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# Analysis of Aqueous Mixtures by Gas Chromatography

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The utilization of some liquids as stationary phases in the analysis of various water-containing mixtures by gas liquid partition chromatography is described and examples given of the separations obtained. The application of the method to quantitative analysis is discussed.

Because of the rapidity with which water can be determined using gas-liquid partition chromatography (GLPC), this method has received considerable attention recently. In order to get good results, the liquid phase should preferably be able to dissolve some of the water. A too high solubility, however, is unsuitable because it results in long elution times. Examples of stationary phases previously used with success are polyethylene glycols [1,2] and a mixture of glycerol and tricresyl phosphate [3]. Data for the columns employed in this work and recommendations for their use are summarized in Table 1.

*Polyethylene glycols.* In the previous investigations [1,2] polyethylene glycols with an average molecular weight of 600 were used. Here, polymers with an average molecular weight of 200 and 400 were tried. There does not seem to be any special advantage in using the higher polymer since the thermal stability diminishes with increasing molecular weight and the vapour pressure of the lower ones is small enough to permit operation at 100°C for long periods. Fig. 1 shows the separation of an aqueous alcoholic mixture on column No. 1. As can be seen, the water band interferes with the *n*-butyl alcohol band. Water travels relatively more rapidly than the alcohols on polyethylene glycol 400 and this causes it to interfere, on column No. 2, with the *n*-propyl alcohol band as well as with the *n*-butyl alcohol band. The separation of an aqueous aldehydic mixture using column No. 1 is shown in Fig. 2. On all columns which are recommended for aldehydes (*cf.* Table 1), formaldehyde travels more slowly than acetaldehyde in spite of its lower boiling point. Obviously the hydrogen bonding forces are responsible for this effect. Examples of the separation of aqueous mixtures of ketones and aqueous mixtures of acids using polyethylene glycols as stationary phases are given in Figs. 3 and 4. The separation of the components in technical diethyl ether using 1 m of column No. 1 and 1 m of column No. 2 in series is shown in Fig. 5. Since this work was completed, Bodnar and Mayeux [4] have reported the use of

*Table 1.* Columns for the gas chromatographic analysis of aqueous mixtures.

| Column No. | Stationary phase (wt %) | Column length (m) | Carrier | The column is recommended for the determination of water in | Approximate elution time (min) of water at 100°C and a flow of 50 ml He/min. |
|---|---|---|---|---|---|
| 1 | Polyethylene glycol (aver. mol. wt 200) (20 %) | 1 | Celite 545 * | Alcohols, ethers, aldehydes, ketones, fatty acids, amines | 3.5 |
| 2 | Polyethylene glycol (aver. mol.wt 400) (20 %) | 1 | Celite 545 * | The same compounds as for column No. 1 | 2 |
| 3 | Glycerol (10 %) plus tricresyl phosphate (10 %) | 1 | Silocel, C22 ** | Alcohols, ethers, aldehydes, ketones | 6.5 |
| 4 | Diglycerol (20 %) $[CH_2(OH)CH(OH)CH_2]_2O$ | 1 | Celite 545 * | The same compounds as for column No. 3 | 5 |
| 5 | Hexantriol (2,4-dihydroxy-3-hydroxymethylpentane) (20 %) | 1 | Celite 545 * | The same compounds as for column No. 3 | 3 |
| 6 | Triethanolamine (20 %) | 1 | Celite 545 * | Alcohols, ethers, formaldehyde, ketones, amines | 5.5 |
| 7 | Tween 80 (polyoxyethylene sorbitan monooleate) (20 %) | 1 | Celite 545 * | Alcohols, ethers, ketones, fatty acids | 1.5 |
| 8 | Tween 80 (5 %) | 2 | Celite 545 * | Fatty acids | 1 *** |
| 9 | Glycerol monooleate (20 %) | 1 | Chromosorb** | Fatty acids | 1.5 *** |

* 60—100 mesh.
** 30—60 mesh.
*** 100°C, 100 ml He/min.

polyethylene glycol 400 and triethylene glycol for the analysis of aqueous mixtures.

