Journal of Chromatography, 591 (1992) 297–301
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 774

Gas chromatography of Titan's atmosphere

III. Analysis of low-molecular-weight hydrocarbons and nitriles with a CP-Sil-5 CB WCOT capillary column

L. Do and F. Raulin*

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

(First received June 21st, 1991; revised manuscript received September 27th, 1991)

ABSTRACT

The systematic calibration of a CP-Sil-5 CB wall-coated open-tubular capillary column (0.15 mm I.D., 2 μm film) with a chemically bonded stationary phase (dimethyl polysiloxane) is reported for the separation of C_1–C_6 hydrocarbons and C_1–C_4 nitriles, at temperatures ranging from 20 to 80°C. Retention indices are given for these solutes at 20°C. Van Deemter curves are also plotted for propionitrile, *n*-hexane and benzene at 20 and 50°C. The column provides good efficiency and resolution, suitable for the conditions required by a flight instrument aboard a Titan probe, such as the gas chromatography–mass spectrometry experiment on the Huygens probe of the Cassini mission.

INTRODUCTION

In the frame of the development of a gas chromatographic–mass spectrometric (GC–MS) instrument [1] for the Titan Huygens probe in the Cassini mission, we are currently studying GC columns which could provide the best conditions for analysing the atmosphere of Titan (a satellite of Saturn) within the constraints of space instrumentation. In previous papers in the series [2,3], we reported the behaviour of porous-layer open-tubular (PLOT) capillary columns in the separation of C_1–C_8 hydrocarbons and C_1–C_4 nitriles. However, in spite of their attractive chromatographic behaviour, recent mechanical tests [4] suggested that such columns do not fulfil all the requirements of space instrumentation: their mechanical strength appears too weak, so far, to resist the severe conditions of a flight instrument, in particular the acceleration and vibration during the launch. The main problem seems to be the degradation of the coating when the column is exposed to such intense vibrations. In this respect, wall-coated open-tubular (WCOT) capillary columns with a chemically bonded stationary phase may be a better choice. In such columns, by means of a chemical reaction, the molecules of the stationary phase are linked among themselves and to the inner wall of the fused-silica tubing [5]. Consequently, transformation of the liquid phase structure into a three-dimensional association system occurs. It gives not only better mechanical resistance but also high thermal stability, decreasing markedly the bleeding of the column [6].

A WCOT capillary column coated with dimethyl polysiloxane such as the CP-Sil-5 CB column (Chrompack, Middelburg, Netherlands) has already shown good behaviour for the simultaneous determination of polar and non-polar low-molecular-weight compounds [7], but there are no data on the behaviour of this type of column relative to nitriles. We report here the results of a detailed chromatographic study of a CP-Sil-5 CB fused-silica capillary column, including the simultaneous separation of mixtures of hydrocarbons and nitriles

0021-9673/92/$05.00

and the Van Deemter curves for some of these compounds.

EXPERIMENTAL

The CP-SIL-5 CB WCOT column (Chrompack) was a 25 m × 0.15 mm I.D. WCOT fused-silica capillary coated with a 2-μm thick film of 100% dimethyl polysiloxane. It was installed in the split mode (splitting ratio generally 305:1) on the same gas chromatograph as described in Part I [2]. The injector and detector temperatures were 100°C. The carrier gas was hydrogen.

Sampling techniques, most of the reagents and the method of determination of the Van Deemter curves were the same as described in Part I [2]. The additional solutes, cyclopropane and 1,3-butadiene, were obtained from Alphagaz–L'Air Liquid (Bois d'Arcy, France) and Aldrich (Strasbourg, France), respectively. Butadiyne was prepared by dehydrochlorination of 1,4-dichloro-2-butyne (Aldrich) with potassium hydroxide in water–dioxane solution [8].

RESULTS AND DISCUSSION

To determine the efficiency of the column and the optimum flow-rate for a gas mixture of hydrocarbons and nitriles, we measured the HETP (H) as a function of the mean linear gas velocity (u) at different temperatures. To plot Van Deemter curves we injected a gas mixture of propionitrile, n-hexane, benzene and methane in constant amounts (7–12 nmol in the injector of the gas chromatograph) at 20 and 50°C.

