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Gas chromatography of Titan's atmosphere VII. Analysis of low molecular weight hydrocarbons and nitriles with cyanopropylphenyl dimethyl polysiloxane capillary columns

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Abstract

Commercial capillary columns having different bonded cyanopropylphenyl/dimethyl polysiloxane ratios were studied for the gas chromatographic (GC) separation of low molecular weight nitriles, saturated and unsaturated hydrocarbons, which are plausible constituents of Titan's atmosphere. Columns having different diameters and film thicknesses were compared in terms of plate height. The data presented show that the columns of small internal diameter coated with a thin stationary phase film provide the best efficiency for the shortest analysis time. These columns are compatible with the requirements of space instrumentation.

Keywords: Titan, atmosphere; Capillary columns; Cyanopropylphenyl dimethyl polysiloxane; Stationary phases, GC; Hydrocarbons; Nitriles

1. Introduction

As reported in previous papers in this series [1–5], we are currently studying gas chromatographic (GC) columns that could provide the separation of most of Titan's atmospheric constituents, given the constraints of space instrumentation within the framework of the Cassini-Huygens mission [6,7]. We previously described the chromatographic behaviour of 5% diphenyl, 95% dimethyl polysiloxane (BPX5) columns in the separation of C₁–C₈ hydrocarbons and C₁–C₄ nitriles [5]. However, there is a need for other selective phases to resolve C₂ hydrocarbons

that cannot be separated on non-polar or lightly-polar phases.

We present here the results obtained for the same type of solutes with cyanopropylphenyl dimethyl polysiloxane wall-coated open tubular (WCOT) capillary columns. As the polarity of the stationary phase increases, most polar solutes are retained longer; so, by decreasing the column temperature we can separate light hydrocarbons (C₂). Furthermore, some of these columns were customized to the Huygens GC–MS instrument. They are WCOT capillary columns of 6% cyanopropylphenyl, 94% dimethyl polysiloxane (Restek MXT1301) and 14% cyanopropylphenyl, 86% dimethyl polysiloxane (Restek MXT1701). Such MXT® columns which use silanized stainless-steel seem to offer many advan-

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tages. With their inert metal column, they can be operated at higher temperatures than usual fused-silica without the fear of breakage. Both fused-silica and stainless-steel MXT® columns offer a high degree of inertness and excellent flexibility. Nevertheless, stainless MXT® columns have the added advantage of being resistant to abrasion and scratches at any GC operating temperature. However, no detailed studies of these columns, including Van Deemter curves, have ever been reported. In addition, no data were available on the behaviour of these columns concerning the separation of solutes as indicated above and, more generally, on the general chromatographic behaviour of these columns.

The purpose of the investigations reported in this paper is to provide such comparative data. To achieve this objective, we measured a number of chromatographic parameters on cyanopropylphenyl dimethyl polysiloxane WCOT capillary columns of different diameters and film thicknesses. The chromatograms of a gaseous mixture of C₁–C₄ nitriles, C₁–C₈ hydrocarbons, benzene and toluene are also presented.

2. Experimental

2.1. Chromatography

The gas chromatograph was a Perkin-Elmer autosystem (USA) equipped with a flame ionisation detector (FID), a thermal conductivity detector (TCD) and a temperature programmer. The chromatograph was connected to a PE-Nelson Turbochrom data acquisition system. The detection time constant was set at 50 ms. The following temperature conditions were used: injector=220°C and detector=

240°C. A split mode was used (with a splitting ratio of 110:1 with the 0.28 mm I.D. columns and 400:1 with the 0.15 mm I.D. columns). Sampling techniques were the same as described previously [5]. The solute vapours were injected through the septum with a 1-ml Hamilton gas syringe equipped with a gas-tight stopcock. Hydrogen was used as the carrier gas.

Table 1 lists the columns used in this study. The column phase ratio, β , is equal to the ratio of the gas phase volume to the stationary phase liquid volume. The columns were obtained from Restek (USA). A specific software (PE-Nelson) was developed for this study and used for determining the height equivalent to a theoretical plate (HETP). Data for HETP vs. linear velocity of the carrier gas were obtained at the operating temperatures for the selected solutes by injecting a mixture of the test solutes with methane as the non-retained compound.

2.2. Analytes

Ethylacetylene (1-butyne) was obtained from Baker (Phillipsburg, NJ, USA). 1-3 Butadiene, pentane, hexane and toluene were obtained from Aldrich (Strasbourg, France). All the other C₁–C₄ hydrocarbons tested were purchased from Alphagaz-1' Air Liquide (Bois d'Arcy, France) and were at least 99% pure. 2-Methyl-2-butene, 1-hexene, benzene, cyclohexene, heptane, cycloheptane, octane, acetonitrile, acrylonitrile and propionitrile were obtained from Prolabo (Paris, France). 1-Pentene and 3-methylpentane was obtained from Fluka (Buchs, Switzerland). Butyronitrile, isobutyronitrile, methacrylonitrile and crotonitrile (mixture of *cis* and *trans* isomers) and 3-butenitrile were obtained from Riedel de Haën (Hannover, Germany).

