

# Gas chromatography of Titan's atmosphere

## VI. Analysis of low-molecular-mass hydrocarbons and nitriles with BPX5 capillary columns

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### Abstract

Wall-coated open-tubular capillary columns (0.15 mm I.D., 12 and 25 m long with a 0.25- $\mu$ m film thickness and 12 m long with a 2- $\mu$ m film thickness with a chemically bonded stationary phase (5% phenyl–95% dimethylpolysiloxane) were used for the gas chromatographic analysis of various mixtures of low-molecular-mass saturated and unsaturated hydrocarbons and nitriles. Retention indices are given for these solutes at 30°C. Van Deemter curves were also plotted for propionitrile, *n*-hexane and benzene at 30°C for both film thicknesses. Both columns proved efficient and yielded good resolution. The analysis of the experimental band broadening on the basis of Golay's equation indicates the important role of the instrumental contribution to band broadening for columns with thin films of stationary phase.

### 1. Introduction

As part of the development of a gas chromatographic–mass spectrometric (GC–MS) instrument destined for the Huygens probe of the Cassini mission [1], we are currently studying GC columns which could provide conditions possible for analysing the atmosphere of Titan, the largest satellite of Saturn [1,2].

We have previously studied PLOT [3–5] and WCOT [5,6] capillary columns for the separation of low-molecular-mass hydrocarbons and nitriles, already detected or likely to be present in Titan's atmosphere. In particular, CP-Sil-5 CB WCOT

columns of 0.15 mm and 0.10 mm I.D., coated with 100% dimethylpolysiloxane, permit the separation of C<sub>1</sub>–C<sub>6</sub> hydrocarbons and C<sub>1</sub>–C<sub>4</sub> nitriles with good resolution. The height equivalent to a theoretical plate (HETP) of these columns was as low as about 0.3 mm at low temperature; they also allow a complete separation of the tested mixtures within less than 35 min at 20°C and in less than 15 min with temperature programming. In order to have several possible column options, we extended this study to other types of WCOT capillary columns with a cross-linked bonded stationary phase because of their low bleed. BPX5 capillary columns (SGE Australia), coated with 5% phenyl–95% dimethylpolysiloxane, are slightly

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more polar than the CP-Sil-5 CB. It has already been shown that these BPX5 columns have good separation properties for the simultaneous determination of polar and non-polar high-molecular-mass compounds. However, no data has been available, so far, on their behaviour pertaining to nitriles and on their capacity for analysing mixtures of low-molecular-mass hydrocarbons and nitriles.

We present here a detailed chromatographic study for 0.15 mm I.D. BPX5 columns coated with 0.25- $\mu\text{m}$  (column A) and 2- $\mu\text{m}$  films (column B) at 30°C. We systematically studied the chromatographic behaviour of these solutes on these BPX5 columns of different film thicknesses and lengths. Plate-height studies of test compounds of each chemical family enable the optimum experimental conditions for the separation to be established.

## 2. Theoretical

The mean plate height,  $\bar{H}$ , may be written as the sum of various contributions [7,8]:

$$\bar{H} = H_g + H_l + H_c \quad (1)$$

where  $H_g$  and  $H_l$  represent the gas-phase and liquid-phase contributions to band broadening, respectively, and  $H_c$  is the extra-column term due to the instrumental contribution. For an open-tubular column,  $H_g$  is related to the outlet carrier gas velocity,  $u_0$ , by the Golay equation [9]:

$$H_g = \left[ \frac{2D_g}{u_0} + \frac{(1 + 6k' + 11k'^2)}{96(1 + k')^2} \cdot \frac{d_c^2}{D_g} \cdot u_0 \right] f \\ = \left( \frac{B'D_g}{u_0} + \frac{C'_g u_0}{D_g} \right) f \quad (2)$$

where  $k'$  is the retention factor,  $d_c$  is the column diameter and  $f$  is a pressure corrector factor [7]. This last parameter is close to 1 for low pressure drops and its maximum value is 9/8 at high inlet pressures.  $D_g$  is the diffusion coefficient of the solute in the mobile phase at atmospheric pressure. For each solute (Table 1),  $D_g$  was calcu-

Table 1  
Calculated diffusion coefficients at 30°C

Solute	$D_g(\text{H}_2)$ ( $\text{cm}^2/\text{s}$ )	$D_g(\text{N}_2)$ ( $\text{cm}^2/\text{s}$ )
Methane	0.7115	0.2270
Hexane	0.3275	0.0823
Propionitrile	0.4496	0.1162
Benzene	0.3842	0.0962

lated according to the Chapman–Enskog equation [10] by using the empirical method for predicting the diffusion coefficients of binary gas-phase systems.

