

Note

Gas chromatography of the atmosphere of Titan

II. Analysis of low-molecular-weight hydrocarbons and nitriles with a potassium chloride-deactivated alumina PLOT capillary column

L. DO* and F. RAULIN

Laboratoire de Physico-Chimie de l'Environnement, Université Paris XII, 94010 Creteil Cedex (France)

(First received December 1st, 1989; revised manuscript received April 3rd, 1990)

We are currently studying gas chromatographic (GC) columns which could be used for analysing the atmosphere of Titan, a satellite of Saturn, from a probe. In Part I¹, we described the chromatographic behaviour of a PoraPLOT Q column in the separation of C₁–C₈ hydrocarbons and C₁–C₄ nitriles¹. We now present the results obtained for the same type of solutes with a potassium chloride-deactivated alumina (Al₂O₃–KCl) porous-layer open-tubular (PLOT) capillary column.

Such a column has already been systematically studied for the analysis of hydrocarbons^{2–4}. It is very powerful for the separation of C₁–C₁₀ hydrocarbons, including alkanes and ethylenic, acetylenic and benzenic compounds. As observed for other PLOT columns, the optimum velocity of the carrier gas is much higher than those obtained with liquid phase coated capillary columns, and for hydrogen it is about twice that for helium. In addition, it was found that this column shows a very high retention for polar compounds, such as alcohols².

However, no quantitative information was available on the behaviour of this column with low-molecular-weight nitriles. For that reason we have studied the separation of mixtures of hydrocarbons and nitriles and the height equivalent to a theoretical plate (HETP) of some of these compounds with the Al₂O₃–KCl PLOT column.

EXPERIMENTAL

The PLOT column (Chrompack, Middelburg, The Netherlands) was of 0.32 mm I.D. It was initially 50 m long and then it was reduced to 10 m. This fused-silica capillary PLOT column was coated with a 5- μ m thick film of aluminium oxide (deactivated by potassium chloride for increased linear adsorption and more symmetrical peaks). The column was mounted in the split mode (splitting ratio 25:1)

on the same gas chromatograph as described in Part I¹. The injector and detector temperatures were 225°C. Hydrogen was used as the carrier gas.

The sampling techniques, reagents and method of determination of the Van Deemter curves were the same as in Part I¹.

RESULTS AND DISCUSSION

A 50-m column of this type was tested initially by injecting some nitriles independently. During these preliminary studies, hydrocyanic acid (HCN), cyanogen (NCCN), cyanoacetylene (HC₂CN), cyanopropyne (CH₃C₂CN) and acetonitrile (CH₃CN) were not eluted, even after several hours at high temperature (*ca.* 200°C). It appears therefore, that the adsorption of these compounds on the alumina surface is very important, probably as a consequence of strong interactions between nitriles, which are Lewis bases, and alumina, which is a Lewis acid. We therefore shortened the column to 10 m in order to optimize the analysis time and observe the elution of nitriles. With this shorter column, the elution of all the nitriles studied may be possible within reasonable times. However, some of them are effectively eluted (mainly HCN, C₂N₂ and the acetylenic nitriles) only if they re injected in relatively large amounts. For instance, with C₂N₂, the minimum injected amount necessary to achieve elution of the solute is about 50 nmol (corresponding to 2 nmol injected onto the column, because of the splitting ratio). For HCN this amount is about 150 nmol (corresponding to 6 nmol injected onto the column). Such behaviour is probably due to irreversible adsorption

