) plus Co (0.95–0.85) from Bi, Cd, and Zn (all 0.05–0.0) with DMSO–80% H_2O–0.6 *M* HCl.

(f) Pb (0.20–0.12) from Co, Fe, Ti, and Zr (all 1.0–0.90) with 20% DMSO–H_2O–30% HCl.

(g) Ti plus Zr (both 1.0–0.85) from Fe (0.71–0.02), Co (0.38–0.09), and Pb (0.45–0.34) with 20% DMSO–H_2O–60% HCl.

The great solvating strength of DMSO is illustrated by the fact that Au, Pb and Ag can be eluted from the resin-paper even though the solvent contains HCl as one component. Gold normally has a very high distribution coefficient in dilute HCl media, and lead and silver chlorides precipitate in other nonaqueous solvents.

CONCLUSIONS

It has been shown that ion-exchange paper chromatography in mixed solvents containing a selective organic extractant yields many useful metal ion separations. Results in many cases are similar to those in columns of resin with the same mobile phase. Sometimes a slight modification of the solvent is required to duplicate column separations, and in still other systems the separations cannot be duplicated.

As a general rule, ions with very high distribution coefficients (>1000) will remain at the origin during paper chromatography, while ions with coefficients below 1 will migrate. We have been unable to formulate any more explicit rules from our studies of ion-exchange paper chromatography employing these complicated solvents, and even this one sometimes fails. For example, the movement of bismuth on resin-paper is often retarded although its batch distribution coefficient indicates that it has little affinity for the resin. As suggested before (*17*), discrepancies between column and paper ion-exchange chromatography are possible due to basic differences in the two techniques or to compositional differences in the stationary phases (e.g., the presence of cellulose).

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