The curves for propionitrile are shown in Fig. 1A. The minimum values of H are 0.5 mm at 20°C and 0.74 mm at 50°C. The linear part of the H *vs.* u curve for this polar compound rises slowly at high velocities of the carrier gas. Fig. 1B shows the curves relating to n-hexane. The minimum values of H are 0.42 mm at 20°C and 0.58 mm at 50°C.

The curves obtained with benzene (Fig. 2) exhibit a relatively flat minimum. It is observed at linear velocities of the carrier gas of *ca.* 30 cm/s. The minimum values of H are 0.31 mm at 20°C, corresponding to 3265 theoretical plates/m and 0.43 mm at 50°C. With the three components stated above, we observed that the column efficiency decreases slightly when the temperature is increased in the range tested. In addition, the efficiency of the column for the selected solutes appears very high according to the observed minimum values of H and the theoretical plate number.

To calibrate the column with a mixture of C_1–C_6 hydrocarbons and C_1–C_4 nitriles, we chose 0.6 ml/min for the outlet flow-rate of the carrier gas. Fig. 3 shows a chromatogram of such a mixture at 20°C.

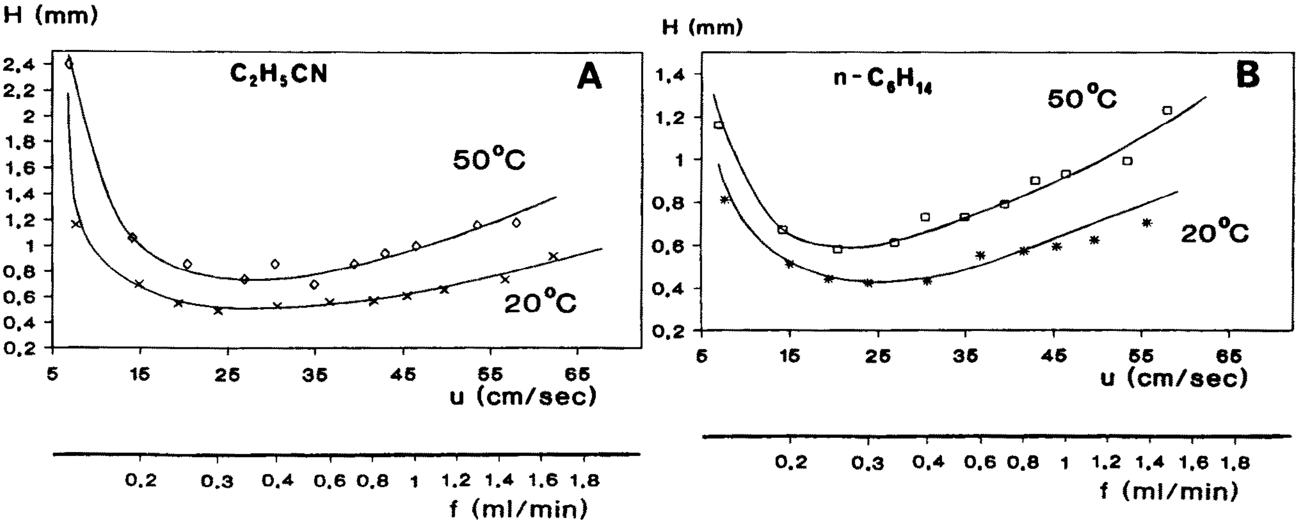

Fig. 1. (A) Propionitrile and (B) n-hexane: variation of the height equivalent to a theoretical plate (H) with the mean linear velocity (u) and outlet flow-rate (f) of the carrier gas (hydrogen) at 20 and 50°C on a 0.15 mm I.D. fused-silica CP-Sil-5 CB WCOT column (2-μm thick coating). Total amounts injected: propionitrile 12 nmol, n-hexane 7 nmol; split mode (305:1).

