

GAS CHROMATOGRAPHIC ANALYSIS OF ALIPHATIC
NITRILES IN AQUEOUS ACIDIC SOLUTION

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INTRODUCTION

Gas chromatography has proved very successful in the analysis of a great variety of organic mixtures. For aqueous solutions, however, separation of the components has been found difficult because of excessive tailing of the water with the stationary phase¹.

Several authors have dealt with this problem in different ways. Suffis and Dean² used non-aqueous extraction prior to injection into the chromatograph and were thus able to separate alcohols from aqueous solutions. Bodner and Mayeux³ analysed only low-boiling compounds which were eluted before the water. For higher boiling compounds Hunter and Ortegren⁴ designed a special combustion tube for oxidizing the fractions emerging from the column. The mixture was absorbed by magnesium perchlorate and the dry carbon dioxide was measured in thermal conductivity cells. The water content in these experiments was up to 50%. An ingenious method was devised by Kung *et al.*¹ who injected the aqueous solution into a calcium carbide precolumn, thus converting all the water into acetylene. By this method they were able to obtain good results with mixtures of alcohols, aldehydes and esters.

In the present work, it was necessary to determine different nitriles in aqueous acidic solutions in the presence of KCl. One method used was the extraction of the nitriles with *o*-dichlorobenzene prior to injection into the column. Results obtained when using this procedure showed that extraction of the nitriles was not complete unless large volume ratios of solvent-aqueous phase were employed. The final stock solutions were too dilute, thus reducing the accuracy of the method.

In this work, a simple method is presented which proved successful in the case of nitriles, and could probably be generalized to some other aqueous solutions. The method involves addition of a five-fold excess of solvent to the aqueous solution, and subsequent dehydration of the mixture with anhydrous Na₂SO₄. The dry organic solution was then injected into the column. It is possible that in some mixtures preferential adsorption of some of the components might take place; this effect is, however, diminished when a good solvent for the organic components is used. It will be shown in the experimental results that no preferential adsorption takes place in the case of the nitriles used in this work.

EXPERIMENTAL

Apparatus

A gas chromatograph Aerograph Model A 350 with a hot wire detector and a 2-m 6 mm i.d. copper spiral column packed with diethylene glycol polyester adipate (LAC-2-R-466, Cambridge, Ind.) and 2% H_3PO_4 on Chromosorb W (25:100, by weight) 30-60 mesh⁵, were used.

Procedure

Mixtures of known composition of nitriles were dissolved in aqueous HCl saturated with respect to KCl. The total nitrile concentration was approximately 15% w/w. 10.25 c.c. of the solution were added to a fivefold excess of *o*-dichlorobenzene* in which about 50 g of anhydrous Na_2SO_4 were present. The mixture was shaken for 5 min until the aqueous phase disappeared and the organic phase was perfectly clear. The solution was filtered and 10-15 μ l injected into the chromatograph.

When monobasic nitriles were analysed, the temperature of the column was kept at 70°, while for the dibasic nitriles the temperature was 220°.

For mixtures of mono- and dibasic nitriles the column was programmed starting at 70°, and raised at the rate of 10° per minute up to 220°.

Elution took place in the following order: acrylo-, propio-, butyronitrile, *o*-dichlorobenzene, succino- and adiponitriles. No trace of water peak was detected when using this procedure.

RESULTS AND DISCUSSION

The results are presented in Table I and a characteristic chromatogram of a mixture of mono- and dibasic nitriles is shown in Fig. 1. The amounts were estimated by measuring the areas under the peaks and it was assumed that the concentration of any nitrile was proportional to its peak area.