The  $H_l$  term can be drawn from the following relationship [9]:

$$H_l = \frac{6k'}{(1 + k')^2} \cdot \frac{d_f^2}{D_l} \cdot ju_0 = C_1 ju_0 \quad (3)$$

where,  $d_f$  is the average thickness of the liquid film,  $D_l$  is the diffusion coefficient of the solute in the stationary liquid phase and  $j$  is the correction factor for gas compressibility. Assuming that the instrument contribution to the plate height is mainly due to the injection profile, we can have [11]

$$H_c = \frac{\sigma_i^2 u_0^2}{(1 + k')^2 L} = Du_0^2 \quad (4)$$

where  $\sigma_i^2$  is the variance of the injection profile and  $L$  is the column length.

As the correction term  $f$  is close to 1, the experimental plate height data can be fitted by the equation

$$H = \frac{B'D_g}{u_0} + C'_g \cdot \frac{u_0}{D_g} + C_1 u_0 + Du_0^2 \quad (5)$$

With experiments performed with a single carrier gas, this equation fits the experimental data well. A linear least-squares fit method can be used and good smoothing is generally observed. However, except for  $B'$ , the relative errors in the determination of the other parameters are as large as 100%. To isolate the  $C_1$  term, Giddings and Schettler [7] introduced a method

based on the use of two different carrier gases. The  $C_1$  contribution is obtained from the difference in plate heights observed at a given  $u_0/D_g$  value. The instrumental plate height  $H_c$  also contributes to this difference in the HETP and must be accounted for, by studying the band broadening of a non-retained compound as a function of mobile phase velocity for two different carrier gases such as hydrogen and nitrogen [8]. At a given  $u_0/D_g$ , the difference in plate heights is then due only to the  $H_c$  term ( $C_1 = 0$ ). For both carrier gases,  $H$  is plotted as a function of  $u_0/D_g$  and a linear least-squares fit program is used to determine the coefficients of the plate-height equation.

### 3. Experimental

#### 3.1. Gas chromatography

Two different WCOT fused-silica capillary columns coated with a film of 5% phenyl–95% dimethylpolysiloxane (BPX5) were studied: a 12-m long column with a film thickness of 0.25  $\mu\text{m}$  (column A) and a 12-m long column with a film thickness of 2  $\mu\text{m}$  (column B). We used a Perkin-Elmer Autosystem gas chromatograph equipped with a flame ionization detector, a thermal conductivity detector and a temperature programmer. It was connected to a PE–Nelson Turbochrom data acquisition system. The detection time constant was set at 50 ms. The injector temperature was 220°C and the detector temperature was 240°C throughout. The split mode was used (with a splitting ratio generally of 60:1) and the sampling techniques were the same as described previously [3]. The solute vapours were injected through the septum with a 1- $\mu\text{l}$  Hamilton gas syringe equipped with a tight stopcock.

The test solutes were propionitrile, hexane and benzene, representing nitrile, alkane and aromatic compounds, respectively.

HETP versus linear velocity of the carrier gas were obtained at 30°C for the selected solutes by injecting a mixture of these solutes with methane, considered as a non-retained com-

pound. Dedicated software (PE–Nelson HETP, developed for this study) was systematically used for determining the HETP from peak broadening.

#### 3.2. Reagents

Allene and cyanogen were obtained from Matheson (East Rutherford, NJ, USA), methylacetylene (propyne) and ethylacetylene (1-butyne) from Baker (Phillipsburg, NJ, USA) and 1,3-butadiene, pentane, hexane and ethylbenzene from Aldrich (Strasbourg, France). All the other  $C_1$ – $C_4$  hydrocarbons tested were obtained from Alphagaz–l'Air Liquide (Bois d'Arcy, France) and were at least 99% pure. 2-Methyl-2-butene, 1-hexene, benzene, cyclohexene, heptane, cycloheptane, 1-octene, octane, acetonitrile, acrylonitrile and propionitrile were obtained from Prolabo (Paris, France), 1-pentene and 3-methylpentane from Fluka (Buchs, Switzerland) and butyronitrile, isobutyronitrile, methacrylonitrile, cyclopropanecarbonitrile, crotonitrile (mixture of *cis* and *trans* isomers) and 3-butenitrile from Riedel-de Haën (Hannover, Germany). Hydrogen cyanide was prepared by acidification of sodium cyanide with sulphuric acid.

