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Note

Gas chromatographic separation of chloronitrobenzenes, nitroanilines and phenylenediamines

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The synthesis of phenylenediamines has been well reviewed in the literature. All isomeric phenylenediamines can be obtained by a two-stage process, involving ammonolysis of chloronitrobenzenes to nitroanilines¹⁻³ and hydrogenation of the latter to phenylenediamines⁴⁻⁷. Commercial solutions are usually mixtures of all isomers, and the separation of these compounds has been accomplished by gas (GC) and thin-layer chromatography (TLC). Good resolution of *o*-, *m*- and *p*-chloronitrobenzenes has been obtained on polyethylene glycols^{8,9}, polyoxyethylene glycol¹⁰ and polypropylene glycol¹¹. Zieliński *et al.*¹² have described the clean and selective GC separation of *o*-, *m*- and *p*-chloronitrobenzenes with QF-1 as the stationary phase using an electron-capture detector. The GC of *o*-nitroaniline has been reported by Gaile and Laitman¹³, while Ościk *et al.*¹⁴ separated *o*-, *m*- and *p*-nitroanilines by TLC.

Qualitative and quantitative analyses of *o*-, *m*- and *p*-phenylenediamines on Triton X-305 have been performed by Bryan¹⁵, and Goldstein *et al.*¹⁶ separated *o*- and *p*-phenylenediamines on UCON 50HB-5100 as the stationary phase.

We have found that cyclohexanedimethanol succinate on Gas-Chrom Q was the best GC system for the separation of chloronitrobenzenes, nitroanilines and phenylenediamines. No such studies have previously been reported.

EXPERIMENTAL

Apparatus

A Giede 18.3.4 gas chromatograph (Berlin, G.D.R.) with two columns, dual differential electrometer and two flame-ionization detectors was used.

Column preparation

The columns were 3.0 m × 4 mm I.D. stainless-steel tubes packed with 3% LAC-796 (cyclohexanedimethanol succinate) on Gas-Chrom Q (60-80 mesh). The stationary phase LAC-796 obtained from Applied Science Labs., State College Pa., U.S.A. was employed. The packed columns were heated at 2°/min from ambient temperature to 220° and then for 18 h at 220° with an argon flow-rate of 20 ml/min.

Reagents

Standard samples of *o*-, *m*- and *p*-chloronitrobenzenes, *o*-, *m*- and *p*-nitro-

anilines and *o*-, *m*- and *p*-phenylenediamines were of analytical-reagent grade. The isomeric phenylenediamines were purified by recrystallization¹⁷ from water and dried under vacuum.

Operating conditions

The column temperature was isothermal at 140° for 22 min, then programmed to 215° at 16°/min and, maintained at that temperature. The detector head temperature was 320°, the injector port temperature 280°, the carrier gas (argon) flow-rate 60 ml/min, the hydrogen flow-rate 60 ml/min, the air flow-rate 320 ml/min and the recorder chart speed 1 cm/min.

Procedure

A portion of the sample was dissolved in three times its weight of ethanol and 2 μ l of the diluted sample were injected on to the column. Standard mixtures were prepared and diluted just prior to analysis in order to minimize errors due to air oxidation.

RESULTS

Fig. 1. shows a chromatogram obtained in the separation of isomeric chloronitrobenzenes, nitroanilines and phenylenediamines. The nine compounds dissolved in ethanol were completely separated in 63 min.

