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GAS CHROMATOGRAPHIC ANALYSIS OF γ-IRRADIATED ANILINE FOR AMINOAROMATIC PRODUCTS

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SUMMARY

Gas chromatographic conditions have been found for the satisfactory analysis of the isomeric diaminobenzenes, the isomeric aminobiphenyls and diphenylamine, the isomeric aminodiphenylamines, and the isomeric 2,2'-, 2,3'-, and 2,4'-diaminobiphenyls. Satisfactory conditions were found for the analysis of 3,3'-, 3,4'-, and 4,4'-diaminobiphenyl as individual components, but not for the analysis of a mixture containing all three isomers.

INTRODUCTION

In a study of the γ-radiolysis of aniline, it was necessary to analyze the irradiated aniline for the three isomeric diaminobenzenes, the three isomeric aminobiphenyls, diphenylamine, the three isomeric aminodiphenylamines, and the six isomeric diaminobiphenyls (one amino group per phenyl ring). A search of the literature revealed information only for the gas chromatographic analysis of the diaminobenzenes[1]. This paper describes the gas chromatographic conditions for the analysis of the aminoaromatic compounds listed above.

EXPERIMENTAL

Materials

The following aminoaromatic compounds were available commercially: *o*-, *m*-, and *p*-diaminobenzene, 2- and 4-aminobiphenyl, diphenylamine, 2- and 4-aminodiphenylamine, and 4,4'-diaminobiphenyl. The following aminoaromatic compounds were prepared by the catalytic reduction of the corresponding nitroaromatic compound: 3-aminobiphenyl, 3-aminodiphenylamine, 2,2'-, 2,3'-, 2,4'-, 3,3'-, and 3,4'-diaminobiphenyl. The crude reduction products were recrystallized from appropriate solvents to obtain satisfactory melting points. The commercial samples were recrystallized if necessary to obtain satisfactory melting points. Stationary phases and packings were obtained from various gas chromatographic suppliers.

Equipment

A Perkin-Elmer Model 900 dual column unit with a hydrogen flame ionization detector was used for all analyses.

Column preparation

Chromosorb W, which was acid washed and DMCS treated, and either 80/100 mesh or 100/120 mesh, was coated initially with 2% sodium hydroxide using methanol as a solvent. The packings of the individual stationary phases were prepared as previously described[2]. For the preparation of a satisfactory packing with Versamid 900, it was found that the best technique was the evaporation of the solvent with gentle stirring on a steam bath. All columns were $\frac{1}{8}$ in. O.D. copper tubing.

Samples

Standard dilute solutions of the various amino compounds in aniline were prepared and used for the different analyses on the various columns.

RESULTS AND DISCUSSION

In an investigation of the radiation chemistry of aniline, some amino compounds that were considered very likely to be among the radiolytic products were the three isomeric diaminobenzenes, the three isomeric aminobiphenyls and diphenylamine, the six isomeric diaminobiphenyls (one amino group per phenyl ring), and the three isomeric aminodiphenylamines. Gas chromatography offered the best analytical method for analyzing the irradiated aniline for these compounds, both qualitatively and quantitatively. A search of the literature revealed only one report on the gas chromatographic analysis of the above compounds. This report gave conditions for the analysis of the diaminobenzenes[1]. Reports were also found in which the use of a support treated with an alkali hydroxide was suggested to reduce tailing in the gas chromatographic analysis of amines[3,4].

In considering stationary phases to be tested, two factors that were taken into consideration were the upper temperature limit and polarity. The three phases that were found to be the most satisfactory were Triton X-305, an alkylaryl polyether alcohol with a temperature limit of 250°; Versamid 900, a polyamide resin with a temperature limit of 275°; and FFAP, which is a condensation product of nitroterephthalic acid and Carbowax 20M (a polyethylene glycol) and which has a temperature limit of 250°. Chromosorb W, acid washed and DMCS treated, was loaded with 2% sodium hydroxide before applying the stationary phase. A loading of 2% sodium hydroxide was found to give the most satisfactory results in reducing the tailing of the peaks of the aromatic amines.

