

OBSERVATIONS ON THE GAS CHROMATOGRAPHIC ANALYSIS OF AQUEOUS ALCOHOLS

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(Received January 10th, 1962)

The gas chromatographic analysis of aqueous solutions is difficult due to the very bad tailing of the water peak produced by adsorption on the support¹. This limits the analysis to those materials which emerge before water, the tailing also necessitating long recovery times².

Various techniques have been developed to circumvent this difficulty, although no simple procedure of directly determining water and organic materials in the presence of each other could be found in the literature. Highly polar stationary phases such as glycerol²⁻⁸, diglycerol^{2,8} and triethanolamine⁵ have been used to increase the retention time of water, thereby increasing the boiling range of organic materials which can be separated, although water still tails badly on these columns. Such polar stationary phases show very poor separating powers for alcohols² and are usually used in combination with other liquids such as polyethylene glycols² or tritolyl phosphate³. Sample conversion^{5,9-13} and support deactivation¹⁴⁻¹⁶ have also been used to overcome these difficulties. Some of these various techniques proposed to prevent or circumvent tailing of polar materials have been examined for their effectiveness in preventing tailing of water. None of the methods examined proved to be applicable.

Silvering the support, a technique applied by ORMEROD AND SCOTT¹⁸ proved tedious and unsuccessful. Only 25 % of the silver used was actually deposited on the support (Chromosorb), representing 30 % of the support weight. With this support no reduction in the tailing of the water peak was observed with dioctyl phthalate as stationary phase.

In an attempt to increase the amount of silver on the support another coating method was used. The support (Chromosorb) was coated with silver nitrate and then heated to 700° to decompose the silver nitrate into metallic silver. Microscopic examination revealed silver globules—even with a second batch which had been heated above the melting point of silver. Neither of these two supports showed any reduction in tailing of the water peak with di-(2-ethylhexyl) sebacate as stationary phase. It would appear that the silver did not wet the support, so that the coat of silver was at best patchy.

Coating Chromosorb with polystyrene also proved to be of no help.

Powdered polyethylene has been successfully used to separate water-methanol mixtures¹⁹, tailing of the water peak being almost completely eliminated. Polyethylene and polypropylene have also been reported as satisfactory stationary phases for the separation of alcohols and other materials²⁰. A column of 1 % paraffin oil on 60-80 mesh polypropylene at 120° showed almost no tailing of the water peak. Unfortunately

after only a few hours the column deteriorated, the packing apparently having sintered in spite of the fact that it was 30° below its softening temperature (stated to be 150°). This support is probably useful at lower temperatures, but was not suitable for the present work as it was desired to work with alcohols up to C_6 . Teflon powder has been reported to prevent tailing²¹.

Stationary phases examined for their separating efficiency for alcohols were Armeen 18D (octadecylamine)²², Carbowax 1540, cetyl alcohol and di-(2-ethylhexyl) sebacate^{23, 24}. Of these the last mentioned gave the best separation of the lower alcohols. Octadecanol has been used at 60° for aqueous alcohols²⁵ and although cetyl alcohol (hexadecanol) gave good separations at 100° the stationary phase was lost rapidly from the column.

SWOBODA² used a dual column of diglycerol and polyethylene glycol 400, the water being back-flushed after emerging from the diglycerol column. By this technique alcohols up to 2-octanol could be separated from water.

The work reported here is similar in principal to that of SWOBODA, sorbitol being used to retain the water, although a dual column with back flushing is not involved. Sorbitol has been used as a mixed stationary phase with Carbowax 1540 to separate cyclohexanol and toluene²⁶. Sorbitol has also been suggested as a water retardant by SCHMAUCH AND DINERSTEIN²⁷. However, as sorbitol alone showed poor resolution for the lower alcohols, it was used in combination with di-(2-ethylhexyl) sebacate.

The column was a 2 m \times 0.25 in. o.d. copper tube packed with Chromosorb (acid washed) 30-60 mesh, coated with 35 % of its weight of a 2.5:1 mixture of sorbitol-di-(2-ethylhexyl) sebacate. This mixture was deposited on the support from a methanol solution. The column was operated at 120° at an inlet pressure of 200 mm of mercury above atmospheric pressure.