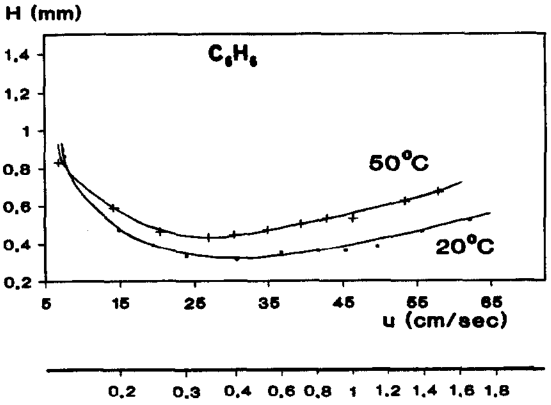

Fig. 2. Benzene: variation of H with u and f as in Fig. 1. Total amount injected: 10 nmol.

With this isothermal condition, several solutes are co-eluted. Ethene is co-eluted with ethyne, 1-butene with isobutene and *trans*- or *cis*-crotononitrile with benzene. Apart from these compounds, all the selected solutes are well separated. Further, the profile of most peaks is sharp and symmetrical. However, the peaks of the non-volatile nitriles show a very slight tailing compared with those of hydrocarbons. This could be due to strong adsorption of nitriles on the stationary phase and slow kinetics of mass transfer between the gas and liquid phases [9]. The elution of all injected solutes is completed in 35 min. The nature of the films of ParaPLOT Q and CP-Sil-5 CB is almost apolar. However, for several hydrocarbons relative to neighbouring nitriles, there are peak inversions between the two columns, as shown in Table I. Apolar or almost apolar hydrocarbons are eluted before the nitrile (*e.g.*, 1-pentene and acrylonitrile, 3-methylpentane and isobutyronitrile) with the CP-Sil-5 CB column but after the nitrile with the PoraPLOT Q column. Hence the stationary phase in the CP-Sil-5 CB column could be slightly less apolar than the adsorbent film in the PoraPLOT Q column.

To improve the separation of solutes and to shorten the analysis time, we programmed the column temperature as a function of time. For the analysis of the same gaseous mixture, we introduced a column temperature programme from 20°C (isothermal for 4 min) at 20°C/min to 80°C (Fig. 4). The separation of all solutes was accomplished in