Calculations of the number of theoretical plates for a column were made with the equation

$$n = 16 \left(\frac{t_R}{\omega}\right)^2$$

where n = plate number, t_R = retention time, and ω = peak width at base[5]. The number of plates required to effect a given separation was calculated with the equation

$$n_{req} = 16 \left[\frac{\alpha}{(\alpha - 1)}\right]^2 \left[\frac{(k+1)}{k}\right]^2$$

where n_{req} is the required number of plates, α is the relative retention, and k is the partition ratio[5]. In the above equation, the calculated required number of plates should give a resolution of 98% separation of two closely spaced peaks. The relative retention, α, is calculated from the equation

$$\alpha_{2,1} = \frac{t'_{R_2}}{t'_{R_1}}$$

where t_R' is the adjusted retention time. The partition ratio, k, is calculated from the equation

$$k = \frac{t_R}{t_A} - 1$$

where t_A = retention time for air or an inert peak. In this work with a flame ionization unit, methane was used as the inert peak. In many cases in calculating the required number of plates, the term $[(k+1)/k]^2$ is negligible when $t_A \ll t_R$ and can be neglected.

In testing new stationary phases, columns of three to five feet in length and 2–5% loading were used. From the initial information obtained from these columns, other columns were prepared for testing. The gas chromatographic conditions that were utilized for the analysis of irradiated aniline for the various aminoaromatic compounds are listed in Table I.

Columns prepared with Triton X-305 were tried first for the separation of the three isomeric diaminobenzenes. These three isomers were completely resolved at 160° on a 3-ft. column packed with 15% Triton X-305 on 80/100 mesh Chromosorb W (AW/DMCS). However, 2-aminobiphenyl and *m*-diaminobenzene overlapped. Since both of these compounds were considered as likely radiolytic products, it would

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

Nitrogen carrier gas was used at a flow rate of 30 ml/min for all analyses.

Compound group	*Stationary phase*[a]	*Loading (%)*	*Column length (ft.)*	*Temperature (°C)*
Diaminobenzenes	Triton X-305	20	10	225
Aminobiphenyls and diphenylamine	Triton X-305	5	5	160° for 16 min; programmed to 190° at 5°/min
2,2′-, 2,3′-, and 2,4′-diaminobiphenyls and 2-, 3-, and 4-aminodiphenylamines	FFAP	6	15	250
	Versamid 900	6	10	230
3,3′-, 3,4′-, and 4,4′-diaminobiphenyls	FFAP	5	5	250

[a] The inert packing used was Chromosorb W, AW/DMCS, coated with 2% NaOH. For the column for the diaminobenzenes, 80/100 mesh was used, and for all other columns, 100/120 mesh was used.

be necessary to have a column which would completely resolve them. The 3-ft. column had 900 plates, and the number of plates calculated to give complete resolution of *m*-diaminobenzene and 2-aminobiphenyl was 8,400. This would have required a column 28 ft. in length which was considered not suitable for this case. Therefore, a 10-ft. column packed with 20% Triton X-305 on 80/100 mesh 2% NaOH loaded Chromosorb W (AW/DMCS) was prepared and tested. This column gave complete resolution of these two compounds. The calculated number of plates for the 10-ft. column was 4,100. A chromatogram of an aniline solution of the three diaminobenzenes and 2-aminobiphenyl on the 10-ft. column of 20% Triton X-305 is given in Fig. 1.