*Glycerol/tricresyl phosphate.* Browning and Watts [3] recommended the use of a stationary phase containing 40 % by weight of glycerol and 26 % by weight of tricresyl phosphate on 34 % by weight of Celite for the analysis of aqueous mixtures. This composition was tried in this laboratory but it was found to be not specially satisfactory. The high liquid content makes the carrier greasy and difficult to pack evenly in the column. Furthermore, high gas velocities are necessary in order to complete the analysis in a reasonable time. However, by diminishing the liquid content to 10 % by weight of glycerol and 10 % by weight of tricresyl phosphate applied on 80 % by weight

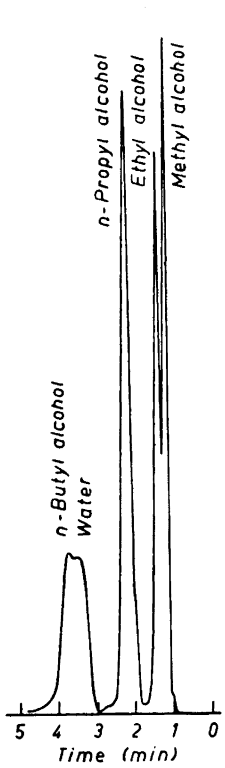


*Fig. 1.* Water-alcohol mixture. Column No. 1. Temperature 100°C. Flow of He 50 ml/min.

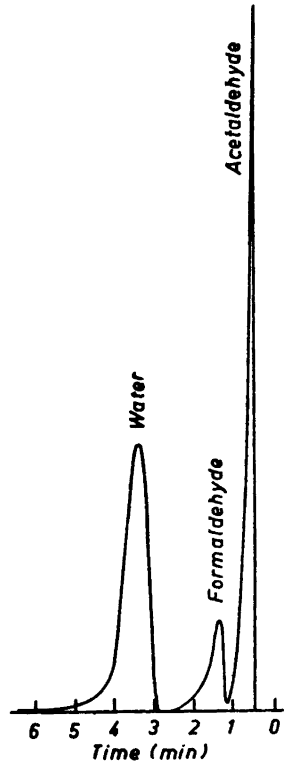


*Fig. 2.* Water-aldehyde mixture. Column No 1. Temperature 100°C. Flow of He 50 ml/min.

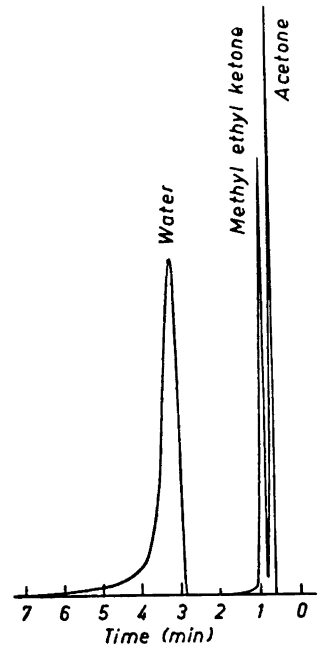


*Fig. 3.* Water-ketone mixture. Column No. 1. Temperature 100°C. Flow of He 50 ml/min.

of Silocel, an easily packed, dry powder with a good separating power was obtained. Because of the relatively long retention time for water on this column (No. 3), it can be used to determine water in all the lower alcohols, including all the $C_4$-alcohols.

*Diglycerol.* The performance of column No. 4 was similar to that of No. 3. The lower alcohols appeared a good distance before the water band. The selectivity of this column for the lower alcohols was low. Thus, methyl, ethyl and *n*-propyl alcohol were not separated but gave instead only one peak. The good thermostability and low volatility of this stationary phase make it very suitable for use in series analyses extending over long periods.

*Hexantriol.* Water and *n*-propyl alcohol appeared in the same place when using this column.

