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Note

Separation of isotopic methanes by gas chromatography

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In connection with the radiolytic study of liquid alkanes in the presence of C^2H_3I it was desirable to develope a simple, fast and efficient gas chromatographic (GC) method for the separation of deuteriated methanes.

The separation of such mixutres has been studied on both packed[1-7] and capillary columns[8]. Since it is generally required that a GC analysis should provide the best separation of a given mixture in the shortest time, the expression R^2/t (R is the resolution of a isotopic pair and t is the time of the analysis) is introduced[9] in order to evaluate the efficiency of a column. When either a 10-m-long column packed with etched glass beads at liquid-nitrogen temperature or a 15-m-long column filled with Porapak Q at different subambient temperatures was used for the analysis of methane isomers we were able to achieve the separation of the pair CH_4–C^2H_4 at R^2/t values of $9 \cdot 10^{-4}$ and $3.7 \cdot 10^{-4}$ sec^{-1}, respectively[10]. These values correspond to those published[6] for the same type of packing. Unfortunately, such columns did not provide the separation of isotopic pairs such as CH_4–$CH_3{}^2H$ and/or C^2H_4–CH^2H_3 which were the most relevant isotopic isomers in our particular case. A partial separation of deuterated methanes was observed on the Graphon column[6] and an almost complete separation of the isomers was observed on the glass capillary column[8]. However, the corresponding R^2/t values were low for CH_4 and $CH_3{}^2H$ (*i.e.*, $3.5 \cdot 10^{-5}$ sec^{-1} with $R = 0.9$ and $9.8 \cdot 10^{-5}$ sec^{-1} with $R = 1.4$, respectively). The main reason for such low values is the considerably long retention times of methanes on these columns. Since R^2/t is directly proportional to the ratio of the volume of the gas phase to that of the liquid phase in the column[9] and this ratio is higher for capillary than for packed columns, we tried to improve the R^2/t ratio for the separation of methanes by modifying the surface activity of the glass capillary column.

EXPERIMENTAL

The glass capillary columns prepared from soft soda-glass tube were etched by using the procedure described by Bruner *et al.*[8]. After the etching procedure the surface of the columns was covered by a thin layer of active silica. The etching solution (10% NaOH) was then passed through one of the columns (45 m long) for an additional

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2 h at 100°. The result of this procedure was the removal of part of the silica layer from the column surface so that only a part of the column was covered by the white active silica.

The column was placed in a home-made holder and was connected to the injection port as well as to the FID inlet of a Perkin-Elmer F-11 Flame Ionization unit. The holder and capillary column were immersed in liquid nitrogen just before the analysis. The test mixture consisting of CH_4, $CH_3{}^2H$, CH^2H_3 and C^2H_4 was prepared from pure gases obtained from Merck Sharp & Dohme (Montreal, Canada). A mixture of He and N_2 (1:1; Carba SA, Switzerland) was used as a carrier gas.

RESULTS AND DISCUSSION

The separation of the four deuterated methane isomers achieved on the 45-m-long modified glass capillary column at liquid-nitrogen temperature is shown in Fig. 1. The separation gives a resolution of the CH_4–$CH_3{}^2H$ pair of $R = 1.57$ at a carrier gas flow-rate of ca. 2 ml/min and a corresponding R^2/t ratio of $1.3 \cdot 10^{-3}$ sec^{-1}. The resolution estimated for the CH_4–C^2H_4 pair from Fig. 1. was ca. 4.3 and $R^2/t = 9 \cdot 10^{-3}$ sec^{-1}. These values are the highest yet published for the pairs mentioned above.

It was observed that the flow-rate of the composite carrier gas (He + N_2) continuously decreased from the moment of immersion of the column into liquid nitrogen. The initial flow-rate of 4 ml/min was reduced to 0.4 ml/min within 300 min. The resolution of the CH_4–$CH_3{}^2H$ pair was improved when the flow-rate was reduced, i.e., the value of R increased from 1.3 to 1.9 when the flow-rate decreased from 4 to 1 ml/min. However, the decrease of the flow-rate resulted in a considerable increase of the retention times and asymmetry of the peaks, leading to a reduction of the R^2/t ratio.
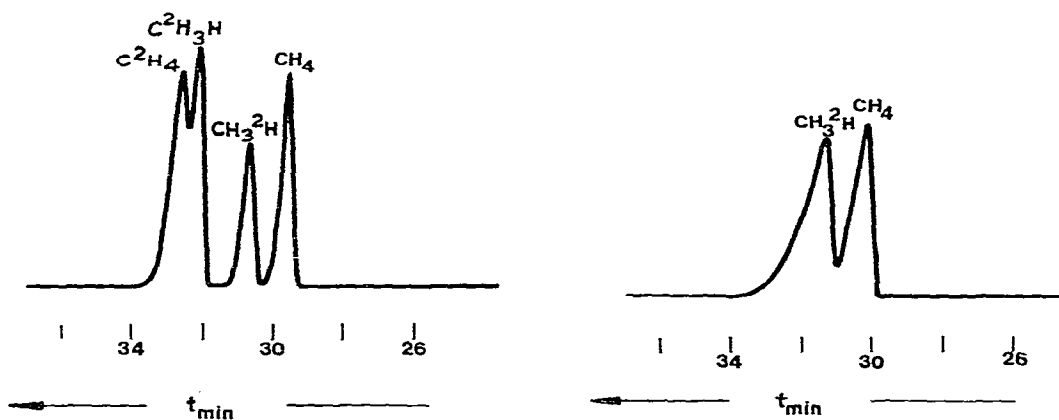

Fig. 1. Separation of a mixture of deuteriated methanes on an etched glass capillary column (45 m × 0.20 mm I.D.) after modification of the surface. Temperature, −190°; carrier gas, He + N_2 (1:1); flow-rate, 2 ml/min.

Fig. 2. Separation of the $CH_3{}^2H$–CH_4 isotopic pair on an etched glass capillary column (15 m × 0.25 mm I.D.). Temperature, −190°; carrier gas, He + N_2 (1:1); flow-rate, 1.3 ml/min.

The experiments with a single gas as the carrier gas showed that when pure helium was used practically no change in the flow-rate was observed within the experimental time interval (300 min) in contrast to the He–N_2 mixture. This finding indicates that the observed decrease of the flow-rate in the case of the He–N_2 carrier gas may be accounted for by a partial condensation of nitrogen in the pores of the active silica having a radius of < 80 Å (ref. 5), resulting in an increased resistance of the column.

The lower resolution for the CH_4–$CH_3{}^2H$ pair ($R = 0.76$) found on the 15-m-long capillary column with a uniform layer of active silica (see Fig. 2), compared with that observed on the modified layer, indicates a more promising way for the optimization of the separation of isotopic methanes. In order to achieve this it is necessary to develop a reproducible procedure for the modification of the activity of the silica layer rather than to use a shorter column with a very active surface.

It has been shown above that the separation of isotopic methanes can be achieved in a very reasonable analysis time. The development of a more convenient surface deactivation method than the use of a He–N_2 mixture as the carrier gas would result in a greater stability of the separation system.

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