Table 1
Characteristics of the MXT capillary columns

Stationary phase	% Cyanopropylphenyl/dimethylpolysiloxane					
	6/94			14/86		
Column	1301A	1301B	1301C	1701A	1701B	1701C
Film thickness (μm)	2.9	1.5	5.5	0.6	1.5	5.5
I.D. (mm)	0.15	0.28	0.28	0.15	0.28	0.28
Phase ratio (β)	12.9	46.7	12.7	62.5	46.7	12.7
Column length (m)	10	15	15	10	15	15

3. Results and discussion

3.1. Efficiency

Fig. 1A shows the Van Deemter curves obtained for benzene at 60°C, with the three different MXT1301 columns coated with 6% cyanopropylphenyl and 94% dimethyl polysiloxane. The MXT1301C column coated with a thick stationary phase film (5.5 μm) exhibits a minimum HETP of 1.9 mm located at a linear velocity of about (10 cm/s) which corresponds to a mean outlet flow-rate of 0.9 ml/min and a relative inlet pressure of 0.2 bar.

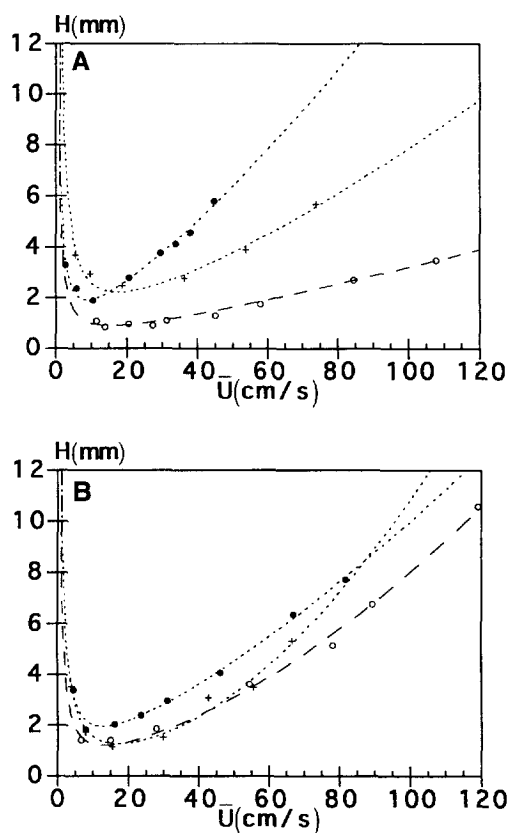


Fig. 1. Plot of the height equivalent to a theoretical plate (H) of benzene versus the mean linear velocity (\bar{U}) of the carrier gas (H_2) at 60°C on: (A) columns MXT 1301: + = column MXT1301A (2.9 μm , 0.15 mm I.D.), \circ = column MXT1301B (1.5 μm , 0.28 mm I.D.), \bullet = column MXT1301C (5.5 μm , 0.28 mm I.D.); (B) columns MXT 1701: + = column MXT1701A (0.6 μm , 0.15 mm I.D.), \circ = column MXT1701B (1.5 μm , 0.28 mm I.D.), \bullet = column MXT1701C (5.5 μm , 0.28 mm I.D.).

The curve shows a sharp minimum in the optimum region. Columns MXT1301A and MXT1301B exhibit a minimum of HETP of 2.4 and 1.2 mm respectively, with a large domain of linear velocities. Column MXT1301B, of lowest film thickness, proved to be more efficient than MXT1301A of smaller internal diameter but having a thicker film.

Fig. 1B shows the HETP plots for the more polar MXT1701 columns (A, B and C) coated with 14% cyanopropylphenyl and 86% dimethyl polysiloxane. Only the data related to benzene are presented, at 60°C as an example. The minimum HETP (1.2 and 2 mm) for the curves obtained with columns MXT1701B and MXT1701C, respectively, of the same internal diameter (0.28 mm) is located at about 12 cm/s linear velocity, corresponding to a mean outlet flow-rate of 1.3 ml/min and a relative inlet pressure of 0.2 bar. A lower efficiency is found for column (MXT1701C) with a thicker film (5.5 μm). The column with a small internal diameter (0.15 mm) and thin film thickness (column MXT1701B) gave the best efficiency (HETP 1.1 mm with benzene) among the columns evaluated, and the minimum of the curve is relatively flat. The results are in agreement with the well-known behaviour [8]: the larger the diameter and the thicker the film, the steeper is the ascending part of the HETP vs. \bar{U} plot (the part corresponding to average linear gas velocities well above optimum). This means that with a smaller-diameter column one can work at relatively high velocities without significant deterioration of column efficiency.

The same conclusion follows when comparing the results related to columns MXT1301B, MXT1301C, and to columns MXT1701B and MXT1701C. With increasing film thickness, a large increase in the slope of the linear portion of the plate height curve is observed, at high velocities of the carrier gas. This shows that the mass transfer in the liquid stationary phase increases with the film thickness.

