

Thin-layer chromatography of *o*-, *m*- and *p*-chloronitrobenzene

Chromatographic studies¹ show that the disubstituted derivatives of benzene, particularly the *meta* and *para* isomers, are difficult to separate. Paper chromatography in neutral systems yields hardly any results. Some slight separation of the *meta* and *para* derivatives could be obtained only under conditions in which salt formation is possible²⁻⁴, that is in an acidic system for the basic substances and in a basic system for the acidic group. Our investigations concerning the separation of *m*- and *p*-chloronitrobenzenes, on which there are no satisfactory literature data available, showed that thin-layer chromatography worked well even in a neutral system. The optimum conditions for separation were determined after testing two types of adsorbent and different types as well as mixed solvents, and using ³⁶Cl-labelled compounds if radiometric evaluation was performed.

Experimental

The experimental technique was similar to that used for the analysis of organic phosphorus and arsenic compounds⁵. For coating the glass plates magnesium silicate (Woelm) and silica gel G (Merck) were used in turn. The coated plates were dried at 110°, for 2 h each. The R_F values were determined on 3 cm × 20 cm glass strips used in the radiometric evaluation, while for a check 20 cm × 20 cm glass plates were used. The R_F values were found to be essentially independent of plate size. The ascending technique was used in glass tanks with ground-in lids. The time of development given in the tables is that for 15–16 cm travelled by the solvent front. 0.04 % Na-fluorescein solution was incorporated in the adsorbent layers during their preparation. The spots were clearly discernible in U.V. light and moderately visible in daylight.

TABLE I

($\bar{R}_F \pm \sigma$) × 100 VALUES ON MAGNESIUM SILICATE ADSORBENT

A = Normal saturation; B = saturation by means of filter paper lining.

Solvent system		Nitro- benzene	<i>o</i> -Chloro- nitro- benzene	<i>m</i> -Chloro- nitro- benzene	<i>p</i> -Chloro- nitro- benzene	Time of develop- ment
Petroleum ether	A	49 ± 1.0	42 ± 1.2	59 ± 0.1	58 ± 0.1	1.5 h
<i>n</i> -Hexane-diisopropyl ether (6:4)	B	44 ± 2.5	43 ± 1.5	49 ± 1.0	53 ± 1.6	45 min
<i>n</i> -Hexane-diisopropyl ether- acetone (7:3:3)	B	54 ± 1.2	53 ± 0.1	55 ± 1.1	59 ± 0.1	50 min
Cyclohexane; 8 % silicone oil	B	27 ± 1.2	20 ± 0.1	29 ± 0.1	29 ± 0.1	1.5 h
Cyclohexane-diethyl ether (2:1); 10 % silicone oil	A	75 ± 2.5	71 ± 1.2	79 ± 3.5	79 ± 2.3	4 h
Cyclohexane-diethyl ether (1:1); 10 % silicone oil	B	54 ± 1.0	48 ± 0.1	55 ± 0.1	61 ± 1.4	1 h
Cyclohexane-diethyl ether- diisopropyl ether (2:1:1)	B	53 ± 2.0	47 ± 0.1	53 ± 1.0	56 ± 1.0	1.5 h
Petroleum ether-diisopropyl ether (1:1)	B	40 ± 1.0	38 ± 0.1	44 ± 1.0	47 ± 0.1	50 min

TABLE II

 $(\bar{R}_F \pm \sigma) \times 100$ VALUES ON SILICA GEL G ADSORBENT

A = Normal saturation; B = saturation by means of filter paper lining.

