

The separation of diazonium salts by thin-layer chromatography

Chromatography has been used to separate many complex mixtures, but rarely has it been concerned with the separation of relatively unstable ionic species¹. Thus, it was of interest to ascertain whether the technique of thin-layer chromatography would be applicable in the separation and identification of diazonium salts.

The diazonium salts used in this study were commercially available chlorozincates and fluoborates, and fluoborates prepared from the chlorozincates by a standard technique². Visualization of the diazo spots by color formation, resulting from the formation of a dye, is rapid and very sensitive. Table I lists the salts studied.

TABLE I
TLC SEPARATION OF DIAZONIUM SALTS

<i>Diazonium salt</i>	<i>R_F of chlorozincate</i>	<i>R_F of fluoborate</i>
2-Ethoxy-4-diethylaminobenzene	0.81	0.81
N-Benzyl-N-ethyl-4-aminobenzene	0.61	*
N-Ethyl-3-methyl-4-aminobenzene	0.58	0.58
4-Morpholinobenzene	0.38	0.38
4-Diethylaminobenzene	0.54	0.54
4-Dimethylaminobenzene	0.31	0.31
2,5-Diethoxy-4-morpholinobenzene	0.85	0.85
4-Diethylamino-2-methylbenzene	0.65	0.65
N-Ethyl-N-2-hydroxy-ethyl-4-aminobenzene	0.53	*
2,5-Dibutoxy-4-morpholinobenzene	0.97	—

* The fluoborate salt would not separate from water.

Because of the heat and light sensitivity of these compounds, the chromatographic separations were carried out at ambient temperatures in a room illuminated with yellow light.

Initially it was assumed that a three-component solvent mixture would be necessary to cause the separation of these ionic compounds. Of the many mixtures tried, only those containing dimethyl sulfoxide were found to move the diazonium salts well on a chromatoplate. The best three-component system found was a 6:1:1 mixture of dimethyl sulfoxide-acetic acid-water. This solvent mixture gave a good separation after a long development time (3 h). Subsequently it was found that a 25:1:5:20 mixture of dimethyl sulfoxide-formic acid (88%)-chloroform-dioxane would give excellent results in 1 h, with little lateral diffusion of the spots. Table I gives the R_F values obtained under the latter conditions. Visualization was accomplished by spraying the developed plate with a blue dye-forming coupler (2,3-dihydroxynaphthalene) followed by treatment with ammonia. It was pointed out to the author and subsequently confirmed in this laboratory that the two stabilizing anions of the diazonium salts have an R_F value of 1.0 under the above experimental conditions³. This suggests that the polar solvent components used stabilize the diazonium cation during the separation.

This method was also found useful in the separation and comparative identification of mixtures of diazo compounds. Identification was readily substantiated by

known techniques after the isolation of the diazonium salt. To accomplish this, a large sample of a specific diazo mixture was separated into bands on a large plate. The bands were sprayed with a methanol solution of zinc chloride (to renew the stabilizing anion) and the plate dried. The band containing the desired diazonium salt was scraped from the plate and extracted with methanol, thus isolating the diazonium compound.

These diazonium compounds on the chromatoplate are readily visible in white light as a yellow band. Their visualization in yellow light is accomplished by the water-spray technique⁴.

The chromatoplates were prepared with a 0.25–0.35 mm layer of silica gel G in the usual manner with Desaga equipment⁵. All diazonium salts were recrystallized prior to use. Spotting solutions of the diazonium compounds were made up in methanol.

IBM Research Laboratory, San Jose, Calif. (U.S.A.)

ROY J. GRITTER

1 E. LEDERER AND M. LEDERER, *Chromatography*, Elsevier, Amsterdam, 1957.

2 H. ZOLLINGER, *Diazo and Azo Chemistry: Aliphatic and Aromatic Compounds*, Interscience, New York, 1961, p. 53.

3 S. HAINING AND M. ORNIK, IBM Vestal Laboratory, Vestal, N.Y., personal communication

4 R. J. GRITTER AND R. J. ALBERS, *J. Chromatog.*, **9** (1965) 52.

5 J. M. BOBBITT, *Thin Layer Chromatography*, Reinhold, New York, 1963

First received July 14th, 1964

Modified May 3rd, 1965

J. Chromatog., **20** (1965) 416–417

Dimethyl sulphoxide as stationary phase in thin-layer partition chromatography on silica gel

Dimethyl sulphoxide (DMS) has been used as a stationary phase in the paper chromatography of carbohydrate formates¹, acetates² and triphenylmethyl ethers³, and in chromatography of inositol acetates⁴ on columns of silica gel. Since silica gel is more convenient than cellulose for spreading as thin layers and is also resistant to heat and to vigorous detecting reagents, it was thought that silica gel might be the most useful support in applying DMS systems to thin-layer chromatography. This expectation proved to be justified.

WICKBERG² observed that α - and β -anomers are better separated on paper treated with DMS as stationary phase than on untreated paper, and this characteristic of DMS systems is maintained when the support is changed from cellulose to silica gel. Several pairs of anomeric acetates were completely separated using one or more moving phase (see Table I), the α -anomers having the higher R_F values (see Table II). However, it is noteworthy that for instance methyl 2-deoxy- α -glucoside triacetate and methyl 2-deoxy- α -galactoside triacetate were not completely separated when the R_F values were less than 0.5. The same was true of the corresponding β -anomers.

J. Chromatog., **20** (1965) 417–419