### 4. Results and discussion

#### 4.1. HETP studies

We systematically applied the theoretical plate-height equation (Eq. 5) to determine the coefficients  $B'$ ,  $C'_g$ ,  $C_1$  and  $D$ . The plate height of test compounds was studied as a function of flow-rate with two different carrier gases. Such an approach enables one to assess the various contributions to solute band broadening and leads to important information. First, for a non-retained compound, it is a convenient way to determine the  $D$  term. For retained compounds, it is then possible to approach the  $C_1$  term, once the  $D$  term of the retained solute has been calculated.

The  $D$  term was determined from a study of

plate height variations with a non-retained compound (methane) using two different carrier gases (hydrogen and nitrogen). The studies were carried out with two different columns with 0.25- and 2- $\mu\text{m}$  stationary phase film thickness.

The variation of  $H$  with  $u_0/D_g$ , as shown in Fig. 1, indicates higher efficiency when nitrogen is used as the carrier gas. The  $\text{N}_2$  curve is systematically lower than the  $\text{H}_2$  curve for both columns coated with a thin or thick stationary phase film. The large difference in the efficiencies observed at high  $u_0/D_g$  value can be explained ( $C_1 = 0$ ) by the instrumental contribution to band broadening, which is very important when  $\text{H}_2$  is used as the carrier gas.

The constants  $B'$ ,  $C'_g$  and  $D$  were determined from the least-squares fit of Eq. 5 to the experimental plate height (Table 2). Table 2 also gives the errors in parameter determination with a 95% confidence interval. In Fig. 1, the corre-

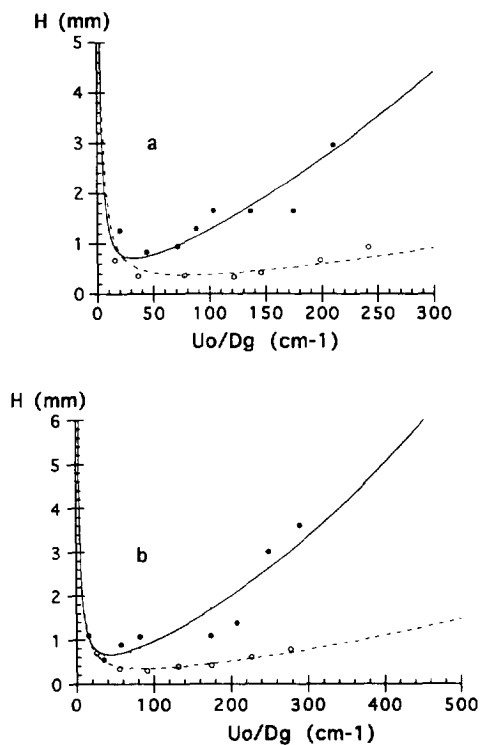


Fig. 1. HETP ( $H$ ) versus  $u_0/D_g$  for methane at 30°C with (●) hydrogen and (○) nitrogen as carrier gases on (a) column A (0.25- $\mu\text{m}$  film thickness) and (b) column B (2- $\mu\text{m}$  film thickness).

Table 2

Coefficients of the plate height equation for a non-retained compound (methane) at 30°C

Column	$B'$ ( $\text{cm}^2/\text{s}$ )	$D$ ( $\text{s}^2/\text{cm}$ )	$C'_g$ (s)
Column A (0.25 $\mu\text{m}$ )	1.8 <u>0.5</u>	$0.10 \cdot 10^{-4}$ <u>0.03</u>	$2.0 \cdot 10^{-4}$ <u>0.3</u>
Column B (2 $\mu\text{m}$ )	1.9 <u>0.3</u>	$0.08 \cdot 10^{-4}$ <u>0.04</u>	$1.5 \cdot 10^{-4}$ <u>0.5</u>

Underlined values correspond to the experimental errors.

sponding model (solid and dashed lines) fits the experimental data well. For both columns, the  $B'$  parameters are close to the theoretical value ( $B' = 2$ ). The use of two different carrier gases led to good precision (about 5%, for a 95% confidence interval) in the determination of the instrumental contribution ( $D$  term). Because of the importance of the  $D$  term, the errors in  $C'_g$  determination are large and the values given in Table 2 are insignificant.

