

CHROM. 6642

## Note

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### Gas chromatographic conditions for the analysis of $\gamma$ -irradiated benzonitrile for cyanoaromatic products

In a study of the  $\gamma$ -radiolysis of benzonitrile, the three isomeric dicyanobenzenes, the three isomeric cyanobiphenyls, and the six isomeric dicyanobiphenyls (one cyano group per phenyl ring) were expected as radiolytic products, and hence, it was necessary to be able to analyze the  $\gamma$ -irradiated benzonitrile for these cyanoaromatic compounds. A search of the literature did not reveal any information on specific conditions for the analysis of these compounds, and this paper describes the gas chromatographic (GC) conditions for the analysis of the cyanoaromatic compounds listed above.

#### *Experimental*

*Materials.* The following cyanoaromatic compounds were available commercially: 1,2-, 1,3-, and 1,4-dicyanobenzene and 4-cyanobiphenyl. The 2- and 3-cyanobiphenyl and the isomeric dicyanobiphenyls (except the 2,2' isomer) were prepared by the Sandmeyer method from the corresponding amino- or diamino-biphenyl. The 2,2'-dicyanobiphenyl was prepared from the corresponding dicarboxylic acid by converting the 2,2'-diacid to the diacid chloride, which was converted to the diamide. The diamide was dehydrated to the 2,2'-dicyanobiphenyl. All of the cyanoaromatic compounds were recrystallized to obtain satisfactory melting points. Stationary phases and packings were obtained from various GC suppliers.

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

*Column preparation.* Both Chromosorb P and Chromosorb W, which were acid washed and DMCS-treated, were utilized as inert packings. The packings of the individual stationary phases were prepared as described previously<sup>1,2</sup>.

*Samples.* Standard dilute solutions of the various cyano and dicyano compounds in benzonitrile were prepared and used for the different analyses on the test columns. The benzonitrile was purified by fractional distillation at reduced pressure and tested for impurities by GC analysis.

#### *Results and discussion*

In an investigation of the radiation chemistry of benzonitrile, the three dicyanobenzenes, the three cyanobiphenyls, and the six dicyanobiphenyls (one cyano group per phenyl ring) were considered very likely to be some of the major radiolytic products. GC offered the best analytical method for analyzing the irradiated benzonitrile, both qualitatively and quantitatively, for the expected radiolytic products. The concentrations of the cyanoaromatic radiolytic products in the irradiated benzonitrile were in the range of approximately  $4 \times 10^{-7}$  to  $3 \times 10^{-6}$  moles/ml.

In considering stationary phases for testing, the upper temperature limit and

polarity were two of the major factors that were considered. A number of columns with different stationary phases were selected for initial screening from those on hand which represented a range of polarities and had upper temperature limits from 200° to 275°. The stationary phases tested with the upper temperature in parenthesis were silicone DC 710 (225°), Versamid 900 (275°), Ucon LB-550X (200°), polyphenyl ether (6 rings) (250°), silicone OV-210 (275°), Triton X-305 (200°), FFAP (250°), and Mer 2 (250°). The stationary phases are listed in order of increasing polarity as reported by McREYNOLDS<sup>3</sup> with one exception. McREYNOLDS reported data for Versamids 930 and 940, which were almost identical. Since the Versamid phases are very similar chemically, the assumption was made that the relative polarity of Versamid 900 would be in the same range as Versamids 930 and 940. The equations used to calculate the number of theoretical plates for a column and the number of plates required to effect a given separation have been reported by HORVATH<sup>4</sup>.

The decision was made to test the stationary phases listed above with the columns on hand utilizing the dicyanobenzenes, which were available commercially. From this preliminary screening, the stationary phases which offered the greatest promise were Versamid 900, Ucon LB-550X, and polyphenyl ether (6 rings). Versamid 900 was selected for additional testing because of the higher temperature limit which would be required for the dicyanobiphenyls. Columns with Chromosorb P and W (each acid washed and DMCS-treated) were tested, and the results with dicyanobenzenes were better with Chromosorb P. From the preliminary screening and testing, calculations indicated that a 10 ft. × 1/8 in. column containing 10% Versamid 900 on 80-100 mesh Chromosorb P (AW/DMCS) should be tested. This column gave good results with the test mixture of the three isomeric dicyanobenzenes. Complete baseline resolution of the 1,4- and 1,3-dicyanobenzenes was not obtained due to the slight tailing of these peaks. A typical chromatogram of the dicyanobenzenes is given in Fig. 1.

Some preliminary testing for the analysis of the cyanobiphenyls was carried out with the Versamid 900 columns on hand and with the 10% Versamid 900 column which was suitable for the analysis of the dicyanobenzenes. From this preliminary work, calculations indicated that a 10 ft. × 1/8 in. column containing 5% Versamid 900 on 80-100 mesh Chromosorb P (AW/DMCS) should be tested. This column gave good results with the test mixture of the three isomeric cyanobiphenyls. Essentially baseline resolution was obtained with the 3- and 4-cyanobiphenyls. A typical chromatogram of the cyanobiphenyls is given in Fig. 2.