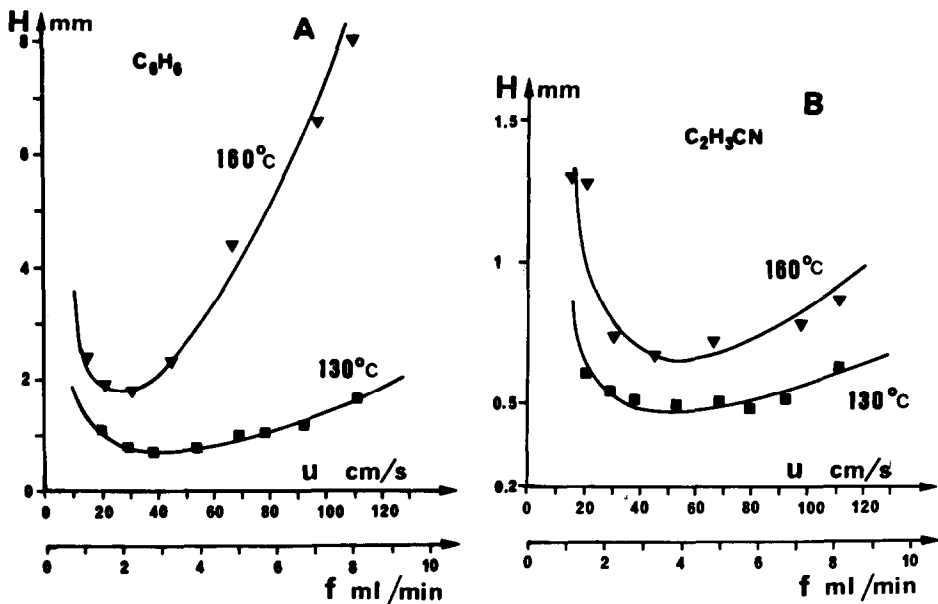


Fig. 1. Variation of the HETP (H) with the mean linear velocity (u) and outlet flow-rate (f) of the carrier gas (hydrogen) at 130 and 160°C on a 10 m \times 0.32 mm I.D. fused-silica Al₂O₃-KCl PLOT column (5 μ m thickness coating) for (A) benzene and (B) acrylonitrile. Total injected amount, benzene 0.6 nmol, acrylonitrile 0.9 nmol; split mode (25:1).

of part of the nitrile and not to chemical reaction with the coating material, as no degradation product was observed during the chromatographic analysis.

We determined the efficiency of the 10-m Al_2O_3 -KCl PLOT capillary column long by measuring the HETP as a function of the linear gas velocity at different temperatures. To plot Van Deemter curves we injected a gas mixture of selected solutes (including in particular methane, benzene and acrylonitrile) at 130 and 160°C.

Fig. 1A shows the curves relating to benzene. The minimum values of H are 0.7 mm at 130°C and 1.8 mm at 160°C. In contrast to the results obtained with PoraPLOT Q¹, the HETP depends markedly on temperature. When the temperature is increased, a large increase in the slope of the linear portion of the HETP vs. u curve is observed at high velocities of the carrier gas. This shows that the C_k term of the Golay equation ($\text{HETP} = B/u + C_g u + C_k u$), which is related to resistance to mass transfer, increases when the temperature increases. This phenomenon may be due to an increase in diffusion into the micropores of the coating material of the column^{5,6}. It has also been observed when chemi-adsorption processes are involved⁷.

The curves for acrylonitrile are shown in Fig. 1B. The column efficiency for this polar compound is much better than that of the PoraPLOT Q column. The minimum values of H are 0.47 mm at 130°C and 0.65 mm at 160°C. With these two latter components, benzene and acetonitrile, we have observed that the column efficiency increases when the temperature decreases in the range of temperatures tested.

For the calibration of the column with C_6 hydrocarbons and C_1 - C_4 nitriles, we used an outlet flow-rate of the carrier gas at 4.4 ml/min. The nitriles are generally eluted after the C_1 - C_6 hydrocarbons. Therefore, the calibration of this column was carried out by injecting a mixture of methane, C_6 hydrocarbons (cyclohexane, 1-hexene and benzene) and C_1 - C_4 nitriles at different temperatures.

Fig. 2A shows a chromatogram of such a mixture at 150°C. All of the injected solutes are separated, with the exception of crotonitriles and 3-butenitrile. For these two solutes, the poor separation is probably connected with strong gas-solid adsorption in the column. They were also not separated at a higher temperature (180°C). The behaviour of this column with respect to the other nitriles is not optimized: C_2N_2 , HCN, 2-methylpropanenitrile and butanenitrile do not give symmetrical peaks. With HCN, the retention time decreases markedly when the temperature increases up to *ca.* 150°C, then remains almost constant between 150 and 180°C. In addition, several peaks appear very large. The elution of all solutes requires at least *ca.* 30 min.

Fig. 2B shows an example of a chromatogram obtained for the same gaseous sample by programming the column temperature (isothermal at 100°C for 2 min, then increased at 25°C/min to 185°C). The separation of all solutes is accomplished in less than 12 min. The peaks of crotonitriles and 3-butenitrile remain flat as before and are unsuitable for quantitative analysis of trace compounds. For the other nitriles, the chromatographic peaks have the same shape as previously.

This study has shown that the Al_2O_3 -KCl PLOT column has a very high retention for nitriles and confirmed the general behaviour of this column relative to polar compounds. Nevertheless, C_1 - C_4 nitriles are eluted from 10 m \times 0.32 mm I.D. Al_2O_3 -KCl PLOT column, but mainly with asymmetric and broad peaks.

Previous studies have demonstrated that a 50 m \times 0.32 mm I.D. fused-silica Al_2O_3 -KCl PLOT column is very effective for the separation of C_1 - C_{10} hydrocarbons