The agreement is satisfactory for the  $D$  term found with both capillary columns. Considering the time constant of the electrometer (50 ms) as a negligible contribution to the lower efficiencies observed at high flow-rates, the mean variance of the injection profile is  $\sigma_i^2 = 0.009 \text{ s}^2$ . In high-speed chromatography using a fluidic injection device [8], the exponential contribution from the current amplifier was the primary source of extra-column band broadening. In the present case it is about 25% of the extra-column contribution and the calculated  $D$  coefficient has to be considered as a global term including both electrometer and instrumental contributions. Therefore, the calculated mean variance of the injection profile is overestimated.

Figs. 2 and 3 illustrate the variation of  $H$  with  $u_0/D_g$  for (A) propionitrile, (B) hexane and (C) benzene on columns with 0.25- and 2- $\mu\text{m}$  film thickness, respectively. The difference in the plate height measured with the two carrier gases ( $\text{H}_2$  and  $\text{N}_2$ ), is due to the diffusion of the solute in the stationary phase and to the extra-column contribution. Table 3 lists the coefficients determined by the least-squares fit of Eq. 5 to the experimental data fixing  $B'$  at its theoretical

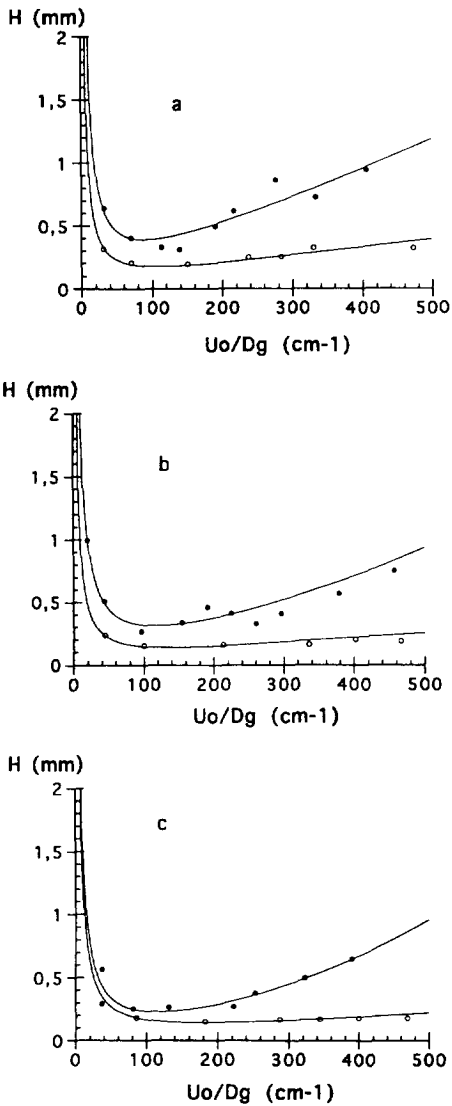


Fig. 2. HETP ( $H$ ) versus  $u_0/D_g$  at 30°C with (●) hydrogen and (○) nitrogen as carrier gases for retained compounds on column A (0.25- $\mu$ m film thickness). (a) Propionitrile; (b) hexane; (c) benzene.

value ( $B' = 2$ ) and  $D = D_{\text{methane}}/(1 + k')^2$ .  $D$  was calculated from the  $D$  (methane) term previously determined, methane being considered as non-retained solute. For the column of small film thickness (Fig. 2), the extra-column effects are the main contribution to HETP, explaining the lower efficiencies observed when hydrogen is used as the carrier gas.

