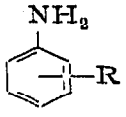
Separation of some aromatic amines by thin-layer chromatography

This work deals with the application of thin-layer chromatography to the separation of some isomeric ring-substituted anilines of the general formula:



where R is: $-CH_3$; $-OH$; $-OCH_3$; $-COOH$; $-NO_2$; $-NH_2$; $-Br$; $-Cl$.

Some of these compounds have already been reported in the literature[1-3], but a more systematic investigation was necessary for our purposes.

Experimental

The chromatoplates were prepared according to the method described by STAHL[4]. Silicagel G* was applied on 20 × 20 cm glass plates** to a thickness of 250 μ and activated at 105° for 1 h. 2 μl of a 5 % ethyl ether solution of each component were applied along a line 2.5 cm from the lower end of the plate and developed by the ascending method.

Five different solvent systems were chosen as mobile phase. They are reported in Table I with the corresponding R_F values. The aromatic amines were revealed by the following techniques:

(1) Direct observation (for coloured products).

(2) Irradiation with U.V. light (365 mμ).

TABLE I

R_F VALUES OF SOME AROMATIC AMINES OBTAINED BY MEANS OF THIN-LAYER CHROMATOGRAPHY ON SILICAGEL G

Solvent system	*ml*				
Dibutyl ether	100	150	50	200	—
Ethyl acetate	100	50	150	—	—
Acetic acid	10	10	10	10	20
n-Hexane	—	—	—	40	—
n-Butanol	—	—	—	—	80
Water	—	—	—	—	100
Aromatic amines	*R_F values*				
o-Toluidine	0.62	0.42	0.64	0.17	0.84
m-Toluidine	0.54	0.29	0.63	0.10	0.83
p-Toluidine	0.40	0.20	0.59	0.05	0.80
o-Aminophenol	0.34	0.24	0.58	0.00	0.80
m-Aminophenol	0.29	0.13	0.53	0.00	0.75
p-Aminophenol	0.06	0.01	0.12	0.00	0.62

(continued on p. 572)

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TABLE I (*continued*)

Aromatic amines	*R_F values*				
o-Aminobenzoic acid	0.62	0.47	0.74	0.44	0.98
m-Aminobenzoic acid	0.50	0.28	0.61	0.12	0.95
p-Aminobenzoic acid	0.59	0.37	0.68	0.29	0.97
o-Anisidine	0.60	0.42	0.70	0.15	0.81
m-Anisidine	0.51	0.30	0.62	0.09	0.80
p-Anisidine	0.11	0.02	0.17	0.02	0.58
o-Nitroaniline	0.69	0.55	0.77	0.52	0.93
m-Nitroaniline	0.64	0.44	0.71	0.36	0.92
p-Nitroaniline	0.58	0.37	0.67	0.29	0.91
o-Phenylenediamine	0.00	0.00	0.00	0.00	0.63
m-Phenylenediamine	0.00	0.00	0.00	0.00	0.53
p-Phenylenediamine	0.00	0.00	0.00	0.00	0.40
o-Bromoaniline	0.81	0.78	0.85	0.69	0.95
m-Bromoaniline	0.70	0.58	0.75	0.44	0.93
p-Bromoaniline	0.61	0.47	0.67	0.27	0.89
o-Chloroaniline	0.78	0.75	0.82	0.66	0.96
m-Chloroaniline	0.68	0.51	0.75	0.40	0.94
p-Chloroaniline	0.60	0.41	0.64	0.22	0.89

(3) Spraying with 5 % $NaNO_2$ in 0.2 *N* HCl solution. After drying at 50° the plate was sprayed with 5 % α-naphthol in methyl alcohol. The amines appear as coloured spots.

(4) Spraying with a 1:1 (v/v) aqueous mixtures of 0.1 *M* $FeCl_3$ and 0.1 *M* $K_3[Fe(CN)_6]$. The amines appear as blue spots.

Conclusions

By determining the R_F values in the solvent systems mentioned in Table I, the components of an unknown mixture of aromatic amines can in most cases be identified.

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