*Triethanolamine.* According to Harvey and Chalkley [5], triethanolamine is unsuitable as a stationary phase for the analysis of aqueous mixtures. This

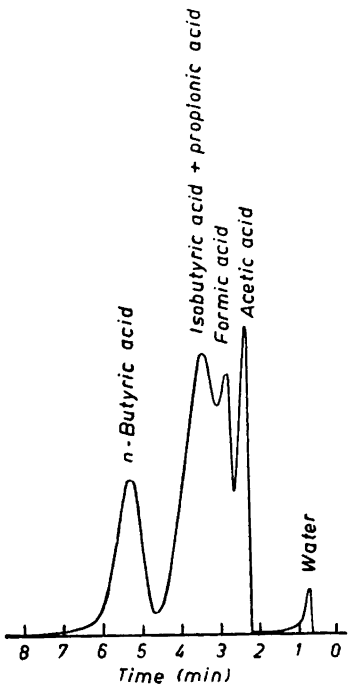


*Fig. 4.* Water-fatty acid mixture. Column No. 2. Temperature 128°C. Flow of He 60 ml/min.

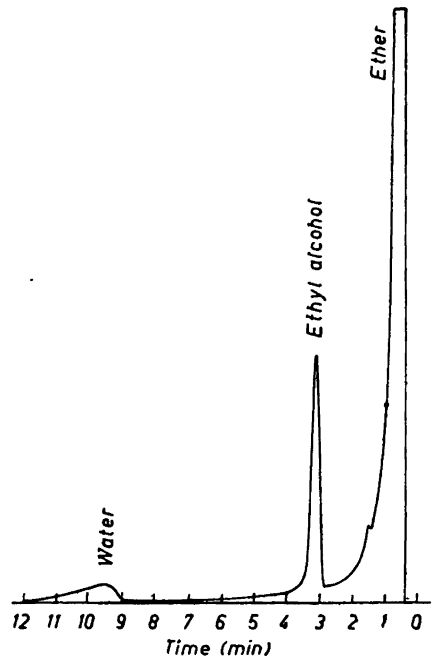


*Fig. 5.* Industrial diethyl ether. Column No. 1 plus column No. 2. Temperature 75°C. Flow of He 100 ml/min.

point of view seems to result from the use of too large a percentage of liquid on the carrier and the use of conditions favouring long retention times. By using 20 % by weight of liquid on Celite and changing the operating conditions, it was found that triethanolamine could be used for the determination of water in all the lower alcohols and in ketones, amines and ethers.

*Tween 80.* Water was eluted rapidly from column No. 7 (*cf.* Table 1). This column seems to be well suited for the determination of small amounts of low boiling alcohols or ketones in aqueous solution (*cf.* Fig. 6). Column No. 8, where the liquid content is diminished to 5 % by weight and the length of the column increased to 2 m, is suitable for the determination of water in the lower fatty acids (*cf.* Fig. 7). If the separation of formic and acetic acid is unnecessary, then a 1 m column is sufficient.

*Glycerol monooleate.* This substance may be used for the analysis of aqueous mixture of fatty acids in the same manner as Tween 80. Only a partial separation of formic and acetic acids can be obtained using column No. 9.

*Columns with hydrophobic stationary phases* have also sometimes been used. Thus Haskin *et al.*[6] utilized a column packed with di(2-ethylhexyl) phthalate for the analysis of an aqueous mixture of ethanol, acetonitrile and triethyla-

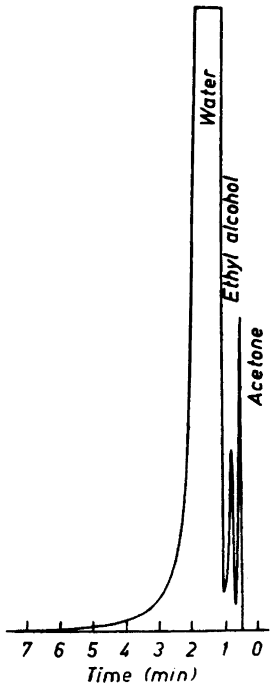


*Fig. 6.* Small amounts of ethyl alcohol and acetone in water. Column No. 7. Temperature 100°C. Flow of He 50 ml/min.