Since the Triton X-305 stationary phase proved satisfactory for the resolution of the three diaminobenzenes and 2-aminobiphenyl, the 3-ft. 15% Triton X-305 and

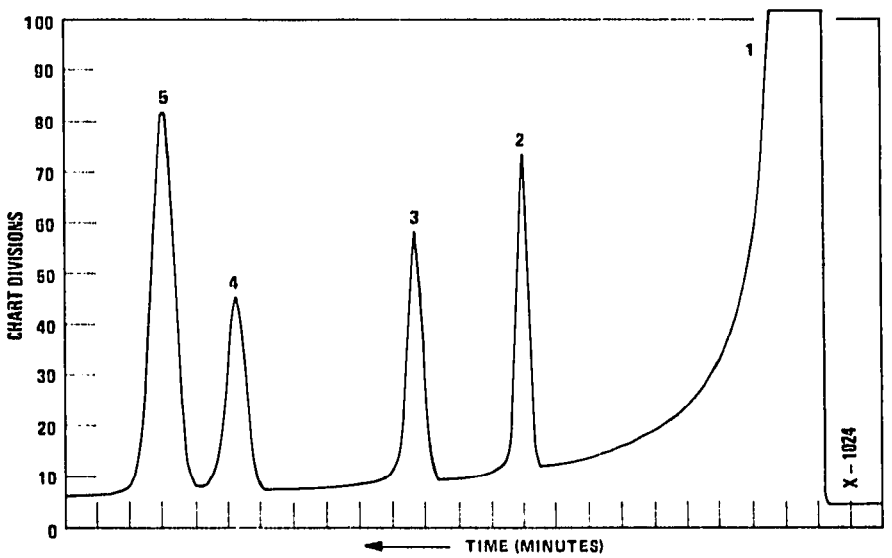

Fig. 1. Chromatogram of 3-μl sample of an aniline solution of the diaminobenzenes and 2-aminobiphenyl. Peaks with retention times: (1) aniline; (2) *o*-diaminobenzene, 12.0 min; (3) *p*-diaminobenzene, 15.3 min; (4) *m*-diaminobenzene, 20.7; (5) 2-aminobiphenyl, 22.9 min.

the 10-ft. 20% Triton X-305 were tried first for the separation of the three aminobiphenyls and diphenylamine. Neither of these columns proved satisfactory for the analysis of the isomeric aminobiphenyls and diphenylamine. The 3- and 4-aminobiphenyl peaks were broad and overlapped on both the 3- and 10-ft. columns. Also, the retention times were too long on the 10-ft. column. Columns of polyphenyl ether (six rings) and Silicone OV-22 (65% phenyl) were tested, and it was found that they did not offer any advantage over the Triton X-305 columns. Since the main objective was to obtain resolution of the 3- and 4-aminobiphenyls in a reasonable time, a 3-ft. 5% Triton X-305 column, using 80/100 mesh Chromosorb W, AW/DMCS with 2% NaOH, was prepared for testing. This column had 450 plates, and the number of plates calculated to give complete separation of 3- and 4-aminobiphenyl was 1,900. A 5-ft. 5% Triton X-305 column using 100/120 mesh Chromosorb W was prepared and tested. This column gave complete resolution of the 3- and 4-aminobiphenyl. Fig. 2 is a chromatogram of the three isomeric aminobiphenyls and diphenylamine on the

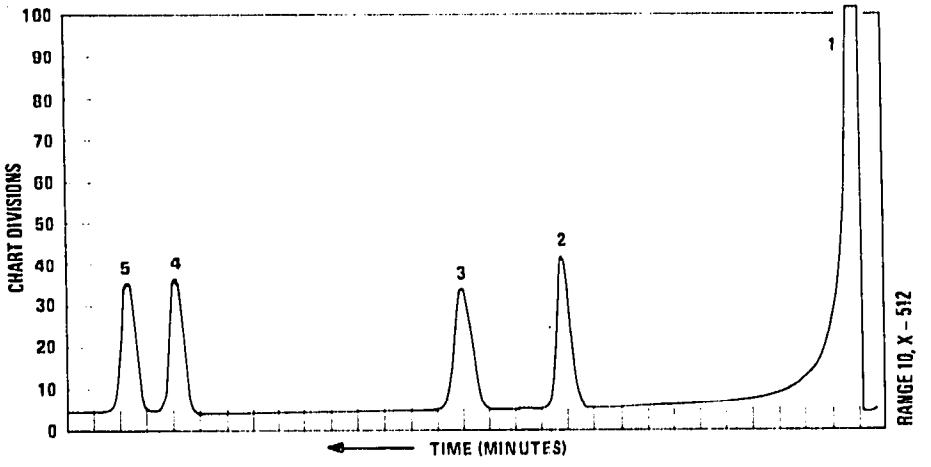

Fig. 2. Chromatogram of 3-μl sample of an aniline solution of the aminobiphenyls and diphenylamine. Peaks with retention times: (1) aniline; (2) 2-aminobiphenyl, 12.2 min; (3) diphenylamine, 16 min; (4) 3-aminobiphenyl, 26.9 min; (5) 4-aminobiphenyl, 28.7 min.