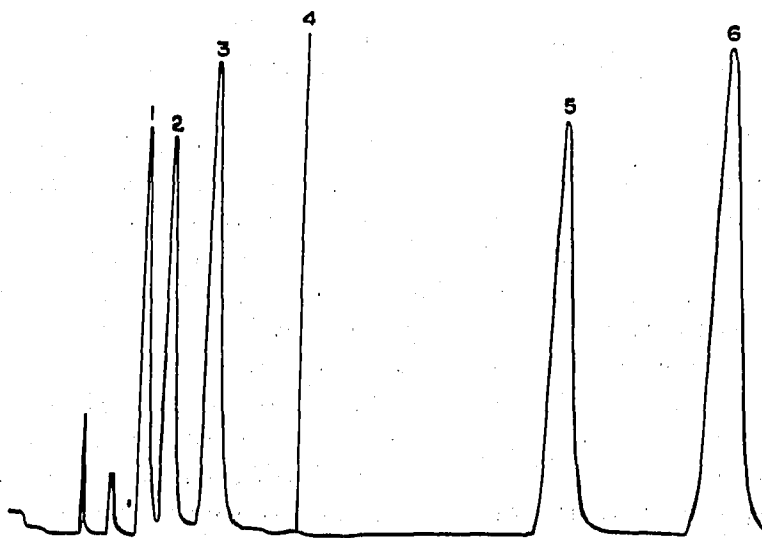


Fig. 1. Chromatogram of a mixture of mono- and dibasic nitriles. (1) Acrylonitrile; (2) propionitrile; (3) butyronitrile; (4) *o*-dichlorobenzene (solvent); (5) succinonitrile; (6) adiponitrile.

* When monobasic nitriles are not present, chloroform may be used as solvent.

TABLE I

No.	Acrylonitrile			Propionitrile			Butyronitrile			Succinonitrile			Adiponitrile		
	% weight taken	% area found	% deviation	% weight taken	% area found	% deviation	% weight taken	% area found	% deviation	% weight taken	% area found	% deviation	% weight taken	% area found	% deviation
1	36.5	35.6	-3.0	37.0	36.1	-3.0	27.0	28.3	+4.3	48.4	47.8	-1.2	51.6	52.2	+1.2
2	31.6	29.6	-6.3	40.1	41.5	+3.7	28.3	29.0	+2.5	36.1	34.8	-3.6	63.9	65.2	+2.0
3	44.2	41.3	-2.5	21.5	22.6	+5.1	34.3	36.1	+5.2	31.0	30.2	-2.6	69.0	69.8	+1.2
4	55.2	55.6	+0.7	11.8	12.5	+5.9	33.0	31.9	-3.3	31.3	29.0	-7.3	68.7	71.0	+3.3
5	60.1	59.4	-1.1	8.6	9.2	+6.9	31.3	31.4	+0.3	14.5	15.0	+3.4	85.5	85.0	-0.6
6															
7															
8															
9															
10															
11	25.0	24.3	-2.8	50.0	49.4	-1.2	25.0	26.2	+5.0	50.0	48.6	-2.8	50.0	50.7	+1.4
12	33.3	34.2	+2.7	33.3	33.7	+1.3	33.3	32.1	-3.4	50.0	52.1	+4.2	50.0	47.2	-5.6
13	33.3	32.5	-2.4	33.3	34.8	+4.2	33.3	32.6	-2.7	50.0	50.8	+1.6	50.0	48.9	-2.2
14	18.8	18.8	0	50.0	49.6	-0.8	31.3	32.5	+3.8	47.5	48.8	+2.7	52.5	51.1	-2.7
15	6.2	6.9	+10.4	62.5	61.0	-2.4	31.3	32.2	+3.2	50.0	49.5	-1.0	50.0	50.5	+1.0
16	10.0	9.8	-7.0	40.0	38.9	-2.8	50.0	51.9	+3.8	50.0	50.5	+1.0	50.0	49.5	-1.0
17	42.8	45.1	+5.3	28.6	28.3	+1.6	28.6	26.4	-7.5	50.0	48.8	-2.4	50.0	51.2	+2.4
18	33.3	33.3	0	33.3	32.3	-3.0	33.3	34.5	+3.6	50.0	50.5	+1.0	50.0	49.5	-1.0
19	50.0	51.8	+3.2	16.7	14.6	-12.8	33.3	33.9	+1.8	28.6	30.8	+9.4	71.4	69.2	-3.1

In experiments in which all the above-mentioned nitriles were analysed together (Nos. 11-19, Table I) the amounts of mono- and dibasic nitriles were calculated on the assumption that each class of nitriles constitutes a 100 % total. An attempt to treat the total area under all peaks as a total of 100 % resulted in poor accuracy in the determination of the separate constituents of the mixture.

It was shown in separate experiments that HCl remained with the Na_2SO_4 phase and did not interfere in the chromatographic analysis. From the results in Table I it can be seen that the individual nitriles can be determined quantitatively with an average error of between 2 and 4 %.

SUMMARY

A mixture of acrylo-, propio-, butyro-, succino- and adiponitriles in aqueous solution in the presence of HCl and KCl was analysed by gas chromatography. The method involved extraction with *o*-dichlorobenzene and drying over anhydrous Na_2SO_4 prior to injection into the chromatographic column. No adverse effect of the drying agent was detected. The same method of drying aqueous solutions for chromatographic analysis could be extended to other systems.

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