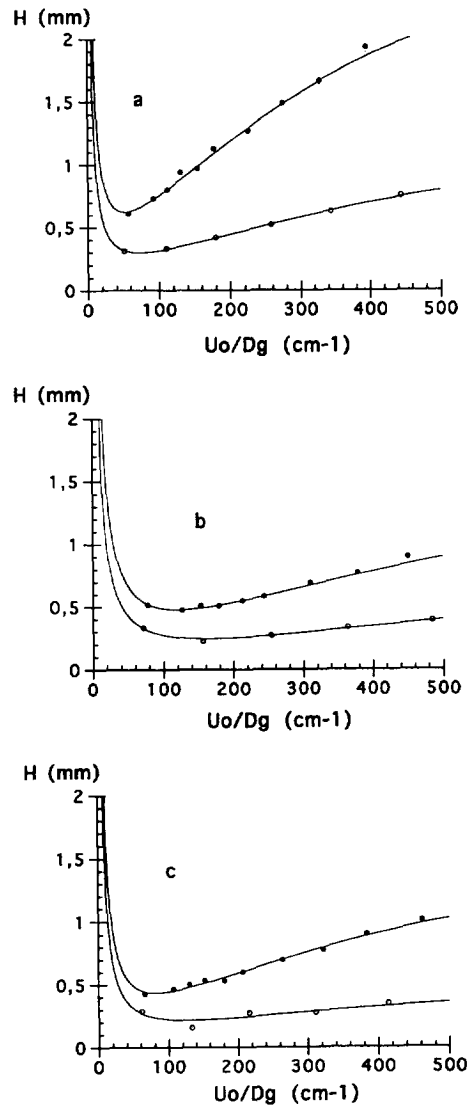


Fig. 3. HETP ( $H$ ) versus  $u_0/D_g$  at 30°C with (●) hydrogen and (○) nitrogen as carrier gases for retained compounds on column B (2- $\mu$ m film thickness). (a) Propionitrile; (b) hexane; (c) benzene.

By plotting  $H - H_c$  versus  $u_0/D_g$  it is possible to determine the  $C_1$  term. As shown in Fig. 4 for benzene, for instance, when the corrective extra-column term is subtracted, the corrected plate heights almost coincide for both carrier gases with column A of small liquid film thickness. The  $C_1$  term is seven times lower than that observed with the column coated with larger amounts of

Table 3

Coefficients of the plate-height equation for retained solutes at 30°C with  $B' = 2$  and  $D$  calculated from Eq. 4 with  $D_{\text{methane}} = 0.09 \cdot 10^{-4} \text{ s}^2/\text{cm}$

Column	Solute	$k'$	$C'_s$ (s)	$C_1$ (s)	$D$ ( $\text{s}^2/\text{cm}$ )	$D_1$ ( $\text{cm}^2/\text{s}$ )
Column A (0.25- $\mu\text{m}$ film thickness)	Propionitrile	1.02	$0.01 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1.8 \cdot 10^{-6}$	
	Hexane	1.04	$0.2 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$1.8 \cdot 10^{-6}$	
	Benzene	2.1	$0.1 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$0.78 \cdot 10^{-6}$	
Column B (2- $\mu\text{m}$ film thickness)	Propionitrile	7.3	$0.05 \cdot 10^{-4}$	$19 \cdot 10^{-4}$	$0.11 \cdot 10^{-6}$	$0.13 \cdot 10^{-4}$
	Hexane	8	$0.2 \cdot 10^{-4}$	$8.9 \cdot 10^{-4}$	$1.11 \cdot 10^{-6}$	$0.26 \cdot 10^{-4}$
	Benzene	16	$0.04 \cdot 10^{-4}$	$10.1 \cdot 10^{-4}$	$0.026 \cdot 10^{-6}$	$0.13 \cdot 10^{-4}$

Underlined numbers are the errors on C values.

stationary phase. The same behaviour is observed with the less retained solutes such as propionitrile or hexane.

At 30°C with column B of larger liquid film thickness, the extra-column effects are then considered as less important because the retention of the tested solutes are larger (Fig. 3). The corresponding plate-height curve shows that it is the diffusion in the stationary liquid phase that mainly explains the lower efficiency observed when hydrogen is used as the carrier gas. The  $C_1$  term of propionitrile is twice as large as that of hexane, although their  $k'$  values are close. A

good precision on  $C_1$  determination is obtained and the diffusion coefficient of the solutes in the liquid stationary phase  $D_1$  were calculated from the  $C_1$  term (Eq. 3). That of hexane is twice as small as that found with benzene and propionitrile. The  $D_1$  coefficients of propionitrile and benzene are similar, revealing a comparable retention mechanism.