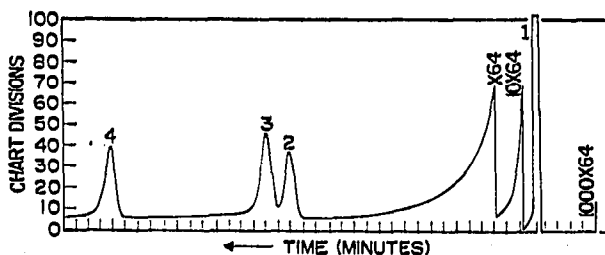


Fig. 1. Chromatogram of a 3- $\mu$ l sample of a benzonitrile solution of the dicyanobenzenes. Peaks are: (1) benzonitrile; (2) 1,4-dicyanobenzene; (3) 1,3-dicyanobenzene; (4) 1,2-dicyanobenzene.

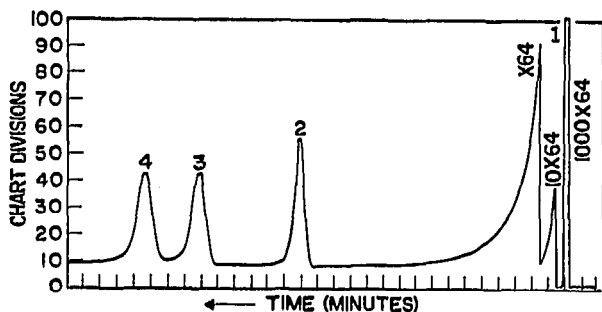


Fig. 2. Chromatogram of a 3- $\mu$ l sample of a benzonitrile solution of the cyanobiphenyls. Peaks are: (1) benzonitrile; (2) 2-cyanobiphenyl; (3) 3-cyanobiphenyl; (4) 4-cyanobiphenyl.

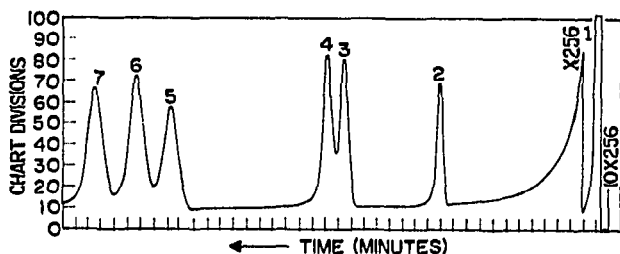


Fig. 3. Chromatogram of a 3- $\mu$ l sample of a benzonitrile solution of the dicyanobiphenyls. Peaks are: (1) benzonitrile; (2) 2,2'-dicyanobiphenyl; (3) 2,3'-dicyanobiphenyl; (4) 2,4'-dicyanobiphenyl; (5) 3,3'-dicyanobiphenyl; (6) 3,4'-dicyanobiphenyl; and (7) 4,4'-dicyanobiphenyl.

Preliminary testing for the GC analysis of the six isomeric dicyanobiphenyls showed that Chromosorb W would be preferable to Chromosorb P. Calculations from the data obtained with a 10 ft. 5% Versamid 900 column and a 10-ft. 8% Versamid 900 column indicated that a 7.5 ft. 8% Versamid column should be tested. This column gave good results with a test mixture of the six isomeric dicyanobiphenyls with a complete analysis of the dicyanobiphenyls requiring approximately 45 min. A typical chromatogram of the dicyanobiphenyls is given in Fig. 3. Additional

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

Compound group	Coating type	Inert packing	Coating (%)	Column length (ft.)	Temperature ( $^{\circ}$ C)
Dicyanobenzenes	Versamid 900	Chromosorb P, AW/DMCS, 80-100 mesh	10	10	180 $^{\circ}$ for 20 min; programmed to 200 $^{\circ}$ at 2 $^{\circ}$ /min
Cyanobiphenyls	Versamid 900	Chromosorb P, AW/DMCS, 80-100 mesh	5	10	205 $^{\circ}$
Dicyanobiphenyls	Versamid 900	Chromosorb W, AW/DMCS, 100-120-mesh	8	7.5	235 $^{\circ}$

work with other Versamid 900 columns in an effort to improve the resolution of the 2,3'- and 2,4'-dicyanobiphenyls and of the 3,3'-, 3,4'-, and 4,4'-dicyanobiphenyls did not produce any improvement in resolution. The GC conditions that were found to be most satisfactory for the analysis of the test solutions of the dicyanobenzenes, cyanobiphenyls, and the dicyanobiphenyls are given in Table I.

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