Under these conditions, alcohols were separated purely by boiling point differences; a plot of the logarithm of the retention times *versus* boiling points produced a straight line. Methanol deviated from the line having a longer retention time than that to be expected from its boiling point. This is probably caused by its high polarity, which may also be the reason why this is the only alcohol which showed any tailing. The retention time of water was sufficiently long to allow the prior emergence of all alcohols boiling below 155° , that is up to *n*-hexanol. The retention time of water relative to the alcohols could be varied by altering the sorbitol-di-(2-ethylhexyl) sebacate ratio.

This column showed no selectivity towards any particular type of alcohol. The following types of alcohols were examined and all obeyed the same boiling point retention time relation: normal primary, normal secondary, isoprimary, isosecondary, tertiary, cyclics such as cyclohexanol, furfuryl and benzyl alcohol and difunctionals such as methylbutenol, methylbutynol and methyl-hydroxy-butanone. Other materials such as benzene, butyl chloride, acetone and dioxane did not obey this relation although acetylacetone did do so.

The column had 550 plates for *n*-butanol and did not effect separations between close boiling isomers such as isoamyl alcohol and active amyl alcohol.

The detection limit for the lower alcohols was found to be 0.1 % (in water) for a 5 μ l sample with a katharometer detector. The detection limit for water (in alcoholic solution) under the same conditions was about 10 %. The water peak showed bad tailing.

This technique has been applied to qualitative analysis and also to the determination of relative amounts of several alcohols in aqueous solutions. It could not be applied directly to quantitative determinations because of the tailing of the water

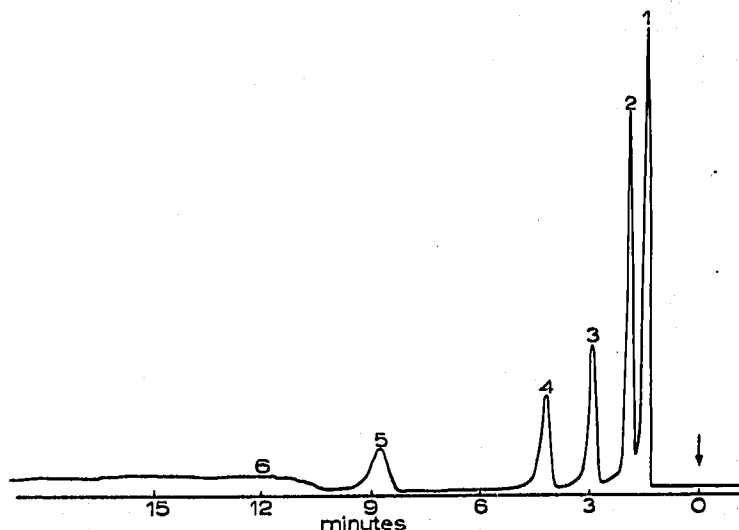


Fig. 1. Chromatogram of lower alcohols and water mixture. Conditions: Column 200 cm \times 0.25 in., 35% 2.5:1 sorbitol-di-(2-ethylhexyl) sebacate on Chromosorb 30-60 mesh at 120°. Inlet pressure 960 mm, outlet pressure 760 mm (atmospheric). Sample 5 μ l. (1) Ethyl alcohol; (2) *n*-propyl alcohol; (3) *n*-butyl alcohol; (4) isoamyl alcohol and active amyl alcohol; (5) *n*-hexyl alcohol; (6) water—low peak due to extreme tailing.

peak, but this may be made possible by employing an internal standard, the water concentration being obtained by difference. Fig. 1 is a chromatogram of an aqueous solution of some of the lower alcohols.

Attempts to use this column for the lower fatty acids failed as water peaks were obtained indicating reaction with the sorbitol.

ACKNOWLEDGEMENT

We are indebted to the Israel Mining Industries for permission to publish this work.

SUMMARY

The qualitative analysis of aqueous alcoholic solutions has been performed by gas chromatography using a mixed stationary phase of sorbitol and di-(2-ethylhexyl) sebacate. Alcohols containing up to six carbon atoms were eluted prior to the water peak.

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