

- 8 D. L. HARDY, D. O. HOLLAND UND J. H. C. NAYLOR, *Anal. Chem.*, 27 (1955) 971.
 9 L. S. MARKOSYAN, *Izv. Akad. Nauk Arm. SSR, Ser. Biol. i Sel'shokhoz. Nauk*, 11, No. 12 (1958) 117.
 10 H. G. KNAUF, P. DIETERLE UND H. ZICKGRAF, *Z. Physiol. Chem.*, 316 (1959) 186.
 11 E. W. SCHERBAKOWA, *Arb. Odessaer Technol. Inst. Nahrungsm. -u. Kulle-Ind.*, 9 (1959) 65.
 12 W. CIUSA UND A. BUCELLI, *Rass. Chim.*, 12 (1960) 17.
 13 K. GRUHN, *Wiss. Z. Friedrich-Schiller-Univ. Jena*, 9 (1960) 593.
 14 C. S. HANES, C. K. HARRIS, M. A. MOSCARELLO UND E. TIJANE, *Can. J. Biochem. Physiol.*, 39 (1961) 163.
 15 B. S. HARTLEY, *Biochem. J.*, 80 (1961) 36P.
 16 P. DE LA LHOSA, C. TERTRIN UND M. JUTISZ, *J. Chromatog.*, 14 (1964) 136.
 17 N. BOUTSCHEFF, *Nahrung*, 9 (1965) 161.
 18 S. M. PARTRIDGE, *Biochem. J.*, 42 (1948) 238.
 19 F.-K. GRUTTE UND B. KOHNKE, *Z. Lebensm.-Untersuch.-Forsch.*, im Druck.

Eingegangen den 10. Juni 1966

J. Chromatog., 26 (1967) 325-327

Some comparisons between column and paper ion-exchange chromatography

Ion-exchange paper chromatography usually yields results comparable to column ion-exchange chromatography when the same solutes, resin and wash liquid are included in the two systems. This has been demonstrated repeatedly by LEDERER and coworkers, for example with some thirty metal ions in anion-exchange systems employing HCl¹. It has been inferred by OSSICINI AND LEDERER² that differences between ion-exchange paper and column experiments are always due to differences in technique, for example frontal analysis of the solvent or other causes of nonequilibrium conditions, which can be detected and hopefully eliminated.

During our work with ion-exchange papers, we reported two discrepancies^{3,4} between paper and column results which we have now studied in detail and tried to explain.

Experimental

The standard procedures we employed for the downward development of paper chromatograms in commercial equipment have already been described⁵. Developed zones were located by spraying with yellow ammonium sulfide. Additional comments on procedure will be given in the discussion of the two systems below.

Vanadium-peroxide system

FRITZ AND ABBINK⁶ separated mercury (II) from vanadium (V) on a column of Dowex 50 (H form) by elution with a solution of 0.010 M sulfuric acid containing 1.0 % of hydrogen peroxide. Vanadium forms an anionic complex⁷ and is rapidly eluted while mercury is cationic⁷ and remains in a tight band on the top of the column.

We were originally unable to separate these ions on hydrogen-form SA-2 cation exchange paper by development with the same solution; vanadium migrated in a compact zone with R_F 0.36 but was contaminated by mercury which formed a long comet extending from the origin out to R_F 0.47⁴. After altering the procedure which

we had routinely been using to change the form of the ion-exchange paper, we were able to achieve a separation of vanadium and mercury comparable to the column.

SA-2 cation-exchange paper contains Amberlite IR-120 strongly-acidic sulfonic acid cation-exchange resin, which is similar to Dowex 50. The paper is commercially supplied in the sodium form. To convert to some other ionic form, we soaked overnight in a 4% solution of an appropriate acid or salt (for example, HCl to convert to the hydrogen form), equilibrated the paper four times for 30 min each with distilled water, and air dried overnight. This paper yielded the unsuccessful separation. If the paper was instead equilibrated eight times for 30 min each with distilled water before drying, the separation was successful. Mercury remained at the origin in a compact zone, and vanadium migrated with R_F 0.33. The original procedure we were using to convert the paper was suggested by an earlier paper⁸ and involved as much washing as we had ever seen specifically suggested. Apparently, however, enough HCl remained in the paper after this treatment to at least partially complex the mercury and cause it to migrate irreversibly as a neutral or weakly anionic complex.