From a practical point of view, the efficiency will be much improved by using a longer column, the instrumental contribution being inversely proportional to the column length. Since the corrected plate height is lower with the column of small film thickness, one will greatly improve the speed and efficiency of analysis by using longer columns of smaller liquid film thickness.

These results explain why in the analytical separations a longer column with a small amount of stationary phase is recommended. The efficiency is improved both by a greater column length and a less important contribution to band broadening, while the analysis speed is increased because of the lower  $k'$  values.

#### 4.2. Separation of complex mixtures

The theoretical study demonstrates the importance of the instrumental contribution when using  $\text{H}_2$  as the carrier gas over the efficiencies observed with column A. In order to lower this

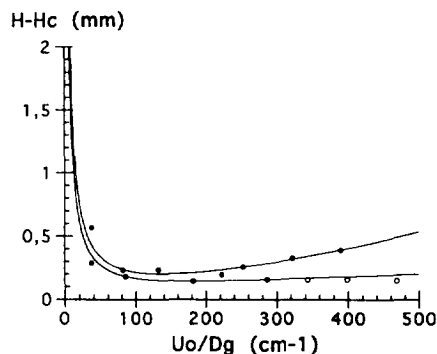


Fig. 4. Correction for extra-column effects. Plot of  $H - H_c$  versus  $u_0/D_g$  for benzene at 30°C with (●) hydrogen and (○) nitrogen as carrier gases on column A (0.25- $\mu\text{m}$  liquid film thickness).

contribution, a longer column was selected (column C) with a total length of 25 m, an I.D. of 0.15 mm and a film thickness of 0.25  $\mu\text{m}$ . Another column having a low instrumental contribution and a length of 12 m (column B) was also used for separating complex mixtures. Analytical separation studies were thus carried out on columns B and C (Fig. 5). Temperature programming was used for both columns in order to shorten the overall analysis time. The low thermal bleeding of the BPX5 columns allows us to use such programming.

The separation of  $C_1$ – $C_6$  hydrocarbons,  $C_1$ – $C_4$  nitriles and some polycyclic aromatic hydrocarbons (PAH) on column C is presented in Fig. 5a. Analytical resolution is achieved for heavy hydrocarbons (above  $C_4$ ), for all nitriles studied and PAH. The analysis time never exceeds 7 min. However, some co-elutions are observed with light hydrocarbons, particularly  $C_2$ .

The separation of  $C_1$ – $C_6$  hydrocarbons,  $C_1$ – $C_4$  nitriles and some PAH on column B is presented in Fig. 5b. The greater film thickness allows a better separation of the light hydrocarbons. The co-elution of methane and  $C_2$  hydrocarbons and the co-elution of ethane and the unsaturated  $C_2$  hydrocarbons have been resolved. However, the co-elution of ethene and ethyne is still observed. Analytical resolution was also achieved for cyanogen, propene and propane, for propyne and allene and for 2-butynitrile, benzene and cyclohexane, with some inversion between the elution times of these compounds. HCN (not injected on column C), is co-eluted with propane and allene. Three new compounds (octane, ethylbenzene and xylene) were also injected as representative of heavy hydrocarbons and PAH, respectively; the analysis time still remains shorter than 10 min.

We also measured the retention indices  $I(i)$  (Table 4), of most of the compounds studied in order to ascertain the behavioral pattern of the column in connection with these solutes. The following equation was used:

$$I(i) = 100 \cdot \frac{\log t'_{R(i)} - \log t'_{R(P_z)}}{\log t'_{R(P_{z+1})} - \log t'_{R(P_z)}} + 100Z \quad (6)$$

where  $t'_R$  is the relative retention time,  $P_z$  and  $P_{z+1}$  correspond to paraffins with  $z$  and  $z+1$  carbon atoms, respectively, and  $i$  corresponds to a solute, the retention time of which is between that of  $P_z$  and  $P_{z+1}$ .

These retention indices at 30°C (Table 4) vary linearly with the carbon number of the solute for a given chemical family. It should be noted that these experimental data are highly reproducible for all solutes, the relative standard deviation being less than 0.5%.