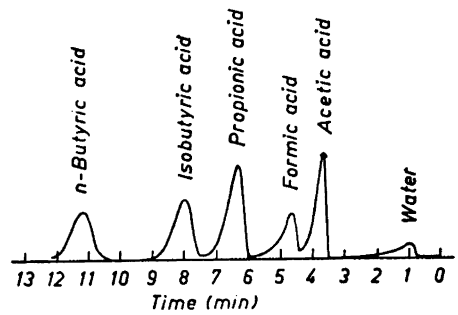


*Fig. 7.* Water-fatty acid mixture. Column No. 8. Temperature 100°C. Flow of He 100 ml/min.

amine. On this column, water is eluted first as a relatively narrow band with a steep front and a tail. We have tried to determine small amounts of water in ethanol by means of a 2 m column containing 30 % by weight of dioctyl phthalate on Celite. It was found, however, that the retention time for water varied with the amount of water in the mixture and increased as the water content decreased. While a good separation was obtained for mixtures containing several per cent water, the separation became bad, thus making quantitative measurements impossible, when the water content was decreased to a few tenths of a per cent.

In the foregoing, a few examples of separations of aqueous mixtures have been given. It should be pointed out, however, that, by varying the column length and using different columns in series and choosing suitable operating variables, aqueous mixtures of almost any kind can be treated successfully.

*Quantitative analysis.* The internal normalization method is very applicable for the quantitative analysis of water in aqueous mixtures. Although it is best suited for the assay of moderate amounts of water, even relatively small amounts of water can be determined by making proper use of the sensitivity switch of the gas chromatograph. In Fig. 8, the chromatogram, using column

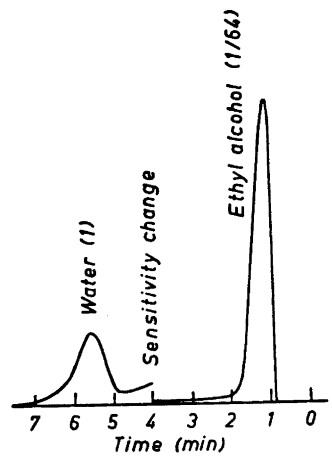


*Fig. 8.* Absolute ethyl alcohol. Column No. 6. Temperature 100°C. Flow of He 50 ml/min. Recorder attenuation shown in brackets.

No. 6, for absolute ethyl alcohol containing about 0.6 % of water is given. The water peak was run at full detector sensitivity and the alcohol peak at 1/64 of its maximum output. By this procedure, the areas under the two peaks are kept similar in size in spite of the large difference in the contents of the two components.

In the internal normalization method, the areas under the peaks are measured. In order to get a reasonably accurate value for the area, the peak should not be too narrow. Several methods are available for broadening a narrow peak, *e.g.* by increasing the paper speed of the recorder, by decreasing the flow of the carrier gas or by decreasing the temperature. It is also possible to increase the length of the column. It has been recommended when using this last method not to add a length of column containing the same stationary phase as the original column but instead to employ one containing a hydrophobic stationary phase, *e.g.* paraffin. In this way, the retention time for the organic component is increased while that for water is changed only to a minor extent. The water peak may, however, become distorted by this procedure.

A convenient and much used method for calculating the area under a peak is to multiply the height of the peak by the width of the peak at half the peak height (half band width). To get a correct value in this way, the peak should not be distorted. To investigate the influence of the tailing of the water peak, often encountered in GLPC-analysis of aqueous mixtures, the following experiment was made. Mixtures of water and ethyl alcohol were made up and analyzed using column No. 6. The area under each peak was measured by two methods. In the first one, the area was obtained by calculating the peak height times half the band width while, in the second, the area was planimetered. The per cent water peak area was calculated and the figures obtained placed in a diagram to give the relationship between the weight per cent of water in the mixture and the per cent area under the water peak. It was found

that, when the area was calculated by multiplying the peak height by half the band width, the deviation from linearity was not greater, than when the area was planimetered. The same result was obtained with mixtures of acetone and water. Thus it does not seem to be necessary to planimeter the water peak in the GLPC-analysis of aqueous mixtures of alcohols and ketones using triethanolamine as the stationary phase. Since the symmetry of the water peaks obtained when using columns Nos. 1—5 was nearly as good as when using column No. 6, it may be concluded that the simpler area calculation method can also be used in these cases. It should, however, be pointed out that, to get accurate values, it is necessary to make a calibration curve. Any deviation from a linear relationship is then revealed. It is also advisable to check the curve from time to time because the column may change its properties during use, *e.g.* by evaporation of the stationary phase or in other ways. For semi-quantitative work, the per cent area under the water peak may be put equal to the weight per cent of water in the mixture.