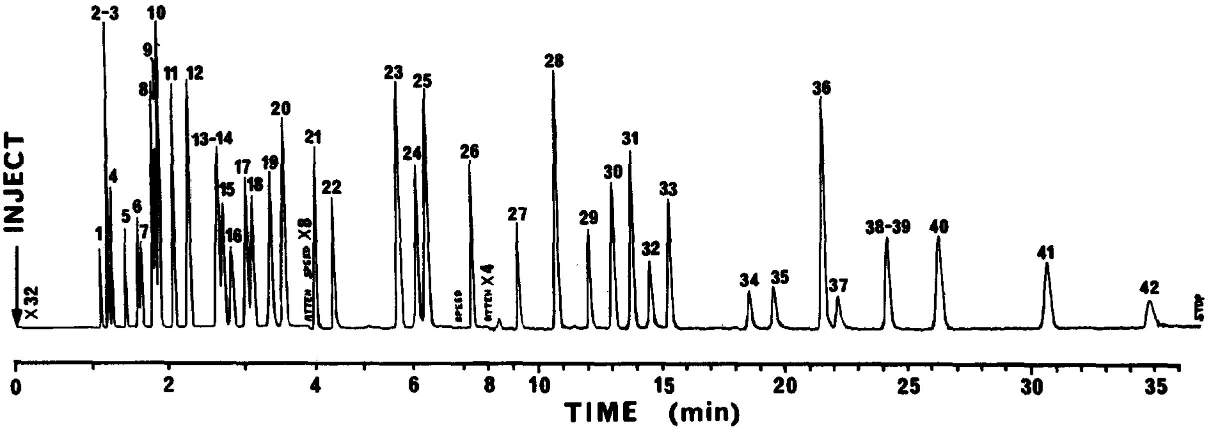

Fig. 3. Gas chromatogram of a gaseous mixture of C_1–C_6 hydrocarbons and C_1–C_4 nitriles on a 25 m × 0.15 mm I.D. CP-Sil 5 CB (2-μm thick coating) fused-silica WCOT column at 20°C. Carrier gas, hydrogen; outlet flow-rate, 0.6 ml/min; amount injected, 1–5 nmol of each constituent; split mode (305:1); flame ionization detector. Peaks: 1 = methane; 2 = ethene; 3 = ethyne; 4 = ethane; 5 = cyanogen; 6 = propene; 7 = propane; 8 = hydrocyanic acid; 9 = propyne; 10 = allene; 11 = cyclopropane; 12 = isobutane; 13 = 1-butene; 14 = isobutene; 15 = 1,3-butadiene; 16 = butane; 17 = *trans*-2-butene; 18 = 1-butyne; 19 = *cis*-2-butene; 20 = butadiyne; 21 = cyanoacetylene; 22 = acetonitrile; 23 = 1-pentene; 24 = acrylonitrile; 25 = *n*-pentane; 26 = 2-methyl-2-butene; 27 = propionitrile; 28 = cyclopentane; 29 = methacrylonitrile; 30 = 3-methylpentane; 31 = 1-hexene; 32 = isobutyronitrile; 33 = *n*-hexane; 34 = *cis*- or *trans*-crotononitrile; 35 = 3-butenenitrile; 36 = 2-butynenitrile; 37 = butyronitrile; 38 = *trans*- or *cis*-crotononitrile; 39 = benzene; 40 = cyclohexane; 41 = cyclohexene; 42 = cyclopropanecarbonitrile.

TABLE I

RETENTION INDICES OF HYDROCARBONS AND NITRILES ON A CP-SIL-5 CB WCOT COLUMN AT 20°C AND (FOR COMPARISON) ON A PORAPLOT Q COLUMN [2] AT 100°C

Reference alkanes are listed in parentheses.

Solute	Retention index	
	CP-Sil-5 CB (20°C)	PoraPLOT Q (100°C)
(Ethane)	200	
Cyanogen	259.2	
Propene	294	
(Propane)	300	300
Hydrogen cyanide	319.9	291.9
Propyne	323.6	
Allene	329.5	
Cyclopropane	348.8	
Isobutane	366	
1-Butane	391	
Isobutene	391	
1,3-Butadiene	394.3	
(Butane)	400	
trans-2-Butene	410.2	
1-Butyne	414	
cis-2-Butene	425	
Butadiyne	431	
Cyanoacetylene	447.6	
Acetonitrile	456.9	
1-Pentene	488.8	489.2
Acrylonitrile	496.4	475.6
(*n*-Pentane)	500	500
2-Methyl-2-butene	520.1	
Propionitrile	545.3	523.3
Cyclopentane	562.6	516.1
Methacrylonitrile	574.9	
3-Methylpentane	583	592.2 (2)[a]
1-Hexene	588.9	592.2 (3)[a]
Isobutyronitrile	594.4	592.2 (1)[a]
(*n*-Hexane)	600	600
cis- or *trans*-crotononitrile	619.8	596.5
3-butenenitrile	625.2	
Cyanopropyne	637.9	
Butyronitrile	638.1	
trans- or *cis*-crotononitrile	647.2	
Benzene	647.2	
Cyclohexane	655.7	
Cyclohexene	671	
Cyclopropyl cyanide	684	
(*n*-Heptane)	700	

[a] Order of appearance of peaks.

less than 16 min, and *cis*- or *trans*-crotononitrile and benzene were separated. The entire analysis time is much reduced, but a drift of the baseline was observed with increasing column temperature. This is due to "bleeding" of the stationary phase, the thickness of which is relatively large (2 μm).

We also measured the retention indices $I(i)$, of the compounds studied in order to obtain a more general view of the behaviour of the column in relation to these solutes. The retention indices are determined from the classical equation

$$I(i) = 100 \cdot \frac{\log t'_{R(i)} - \log t'_{R(P_z)}}{\log t'_{R(P_{z+1})} - \log t'_{R(P_z)}} + 100Z$$

where t'_R is the relative retention time, P_z and P_{z+1} correspond to the paraffins with z and $z+1$ carbon atoms, respectively, and i correspond to a solute, the retention time of which is between that of P_z and P_{z+1}. These retention indices at 20°C (Table I) vary linearly with the carbon number of the solute for a given chemical family. It must be pointed out that these experimental values appeared to be highly reproducible for most of all solutes, the relative error being less than 0.8%.