5-ft. 5% Triton X-305 column. On this column, the 2-aminobiphenyl and *m*-diaminobenzene, which are completely resolved on the 20% Triton X-305 10-ft. column, are not resolved. On some columns 2,2'-diaminobiphenyl has a retention time very close to that of 4-aminobiphenyl. However, it is completely resolved from 4-aminobiphenyl on this column with a retention time of 32.3 min for the conditions used for the chromatogram in Fig. 2.

It was found convenient to analyze the isomeric 2,2'-, 2,3'-, and 2,4'-diaminobiphenyls and the isomeric 2-, 3-, and 4-aminodiphenylamines as one group. The 2,2'-diaminobiphenyl and 2-aminodiphenylamine are easily resolved from the other four amino compounds. The major difficulty in analyzing for the 2,3'- and 2,4'-diaminobiphenyl and 3- and 4-aminodiphenylamine is the overlap of peaks on the various columns tested. Stationary phases initially tested and found unsatisfactory were

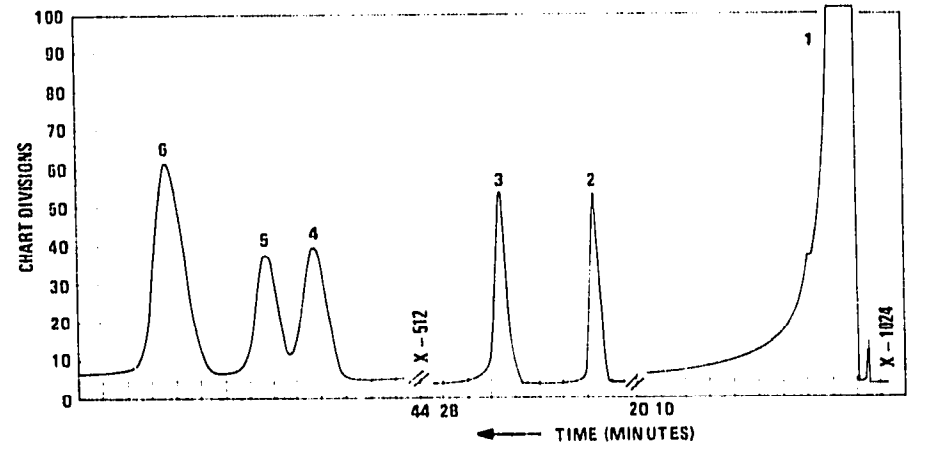

Fig. 3. Chromatogram of 3-μl sample of an aniline solution of the three isomeric aminodiphenylamines and of three of the isomeric diaminobiphenyls. Peaks with retention times: (1) aniline; (2) 2,2'-diaminobiphenyl, 21.6 min; (3) 2-aminodiphenylamine, 25.6 min; (4) 4-aminodiphenylamine, 48.3 min; (5) 2,3'-diaminobiphenyl, 50.3 min; (6) 2,4'-diaminobiphenyl and 3-aminodiphenylamine, 54.3 min.