Instead of applying the internal normalization method, it is often best to base the quantitative measurements on the peak height or peak area of one or a few of the components in the mixture using either the internal standard or fixed volume method. If the latter method is employed, it is necessary to add exactly the same volume every time. The Agla micrometer syringe or capillary pipettes may be used. Recently a method for injecting exact volumes by means of ordinary syringes has also been described [7]. To exemplify the use of these methods, their application to the analysis of a water-acetone mixture will be described. In the fixed volume method, an exact volume of the mixture is injected and separated on, for example, column No. 1 (*cf.* Fig. 3). The height of the acetone peak is measured. To get the best accuracy, the procedure is repeated several times and the mean value of the acetone peak heights is taken. The per cent acetone in the mixture is read from a calibration curve obtained by injecting the same volume of mixtures containing known amounts of water and acetone using the same experimental conditions and measuring the heights of the acetone peaks. The water content is obtained by difference.

If the internal standard method is applied, a known amount of methyl ethyl ketone is added to the mixture of unknown composition as an internal standard and the mixture is run as before on column No. 1 (*cf.* Fig. 3). The height of the two ketone peaks is measured and the ratio calculated. From this ratio, the per cent acetone is obtained using a calibration curve giving the ratio of per cent acetone to per cent methyl ethyl ketone as a function of the ratio of the peak height of acetone to the peak height of methyl ethyl ketone. This method is somewhat more laborious than the former one but it generally gives the most accurate values since minor fluctuations in the operating variables are compensated for. For comparison, the analysis values for a mixture of acetone and water using the internal normalization method, fixed volume method and internal standard method using column Nos. 6 and 1 are given in Table 2. It is obvious that the fixed volume method is inferior in accuracy to the other two in this case. However, the accuracy of the fixed volume method increases when the acetone content decreases since the relative injection error decreases when larger volumes can be injected.

*Table 2.* Analysis values for a water-acetone mixture obtained by various methods.

| Method | Acetone (wt %) | | Water (wt %) | | Column No. |
|---|---|---|---|---|---|
| | True value | Observed | True value | Observed or calculated | |
| Internal normalization | 11.1 | 11.2<br>11.2<br>11.4 } 11.3 | 88.9 | 88.8<br>88.8<br>88.6 } 88.7 | 6 |
| Internal * standard | 11.1 | 11.0<br>11.1<br>11.2 } 11.1 | 88.9 | 88.9 ** | 7 |
| Fixed volume *** | 11.1 | 10.9<br>11.8<br>11.4 } 11.4 | 88.9 | 88.6 ** | 7 |

* Internal standard methyl ethyl ketone.
** Calculated as difference from the acetone value.
*** Injected volume 6 $\mu$l.

For trace analyses, the internal standard method or fixed volume method must be used. The measurement is in this case always based on the trace component or components. Either the peak height or peak area is used. It should be pointed out that, when using the peak height, peak height maxima are generally not seriously affected by a certain amount of overlap. As the water peak is generally rather flat, measurements of trace amounts of water must be based on the area of the water peak which impairs the accuracy and sensitivity somewhat.

## EXPERIMENTAL

The analyses were performed using a Perkin Elmer Vapour Fractometer Model 154. The columns were made from aluminum tubing of 4 mm internal diameter.

The liquids used as stationary phases were heated in vacuum in a stream of nitrogen to remove low boiling impurities. Diglycerol was obtained from May and Baker Ltd, Dagenham, England, and hexantriol, Tween 80 and glycerol monooleate from T. Schuchardt, München, Germany. The other compounds used as stationary phases may be obtained from any chemical firm.

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