Under isothermal conditions (20°C), the detection limit (signal twice the baseline noise) corresponds to an absolute amount of solute in the column of less than about 10^{-12}–10^{-13} mol for C_2–C_3 hydrocarbons, HCN and cyanoacetylene. This limit comes mainly from the detection sensitivity (flame ionization detector) and not from the column. For the same organics, the amounts that will be injected into the GC–MS instrument are expected to be in this range or even higher. Therefore, this column should be compatible with the GC–MS analysis on the Huygens probe, at least in terms of sensitivity.

The results demonstrate that a 25 m × 0.15 mm I.D. fused-silica CP-Sil-5 CB (film thickness 2 μm) WCOT column is efficient for the separation of C_1–C_6 hydrocarbons and C_1–C_4 nitriles at low temperature. Moreover, faster analysis was achieved by temperature programming; however, the bleeding of the stationary phase may decrease significantly the signal-to-noise ratio of the GC–MS instrument of the Huygens probe. To reduce the analysis time under isothermal conditions, the column length could be shortened while the thickness of the film is decreased in order to reduce the bleeding of the stationary phase during temperature programming. If the column is so modified, it can be used for faster

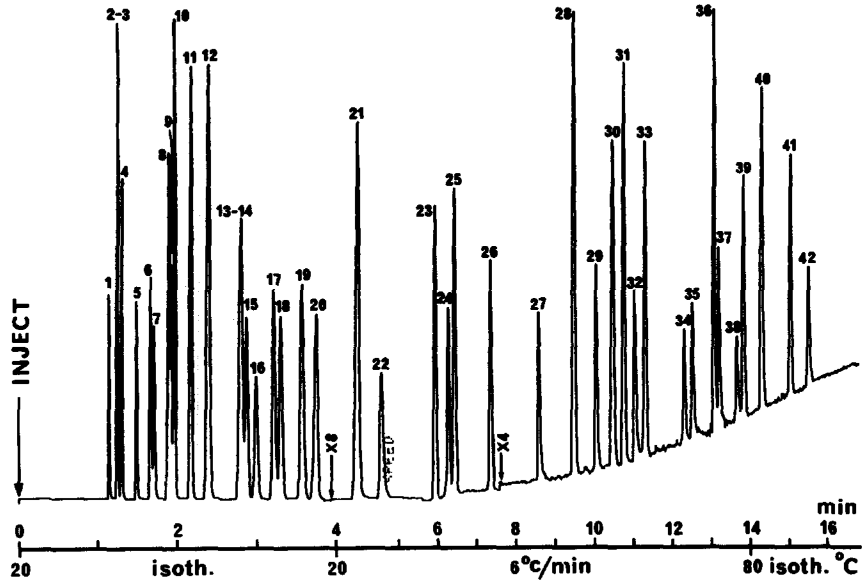

Fig. 4. Chromatogram obtained under the same conditions as in Fig. 3, but with temperature programming of the column: isothermal for 4 min at 20°C, then increased at 6°C/min to 80°C. Peak numbers as in Fig. 3.

analysis and with a lower inlet pressure of the carrier gas.

ACKNOWLEDGEMENTS

We thank Dr. G. Gaspar and J. de Zeeuw for their help with this work. This study was supported by a grant from the Centre National d'Etudes Spatiales.

REFERENCES

1 H. Niemann, *Proposal to ESA Cassini Mission: Huygens Probe*, NASA–Goddard Space Flight Center, Greenbelt, MD, (1990).
2 L. Do and F. Raulin, *J. Chromatogr.*, 481 (1989) 45.
3 L. Do and F. Raulin, *J. Chromatogr.*, 514 (1990) 65.
4 H. Niemann, personal communication.
5 *Chrompack News, No. 13*, Chrompack, Middelburg, 1986, p. 1.
6 *Chrompack News, No. 12*, Chrompack, Middelburg, 1986, p. 3.
7 *Chrompack News, No. 12*, Chrompack, Middelburg, 1985, p. 4.
8 K. K. Georgieff and Y. Richard, *Can. J. Chem.*, 36 (1958) 1280.
9 G. Guiochon and C. L. Guillemin, *Quantitative Gas Chromatography*, Elsevier, Amsterdam, 1988.