## 5. Conclusion

This study has shown that BPX5 columns give a very high resolution for nitriles and confirms the general behaviour of these columns for polar compounds. Consequently, the adsorption of these polar compounds on the stationary phase surface does not change its chromatographic behaviour relative to hydrocarbons. Such columns could be suitable for use in GC–MS studies. Both columns B and C offer a good separation power for saturated and unsaturated hydrocarbons, PAH and nitriles, in a relatively short time, but require temperature programming. Such conditions are not convenient for space GC instrumentation, because they increase markedly the duration of the analytical cycle and the complexity of the instrument and its software. In fact, in the case of the Titan probe, the use of a GC–MS instrument reduces the importance of co-elution problems, especially if the co-eluted compounds have well differentiated chemical properties and consequently different mass fragmentations. This is the case with HCN and propene. Columns B and C are both compatible within the constraints of the Cassini–Huygens mission (temperature between 30 and 100°C, flow-rate about 0.3–0.4 ml min<sup>-1</sup>, analysis time shorter than 10 min and column head pressure between 0.7 and 0.8 bar). A good separation of heavy hydrocarbons and nitriles is achieved on column C but its length of 25 m is far too great and cumbersome. The length of column B is acceptable and a better analytical resolution is achieved for light hydrocarbons.

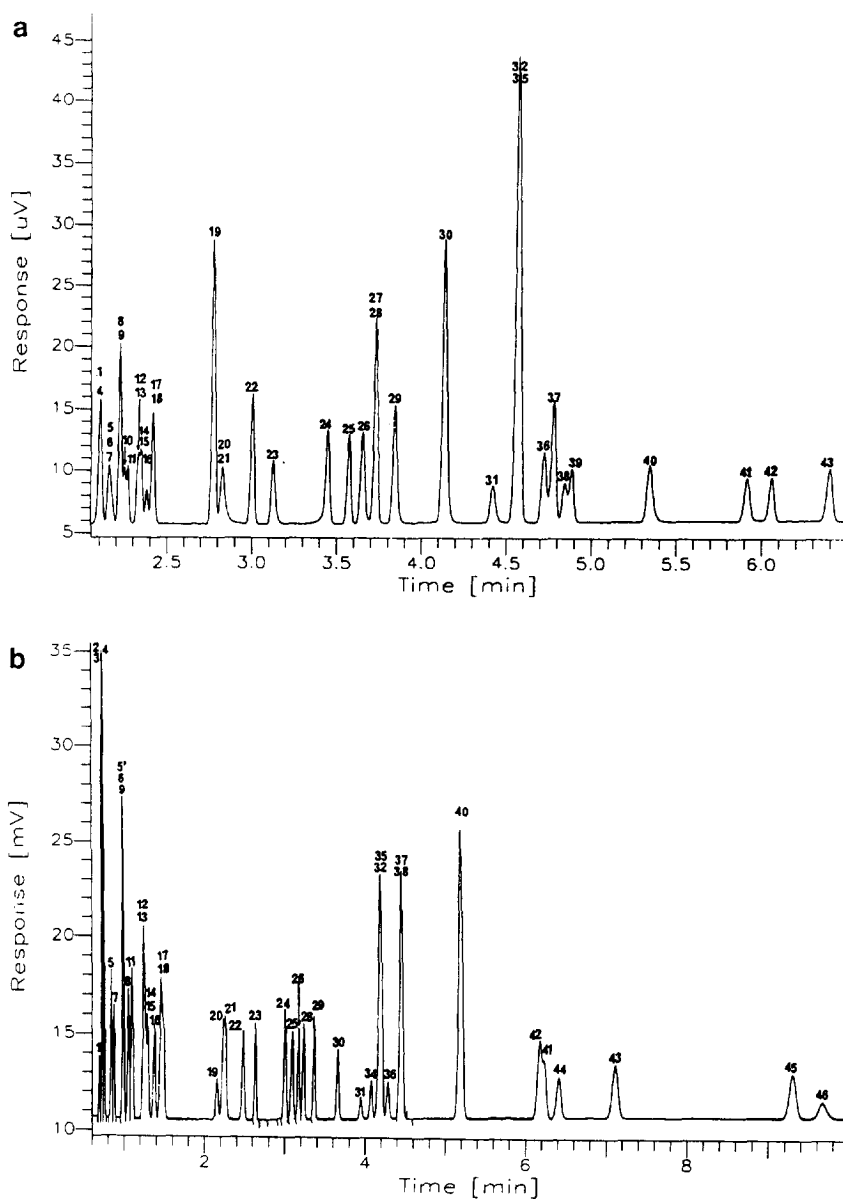


Fig. 5. GC analysis of a gaseous mixture of  $C_1$ - $C_6$  hydrocarbons, PAH and  $C_1$ - $C_4$  nitriles. (a) On a  $25 \text{ m} \times 0.15 \text{ mm}$  I.D. BPX5 ( $d_f = 0.25 \text{ }\mu\text{m}$ ) fused-silica WCOT column. Temperature, isothermal for 1.5 min at  $30^\circ\text{C}$ , then increased at  $30^\circ\text{C}/\text{min}$  to  $100^\circ\text{C}$ ; carrier gas,  $\text{H}_2$ ; outlet flow-rate,  $0.33 \text{ ml}/\text{min}$ ; inlet pressure,  $0.8 \text{ bar}$ . (b) On a  $12 \text{ m} \times 0.15 \text{ mm}$  I.D. BPX5 ( $d_f = 2 \text{ }\mu\text{m}$ ) fused-silica WCOT