polyphenyl ether (6 ring), OV-25 (a silicone with 75% phenyl), OV-210 (a trifluoropropyl silicone), and OV-225 (a cyanopropylphenyl silicone). The FFAP stationary phase was found to offer the best possibility of resolving this group of amino compounds. A 5-ft. column of 5% FFAP gave good peak shapes for the individual amino compounds of this group. The 2,3'-diaminobiphenyl and the 4-aminodiphenylamine were not completely resolved, and the 2,4'-diaminobiphenyl and 3-aminodiphenylamine had the same retention time. The 5-ft. column had 1,600 plates, and the number of plates required to resolve the 2,3'-diaminobiphenyl and the 4-aminodiphenylamine was 4,000. A 15-ft. column of 6% FFAP was prepared and tested. This column had 11,000 plates. Fig. 3 is a chromatogram of an aniline solution of the three isomeric aminodiphenylamines and the three isomeric diaminobiphenyls on the 15-ft. column of 6% FFAP. Peaks number 4 and 5 show that the 4-aminobiphenylamine and 2,3'-diaminobiphenyl are not completely resolved. Peak number 6 shows that no resolution of 2,4'-diaminobiphenyl and 3-aminodiphenylamine is obtained. The resolution of these two amines was the next objective. Some previous work with Versamid 900

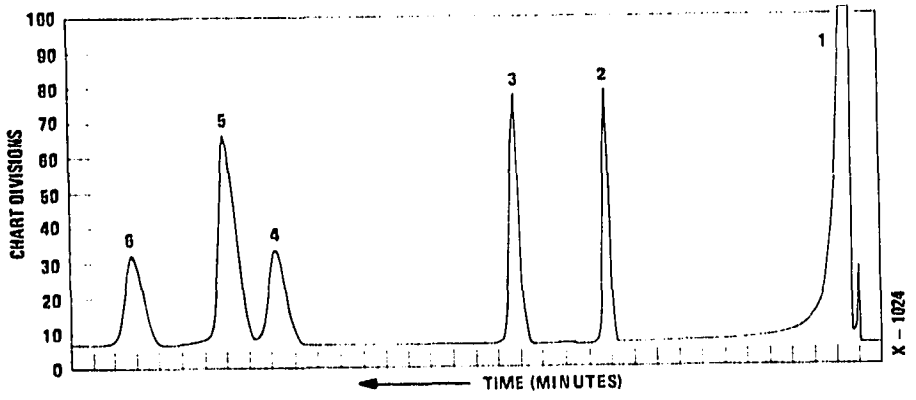

Fig. 4. Chromatogram of 3-μl sample of an aniline solution of the three isomeric aminodiphenylamines and of 2,2'-, 2,3'-, and 2,4'-diaminobiphenyl. Peaks with retention times: (1) aniline; (2) 2,2'-diaminobiphenyl, 13.1 min; (3) 2-aminodiphenylamine, 16.7 min; (4) 2,3'-diaminobiphenyl, 26.7 min; (5) 4-aminodiphenylamine and 2,4'-diaminobiphenyl, 29 min; (6) 3-aminodiphenylamine, 33.1 min.

indicated that this phase offered some possibilities for the resolution of 2,4'-diaminobiphenyl and 3-aminodiphenylamine, based on the retention times of 3- and 4-aminodiphenylamine and 2,4'-diaminobiphenyl. A new 10-ft. column of 6% Versamid 900 was prepared and tested. This column had 7,700 plates. Fig. 4 is a chromatogram of an aniline solution of the three aminodiphenylamines and the 2,2'-, 2,3'-, and 2,4'-diaminobiphenyl on the 10-ft. column of 6% Versamid 900. The 3-aminodiphenylamine is completely resolved from the 2,4'-diaminobiphenyl. However, the 4-aminodiphenylamine and 2,4'-diaminobiphenyl elute as one peak. In irradiated aniline, the yield of the radiolytic product 2,4'-diaminobiphenyl is obtained by difference.