This explanation involving complexing by residual chloride is substantiated by the fact that when the paper was converted by soaking in 4% H_2SO_4 , HNO_3 or $HClO_4$, followed by only four water equilibrations, a separation agreeing with column chromatography resulted: vanadium had R_F 0.36 and mercury remained at the origin in each case. These results emphasize the importance of thoroughly washing ion-exchange paper after conversion in order to avoid possibly anomalous results.

Tin-tartaric acid systems

Tin(IV) and copper(II) ions were separated by column elution chromatography on Amberlite IR-120 cation-exchange resin (ammonium form) with 0.33 *M* tartaric acid as eluent⁹. Tin forms an anionic complex with tartrate which is not sorbed by the resin while the copper (and many other ions such as Pb^{+2} , Ba^{+2} , Al^{+3} , Cr^{+3} , etc.) is uncomplexed and strongly sorbed.

We reported earlier that this separation could not be reproduced on ion-exchange paper (SA-2) containing the same resin in the same ionic form by development with the same wash liquid because both the tin and copper remained at the origin ($R_F < 0.15$)³. Because we also found that tin was not sorbed from tartaric acid on Whatman No. 1 cellulose paper, we suggested that the anomalous results for tin might be due to sorption by binder chemicals in the ion-exchange paper³. We have since been informed by the manufacturer of this paper that SA-2 paper supposedly contains no binder but is a mixture only of cellulose and resin¹⁰. We therefore began to look for other disturbing effects, such as those suggested by OSSICINI AND LEDERER², which we could exclude so that the paper and column results would agree.

To determine whether the solvent was altered by passing through the paper, we allowed 0.33 *M* tartaric acid to descend as usual over almost the entire length of a 30 cm strip of dry ammonium-form paper, and then sprayed with various reagents to measure the distribution of tartaric acid along the paper. Hydrogen ions were detected by spraying with universal indicator (and other pH indicators) and tartrate ions with $KMnO_4$ or $FeCl_3$ solutions. The H^+ front was somewhat difficult to locate exactly but had an R_F value of at least 0.85; the tartrate front was identical to the bulk solvent front (R_F 1.0). These results indicated no significant frontal development of the solvent and therefore no deficiency of complexing agent during development of the tin.

So that the ion-exchange paper more closely simulated an ion-exchange column, some paper was soaked overnight in the wash liquid and then dried only enough so that the solvent front could be observed during development. This left a reserve of tartaric acid in the paper, although not nearly so much as would be present in a properly prepared column. Again, both the copper and tin were found at the origin after development.

Different forms of ion-exchange paper were tried (hydrogen form, sodium form, etc.), and the tin was sorbed at the origin in every case.

In order to somewhat simulate the ion-exchange paper, a mixture of 50 % (by weight) of Amberlite CG-120 ammonium-form cation exchange resin (200–400 mesh) and 50 % Whatman cellulose powder (CF-12; 200 mesh) was intimately mixed and spread in a thin layer on a glass plate using equipment and procedures already described¹¹. Development with 0.33 *M* tartaric acid gave the expected separation: copper had R_F 0.0 and tin R_F 1.0. A column of this resin–cellulose mixture gave a separation of copper and tin identical to a column of resin alone. These results indicate that it is not simply the combination of cellulose and resin in the ion-exchange paper that is the basis of the problem.

Other related experimental results which we obtained were as follows: tin was at the solvent front when developed with tartaric acid on a thin layer of cellulose or in a column of cellulose. Also, tin and copper separated as expected when developed in a horizontal position¹² on an unbound thin layer of Amberlite CG-120 resin.

Discussion

There are several possible explanations for the anomalous sorption of tin from tartaric acid on SA-2 ion-exchange paper despite: (1) the absence of sorption on cellulose or comparable ion-exchange resin in any related system; (2) the absence of frontal effects for the solvent; and (3) the absence of any obvious precipitation when the zones were spotted at the origin. Perhaps there are some binder or foreign chemicals present in the finished ion-exchange paper of which the manufacturers are unaware; perhaps during the manufacture of the paper, the resin or cellulose changes in some way so that either or both then becomes able to sorb tin; or perhaps there is a synergistic effect of cellulose and resin arising during the manufacture of the paper which complicates the situation. In any case, when using standard, recognized techniques for column and paper experiments with the same resin, one does not necessarily get the same result for every solute with a given wash liquid. And as we have shown above, the reasons for the discrepancies may or may not be due to differences in technique, and may or may not be easy to locate and correct.