Solvent system		Nitro- benzene	<i>o</i> -Chloro- nitro- benzene	<i>m</i> -Chloro- nitro- benzene	<i>p</i> -Chloro- nitro- benzene	Time of develop- ment
Diethyl ether	A	96 ± 0.1	92 ± 0.1	96 ± 0.0	97 ± 0.1	1.5 h
Diethyl ether	B	83 ± 1.6	79 ± 2.3	85 ± 0.1	85 ± 0.1	40 min
Diisopropyl ether	A	85 ± 2.7	82 ± 1.9	87 ± 3.9	92 ± 0.1	1.5 h
Diisopropyl ether	B	67 ± 2.4	60 ± 1.5	70 ± 1.7	74 ± 2.0	55 min
<i>n</i> -Hexane	A	9 ± 0.8	8 ± 1.4	13 ± 1.7	11 ± 0.3	1 h
<i>n</i> -Hexane	B	4 ± 0.1	4 ± 0.1	6 ± 0.1	5 ± 0.1	45 min
Cyclohexane	A	12 ± 0.1	12 ± 1.8	13 ± 1.2	12 ± 1.0	2 h
Cyclohexane	B	4 ± 0.1	5 ± 0.1	6 ± 0.1	5 ± 0.1	1.5 h
Petroleum ether	A	13 ± 0.6	12 ± 0.4	17 ± 1.4	15 ± 0.9	1.5 h
Petroleum ether	B	6 ± 0.1	6 ± 0.1	8 ± 0.1	7 ± 0.1	40 min
<i>n</i> -Hexane-diisopropyl ether (6:4)	A	77 ± 0.2	63 ± 1.3	80 ± 1.5	85 ± 1.1	1 h
	B	44 ± 1.4	35 ± 0.2	47 ± 0.1	56 ± 0.2	30 min
<i>n</i> -Hexane-diisopropyl ether (9:2)	A	69 ± 2.6	51 ± 1.8	71 ± 1.5	80 ± 1.6	1 h
	B	39 ± 1.4	27 ± 0.1	41 ± 0.3	50 ± 0.1	30 min
<i>n</i> -Hexane-diisopropyl ether- acetone (7:3:3)	B	52 ± 1.5	47 ± 1.7	53 ± 1.6	58 ± 1.5	20 min
<i>n</i> -Hexane-petroleum ether- ethyl acetate (30:95:5)	B	27 ± 0.2	20 ± 0.2	29 ± 0.1	35 ± 0.3	30 min
<i>n</i> -Hexane-petroleum ether-ethyl acetate-diisopropyl ether (30:45:5:20)	B	39 ± 1.0	32 ± 0.2	43 ± 0.2	50 ± 0.2	30 min
Cyclohexane; 8% silicone oil	B	18 ± 1.3	13 ± 0.2	22 ± 0.3	24 ± 2.1	35 min
Cyclohexane-diethyl ether (2:1); 10% silicone oil	A	68 ± 2.6	56 ± 2.5	70 ± 3.1	79 ± 1.3	1 h
	B	42 ± 1.5	33 ± 1.1	39 ± 0.3	51 ± 1.6	45 min
Cyclohexane-diethyl ether- diisopropyl ether (2:1:1)	B	43 ± 1.8	38 ± 1.7	47 ± 1.4	52 ± 1.4	35 min
Petroleum ether-diisopropyl ether (1:1)	B	47 ± 0.3	42 ± 1.3	52 ± 1.3	58 ± 0.3	20 min
Petroleum ether-ethyl acetate (85:15)	B	43 ± 1.8	35 ± 2.6	45 ± 1.2	51 ± 1.1	30 min
Petroleum ether-ethyl acetate (95:5)	B	32 ± 1.2	24 ± 0.1	34 ± 0.1	41 ± 1.3	25 min
Petroleum ether-ethyl acetate- diisopropyl ether (6:2:2)	B	50 ± 5.8	45 ± 2.4	54 ± 2.0	57 ± 1.5	25 min
Petroleum ether-ethyl acetate- diisopropyl ether (8:2:2)	B	42 ± 1.2	36 ± 0.1	48 ± 0.1	53 ± 2.0	30 min

Results and discussion

The R_F values of the compounds chromatographed using different solvents are shown in Table I for magnesium silicate, and in Table II for silica gel adsorbent.

The separation is seen to be better and usually faster on silica gel.

It is of interest to note that for pure hydrocarbon solvents the R_F values increase in the order *ortho*, *para*, *meta*, while for non-hydrocarbons (e.g. diisopropyl ether) the order of increase changes to *ortho*, *meta*, *para* independently of the type of adsorbent and the degree of saturation of the system. In the case of solvent mixtures, the latter order asserts itself even if the hydrocarbon component is of higher concentration.

Another feature of interest is that the mixture of cyclohexane and diethyl ether containing silicone oil permits a satisfactory separation of the derivatives in question, although neither of the components works if used alone. Similarly, the individually unsuitable *n*-hexane if added to diisopropyl ether appreciably improves the degree of separation and substantially reduces the time taken by the analysis as compared with the results achievable with the latter when used alone.

For the simultaneous identification of the three isomers, mixtures of *n*-hexane and diisopropyl ether at various relative concentrations, as well as a mixture of cyclohexane and diethyl ether (2:1) with silicone oil, on Silica Gel adsorbent was found to be the most successful. This holds also for the separation of the *ortho* and *para* isomers, while the *ortho* and *meta* isomers can be separated well not only with the above mixtures, but can also be resolved by a combination of petroleum ether with ethyl acetate or diisopropyl ether on Silica Gel and also by pure petroleum ether on magnesium silicate adsorbent. Of the three derivatives, the *m*-chloronitrobenzene is the most difficult to separate from nitrobenzene. It can be done with petroleum ether on magnesium silicate adsorbent or with mixtures of petroleum ether and diisopropyl ether (1:1) or with a mixture of petroleum ether, ethyl acetate and diisopropyl ether (8:2:2) on Silica Gel G adsorbent.

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