column. Temperature, isothermal for 1.6 min at  $40^\circ\text{C}$ , then increased at  $45^\circ\text{C}/\text{min}$  to  $100^\circ\text{C}$ ; carrier gas,  $\text{H}_2$ ; outlet flow-rate,  $0.44 \text{ ml}/\text{min}$ ; inlet pressure,  $0.70 \text{ bar}$ . Peaks: 1 = methane; 2 = ethene; 3 = ethyne; 4 = ethane; 5 = cyanogen; 5' = hydrocyanic acid; 6 = propene; 7 = propane; 8 = propyne; 9 = allene; 10 = cyclopropane; 11 = isobutane; 12 = 1-butene; 13 = isobutene; 14 = butadiene; 15 = butane; 16 = *trans*-2-butene; 17 = butyne; 18 = *cis*-2-butene; 19 = 1-pentene; 20 = acetonitrile; 21 = pentane; 22 = 2-methyl-2-butene; 23 = acrylonitrile; 24 = cyclopentane; 25 = 3-methylpentane; 26 = propionitrile; 27 = 1-hexene; 28 = hexane; 29 = methacrylonitrile; 30 = isobutyronitrile; 31 = *cis*- or *trans*-crotononitrile; 32 = 3-butenenitrile; 33 = 2-butyne; 34 = benzene; 35 = cyclohexane; 36 = butyronitrile; 37 = cyclohexene; 38 = *cis*- or *trans*-crotononitrile; 39 = *n*-heptane; 40 = cyclopropanecarbonitrile; 41 = toluene; 42 = 1-octene; 43 = cycloheptane; 44 = octane; 45 = ethylbenzene; 46 = xylene.



Table 4  
Retention indices of hydrocarbons and nitriles on columns B and C at 30°C

Solute	Retention index	
	Column B	Column C
Propane	300	300
Cyclopropane	356	357
Propyne	339	357
Butane	400	400
1,3-Butadiene	400	400
<i>trans</i> -2-Butene	413	414
<i>cis</i> -2-Butene	426	431
1-Butene	394	394
Isobutene	394	368
1-Pentene	480	510
Acetonitrile	504	500
<i>n</i> -Pentane	500	500
Acrylonitrile	540	544
Cyclopentane	572	573
Propionitrile	595	592
Hexane	600	600
Methacrylonitrile	614	611
Isobutyronitrile	643	638
<i>cis</i> - Or <i>trans</i> -crotonitrile	664	661
3-Butenenitrile	680	673
Butyronitrile	694	686
<i>cis</i> - Or <i>trans</i> -crotonitrile	699	696
Cyclohexene	689	685
Heptane	700	700

However, ethene and ethyne are still co-eluted. The theoretical study shows the importance of increasing retention times in order to decrease the instrumental contribution to band broadening. Therefore, column B may clearly be selected as one of the chromatographic columns of the GC instrument to be shipped on the Titan probe.

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