Other workers have reported such discrepancies which remain unexplained. For example, LEDERER AND SARACINO¹³ noted differences in the behavior of gallium (III) in HClO_4 on SA-2 paper compared with column experiments performed by NELSON *et al.*¹⁴. This was attributed to differences between the IR-120 resin in the ion-exchange paper and the Dowex 50 resin employed in the column studies. This may well be the explanation, although we have never noted any significant differences between these two resins. It could be verified by repeating the column experiments with the Amberlite resin.

CASSOL *et al.*¹⁵ reported the adsorption of tin (IV) fluoride on the cellulose network of various anion-exchange papers. QURESHI AND QURESHI¹⁶ also mentioned the

adsorption of metal ions on the cellulose of stannic phosphate impregnated papers. Results obtained on such papers would of course not compare with results on columns of the same sorbent. These differences would not be due to technique but to the presence of cellulose in one system and its absence in the other. As suggested above, if binder chemicals are also present in the ion-exchange paper, this would be a further difference in the chromatographic system which could lead to results different than those obtained from batch or column ion-exchange experiments. It is well known that the presence of binders in thin-layer chromatography occasionally causes results different from those obtained in columns of the same adsorbent¹⁷.

In conclusion, we suggest that although the migration of ions in ion-exchange paper chromatography can usually be predicted from batch equilibrium and column chromatography (and *vice versa*), one must be aware of possible discrepancies, which may be due to differences in technique² or to basic differences in the stationary phase of the chromatographic systems being used.

Acknowledgement

K. M. R. was a participant in Lafayette's N.S.F. Undergraduate Research Program.

Department of Chemistry, Lafayette College, Easton, Pa. 18042
(U.S.A.)

JOSEPH SHERMA
KENNETH M. RICH

- 1 M. LEDERER AND L. OSSICINI, *J. Chromatog.*, 13 (1964) 188.
- 2 L. OSSICINI AND M. LEDERER, *J. Chromatog.*, 17 (1965) 387.
- 3 J. SHERMA AND C. W. CLINE, *Anal. Chim. Acta*, 30 (1964) 139.
- 4 J. SHERMA, *Talanta*, 11 (1964) 1373.
- 5 J. SHERMA, *Talanta*, 9 (1962) 775.
- 6 J. S. FRITZ AND J. E. ABBINK, *Anal. Chem.*, 34 (1962) 1080.
- 7 J. SHERMA, G. H. EVANS, H. D. FRAME AND H. H. STRAIN, *Anal. Chem.*, 35 (1963) 224.
- 8 M. LEDERER AND F. RALLO, *J. Chromatog.*, 7 (1962) 552.
- 9 J. SHERMA AND A. K. BRYDEN, *Chemist-Analyst*, 52 (1963) 69.
- 10 J. GULDALIN, H. Reeve Angel and Co., Clifton, N. J., personal communication.
- 11 J. SHERMA AND L. V. S. HOOD, *J. Chromatog.*, 17 (1965) 307.
- 12 M. MOTTIER AND M. POTTERAT, *Anal. Chim. Acta*, 13 (1955) 46.
- 13 M. LEDERER AND F. SARACINO, *J. Chromatog.*, 15 (1964) 80.
- 14 F. NELSON, T. MURASE AND K. A. KRAUS, *J. Chromatog.*, 13 (1964) 503.
- 15 A. CASSOL, L. MAGON AND R. BARBIERI, *J. Chromatog.*, 19 (1965) 57.
- 16 M. QURESHI AND S. QURESHI, *J. Chromatog.*, 22 (1966) 198.
- 17 B. BAEHLER, *Schweiz. Apotheke-Ztg.*, 99 (1961) 543.

Received June 9th, 1966

J. Chromatog., 26 (1967) 327-330