The resolution of the isomeric 3,3'-, 3,4'-, and 4,4'-diaminobiphenyls from one another has presented a difficult problem, and no satisfactory solution has been found for the resolution of these amino compounds. A number of stationary phases were tested in an effort to find satisfactory conditions to resolve the three isomers. Of the stationary phases tested, the following phases gave good peak shapes for aniline

solutions of the individual isomers with reasonable retention times: polyphenyl ether (7 rings), Silicone OV-25 (75% phenyl), Mer-2 (a polyphenylpolyester), Versamid 900 and FFAP. The major difficulty in obtaining separation of these three isomers is that the retention times of the individual isomers are very close on the phases tested. The results with the 5-ft. column of 5% FFAP will illustrate the difficulty of resolving these three isomers. The retention times of the isomers on a 5-ft. 5% FFAP column at 250° were: 3,3'-diaminobiphenyl, 12 min; 4,4'-diaminobiphenyl, 13.3 min; and 3,4'-diaminobiphenyl, 13.5 min. A chromatogram of 3,3'-diaminobiphenyl in aniline is shown in Fig. 5, and a chromatogram of an aniline solution of 3,3'- and 3,4'-diaminobiphenyl, in Fig. 6. The chromatograms in Figs. 5 and 6 were obtained with the 5-ft 5% FFAP column. The 5-ft. 5% FFAP column had 2,300 plates. The number of

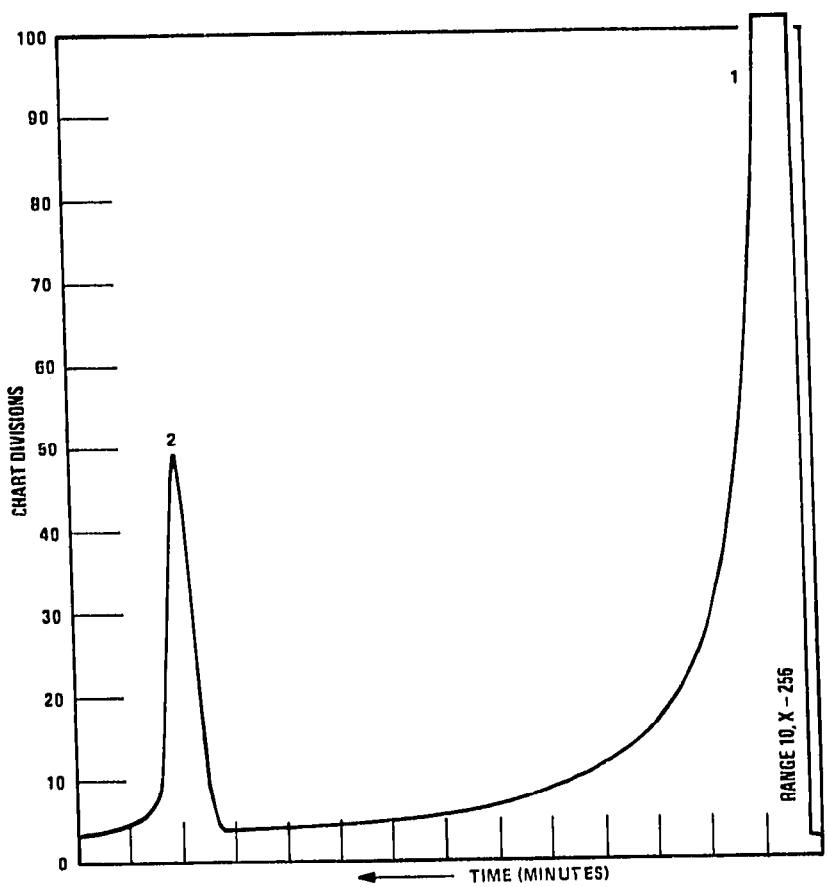

Fig. 5. Chromatogram of 3-μl sample of an aniline solution of 3,3'-diaminobiphenyl; retention time, 12 min.

calculated plates that would be required to resolve 3,4'- and 4,4'-diaminobiphenyl is 73,000. Based on the number of plates in the 5-ft. column, this would require a column 228 ft. in length which is not a practical solution. Additional work is being done in an effort to find satisfactory gas chromatographic conditions for the resolution of 3,3'-, 3,4'-, and 4,4'-diaminobiphenyl.