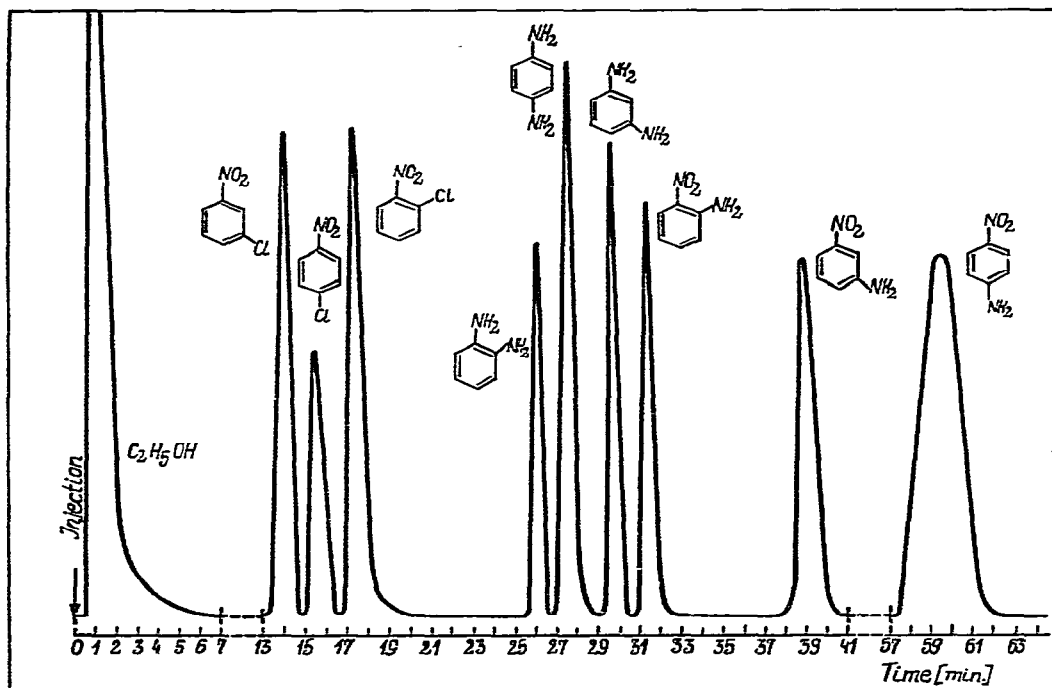


Fig. 1. Chromatogram of chloronitrobenzenes, nitroanilines and phenylenediamines. For gas chromatographic conditions, see under *Operating conditions*.

We obtained good results in the analysis of 0.01–0.5% (w/w) solutions of all of the compounds investigated. The retention times and boiling points are presented in Table I.

The rapid GC method described, without the need for preliminary separation, is of interest in technological process control.

TABLE I

RETENTION TIMES AND BOILING POINTS OF SOLVENT, CHLORONITROBENZENES, NITROANILINES AND PHENYLENEDIAMINES

Compound	Retention time (min)	Boiling point ¹⁸ (°C)
Ethanol	1.16	78.3
<i>m</i> -Chloronitrobenzene	14.00	235.6
<i>p</i> -Chloronitrobenzene	15.66	241.9
<i>o</i> -Chloronitrobenzene	17.63	245.7
<i>o</i> -Phenylenediamine	20.16	256–258
<i>p</i> -Phenylenediamine	27.53	267
<i>m</i> -Phenylenediamine	29.70	284–287
<i>o</i> -Nitroaniline	31.46	284.1
<i>m</i> -Nitroaniline	39.10	306.4
<i>p</i> -Nitroaniline	59.75	331.7

REFERENCES

- 1 BIOS, Final Rep., 1147, J. G. Farbemindustrie, Höchst.
- 2 K. H. Saunders, *U.S. Pat.*, 1,911,711 (1933); *C.A.*, 27 (1933) 3952.
- 3 W. H. Williams, R. D. Holmes and H. F. V. Feuehauf, *U.S. Pat.*, 2,432,551 (1947); *C.A.*, 42 (1947) 2620e.
- 4 J. Levy, *U.S. Pat.*, 3,230,259 (1966); *C.A.*, 64 (1966) 11126c.
- 5 C. G. Wickham, *Brit. Pat.*, 1,077,920 (1967); *C.A.*, 67 (1967) 99833s.
- 6 B. Mees and J. Ribka, *Ger. Pat.*, 2,140,787 (1973); *C.A.*, (1973) 124264u.
- 7 G. S. Samuelsen, V. L. Garick and G. B. L. Smith, *J. Amer. Chem. Soc.*, 72 (1950) 3872.
- 8 M. M. Nemova, V. N. Pertsova and S. L. Dobyichin, *Tr. Gos. Inst. Prikl. Khim.*, 62 (1969) 173.
- 9 V. N. Pertsova, M. M. Nemova and S. L. Dobyichin, *Tr. Gos. Inst. Prikl. Khim.*, 62 (1969) 171.
- 10 V. J. Ostrovski, J. J. Bat, P. N. Ovczinnikov and G. G. Shuvalova, *Tr. Gos. Inst. Prikl. Khim.*, 62 (1969) 175.
- 11 N. P. Sokolova, Z. M. Skulskaya and A. A. Balandin, *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.*, 10 (1966) 1861.
- 12 W. L. Zieliński, Jr., L. Fishbein and R. O. Thomas, *J. Chromatogr.*, 30 (1967) 77.
- 13 A. Gaile and I. I. Laitman, *Zh. Fiz. Khim.*, 41 (1967) 2886.
- 14 J. Ościk and G. Chojnacka, *Chem. Anal. (Warsaw)* 12 (1967) 1213.
- 15 H. W. Bryan, *Anal. Chem.*, 36 (1964) 2025.
- 16 S. Goldstein, A. A. Kopf and R. Feinland, *Proc. Joint. Conf. Cosmet. Sci.*, (1968) 19; *C.A.*, 70 (1969) 109098j.
- 17 A. I. Vogel, *A Text Book of Practical Organic Chemistry*, Longmans, Green and Co. Ltd., London, 3rd ed., 1956.
- 18 R. H. Perry and C. H. Chilton, *Chemical Engineer's Handbook*, McGraw-Hill, Ind., New York, 5th ed., 1973.