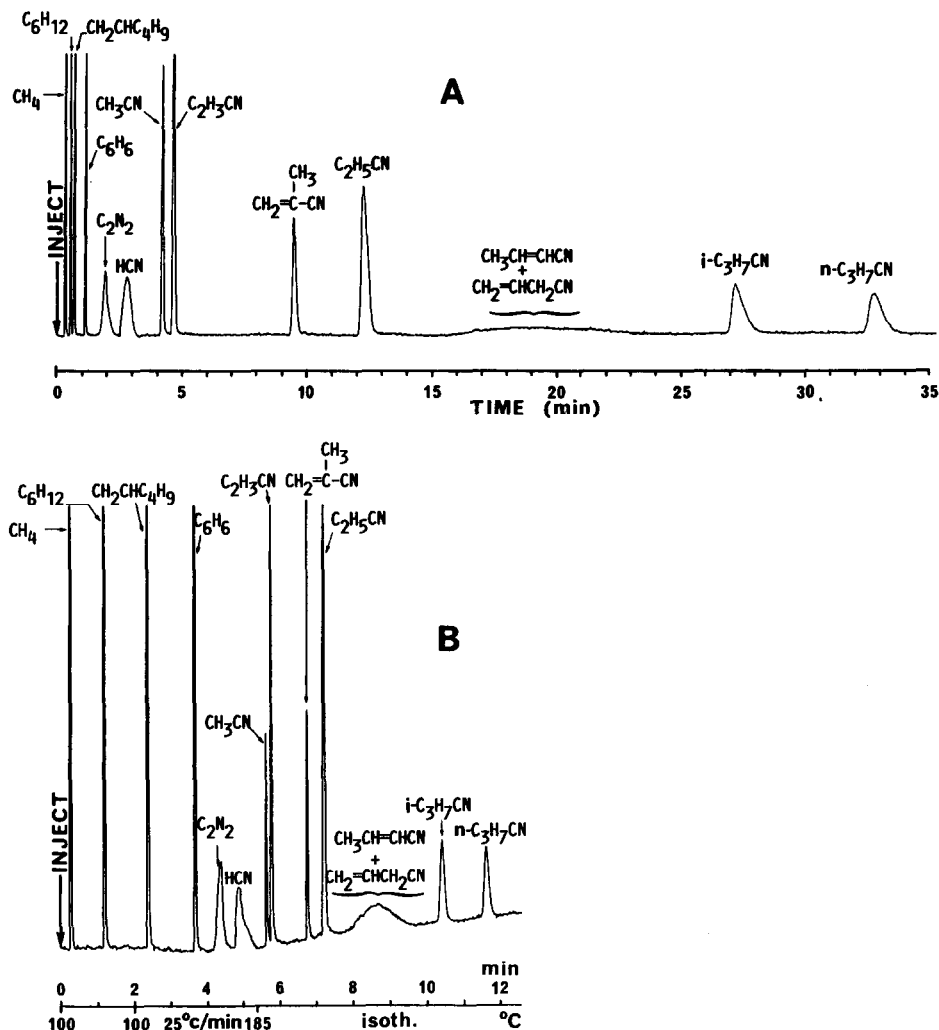


Fig. 2. Gas chromatogram of a gaseous mixture of methane, C_6 hydrocarbons (cyclohexane, 1-hexene and benzene) and C_1 - C_4 nitriles, (A) at 150°C and (B) with temperature programming (2 min isothermal at 100°C , then increased at $25^\circ\text{C}/\text{min}$ to 185°C). Carrier gas, hydrogen; outlet flow-rate, 4.4 ml/min; total amount injected, 10-30 nmol (hydrocarbons and C_1 - C_4 nitriles), 50 nmol (C_2N_2) and 150 nmol (HCN); split mode (25:1); flame ionization detector.

at low temperatures²⁻⁴. Under these conditions nitriles are not eluted even after several hours. Hence the presence of nitriles does not prevent the use of this column for the rapid GC analysis of light hydrocarbons. In addition, it must be pointed out that no noticeable change in retention times was observed for the hydrocarbons studied after several injections of nitriles in relatively large amounts. Consequently, the adsorption of these polar compounds on the alumina surface does not seem to markedly alter its characteristics and does not change its chromatographic behaviour relative to the hydrocarbons. Such a column could be suitable for use in GC-mass

spectrometric experiments in the Cassini mission, specifically for the analysis of the hydrocarbons present in Titan's atmosphere.

ACKNOWLEDGEMENTS

We thank Dr. G. Gaspar and J. de Zeeuw for their help during the preparation of this work. This study was supported by a grant from the Centre National d'Etudes Spatiales. We also thank the referees for fruitful comments and suggestions.

REFERENCES

- 1 L. Do and F. Raulin, *J. Chromatogr.*, 481 (1989) 45.
- 2 J. de Zeeuw, R. C. M. de Nijs and L. T. Henrich, *J. Chromatogr. Sci.*, 25 (1987) 71.
- 3 J. de Zeeuw, R. C. M. de Nijs, J. C. Buijten, J. A. Peene and M. Mohnke, *Int. Lab.*, December (1987) 52.
- 4 J. de Zeeuw, R. C. M. de Nijs, J. C. Buijten, J. A. Peene and M. Mohnke, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 162.
- 5 A. G. Altenau and L. B. Rogers, *Anal. Chem.*, 36 (1964) 1726.
- 6 J. E. Oberholtzer and L. B. Rogers, *Anal. Chem.*, 41 (1969) 1590.
- 7 M. T. Ivanova and A. A. Zhukhovitskii, *Russ. J. Phys. Chem.*, 41 (1967) 1030.