In addition to the conditions given above for the analysis of the isomeric diaminobenzenes, these amines can be resolved with very sharp peaks on a 15-ft. 6%

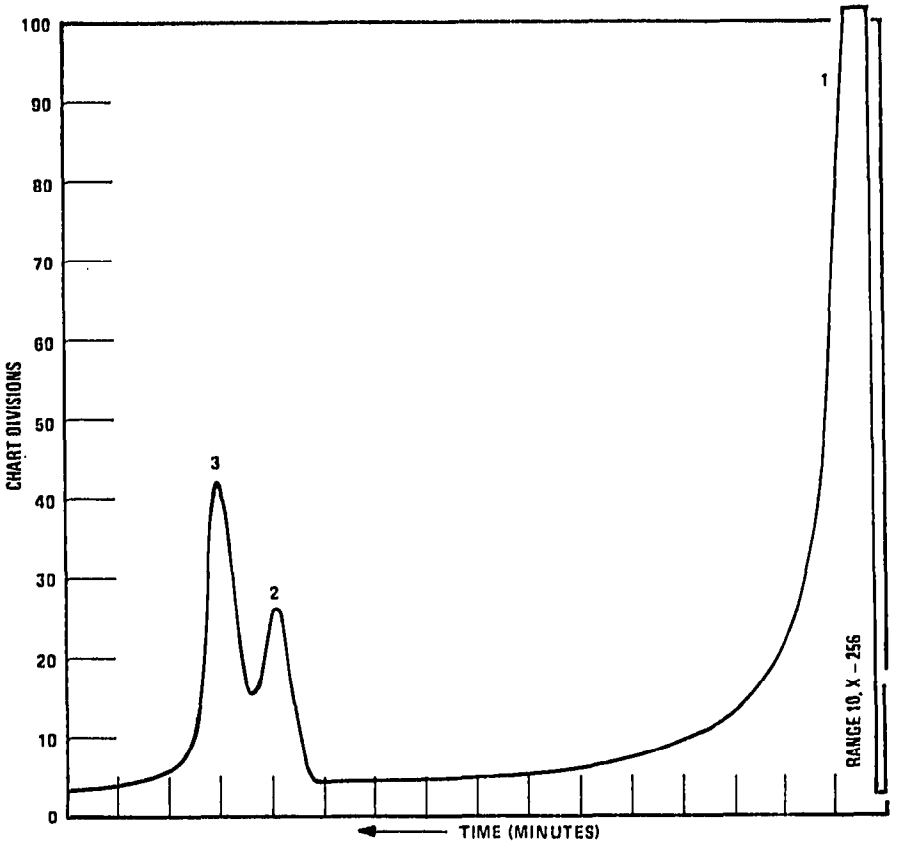

Fig. 6. Chromatogram of 3-μl sample of an aniline solution of 3,3'- and 3,4'-diaminobiphenyl. Peaks with retention times: (2) 3,3'-diaminobiphenyl, 12 min; (3) 3,4'-diaminobiphenyl, 13 min.

FFAP column at 230°. The retention times were: *o*-diaminobenzene, 7.7 min; *p*-diaminobenzene, 9.5 min; and *m*-diaminobenzene, 12.7 min. *m*-Diaminobenzene and 2-aminobiphenyl, however, overlap on this column under these conditions. Also, the isomeric aminobiphenyls and diphenylamine can be resolved with excellent peaks on a 15-ft. 6% FFAP column at 240°. The retention times were: 2-aminobiphenyl, 9.9 min; diphenylamine, 11.2 min; 3-aminobiphenyl, 22.9 min; and 4-aminobiphenyl, 25.4 min.

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REFERENCES

1 W. H. Bryan, *Anal. Chem.*, 36 (1964) 2025.
2 J. A. Knight, *J. Chromatogr.*, 48 (1970) 526.
3 A. W. Decora and G. U. Dineen, in H. J. Noebels, R. F. Wall and N. Brenner (Editors), *Gas Chromatography*, Academic Press, New York, 1961, p. 33.
4 E. D. Smith and R. D. Radford, *Anal. Chem.*, 33 (1961) 1161.
5 C. Horváth, in L. S. Ettre and A. Zlatkis (Editors), *The Practice of Gas Chromatography*, Interscience Publishers, New York, 1967, pp. 129–238.