Table 2 summarizes the gas chromatographic properties of columns having the same stationary phase and internal diameter but different film thicknesses, using pentane, acetonitrile and benzene as test solutes. The best efficiency was obtained with columns having the lowest film thickness (1.5 μm). With pentane, minimum HETP values are 1.4 and 2.1 mm for 1301B and 1701B MXT columns,

Table 2

Retention factor k' , HETP_{min} and enthalpy of dissolution (ΔH) of pentane, acetonitrile and benzene on columns MXT1301B and C and 1701B and C at 60°C

Solute	Parameters	Column			
		MXT1301B	MXT1701B	MXT1301C	MXT1701C
Pentane	k'	0.6	0.4	1.9	1.4
	H_{\min} (mm)	1.4	2.1	3.1	3.1
	ΔH (KJ/mol)	-21.2	-20.9	-22.5	-20.7
Acetonitrile	k'	1.0	1.1	3.5	4.6
	H_{\min} (mm)	1.4	1.4	2.0	2.0
	ΔH (KJ/mol)	-24.0	-26.6	-25.5	-26.5
Benzene	k'	2.8	2.2	9.6	9.1
	H_{\min} (mm)	1.2	1.2	1.9	1.9
	ΔH (KJ/mol)	-27.3	-30.2	-27.1	-29.1

respectively, instead of 3.1 mm for the 5.5 μm film thickness columns. With acetonitrile, the best efficiency is also observed for columns MXT1301B and MXT1701B, with a minimum HETP of 1.4 mm. The same result is found for benzene with a minimum HETP of 1.2 mm on the columns of 1.5 μm film thickness [9].

3.2. Thermodynamics of retention

As a first approximation, the retention factor k' , related to a given solute, varies with temperature, according to the Clausius-Clapeyron equation [8]: $\ln k' = \Delta H_s / RT = \text{constant}$, where ΔH_s is the enthalpy of solution of the solute. As expected, linear relationships were obtained between $\ln k'$ and $1/T$ for the selected solutes on column MXT1301B (see Fig. 2). Similar plots (not shown here) were obtained on the other columns. The lines in Fig. 2 appear parallel, indicating that the solute enthalpies (of dissolution) for these compounds are nearly the same. A closer look reveals that the lines diverge slightly at low temperatures. This observation is in full agreement with the well known GC empirical law, i.e. GC separations are usually better at low temperatures [8].

The enthalpy of dissolution of the selected solutes listed in Table 2 were calculated from the plots, using a linear regression analysis. The data shows that the absolute values of the dissolution enthalpies increase when k' increases. For a given stationary phase there is no significant difference between the

adsorption enthalpies measured on the columns having two different film thickness. With a polar solute, such as acetonitrile, the absolute values of ΔH_s increases with increasing column polarity. The inverse phenomenon is observed with pentane. As expected, for a non-polar solute, the absolute value of the ΔH_s of pentane is larger with the less polar stationary phase (MXT1301) than that observed with the polar MXT1701 columns. This result agrees with classical behaviour of stationary phase and shows that the retention of alkanes on the polar stationary phase is not influenced by the adsorption at the liquid surface interface.

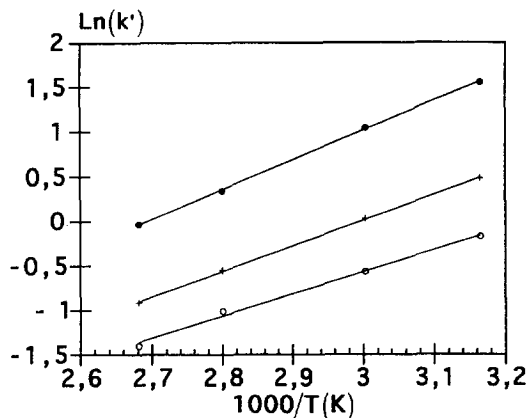


Fig. 2. Variation of the retention factor $\ln k'$ versus $1/T$: example of column MXT1301B. Solutes: (○) pentane, (+) acetonitrile, (●) benzene.

3.3. Analytical application

Fig. 3 shows the chromatograms of a complex mixture containing C_1 – C_8 hydrocarbons and C_1 – C_4 nitriles using columns MXT1301A, MXT1701A, MXT1301B and MXT1701C. All the chromatograms show a good separation of the heavy hydrocarbons and nitriles under the stipulated conditions. But the separation of C_2 hydrocarbons appears quite difficult to achieve, especially that of ethene and ethane. However, by lowering the temperature of the column down to values below 30°C , it was possible to obtain such a separation with MXT1301C and MXT1701C columns having the highest film thickness ($5.5\ \mu\text{m}$).

An example of such separation for light hydrocarbons (methane, ethene, ethane and ethyne) at 20°C , with an inlet pressure of about 0.05 bar, is shown in Fig. 4.

Fig. 3 provides a comparison of selectivity of the stationary phase 6% cyanopropylphenyl (1301) and 14% cyanopropylphenyl (1701). For the resolution of polar compounds (nitriles), the high polarity of 14% cyanopropylphenyl is needed. The co-elution of hexane and acrylonitrile observed with column MXT1301A (Fig. 3A) is suppressed with column MXT1701C (Fig. 3D), although both columns MXT1301A and MXT1701C have about the same β (12.7–12.9). Chromatograms obtained with columns

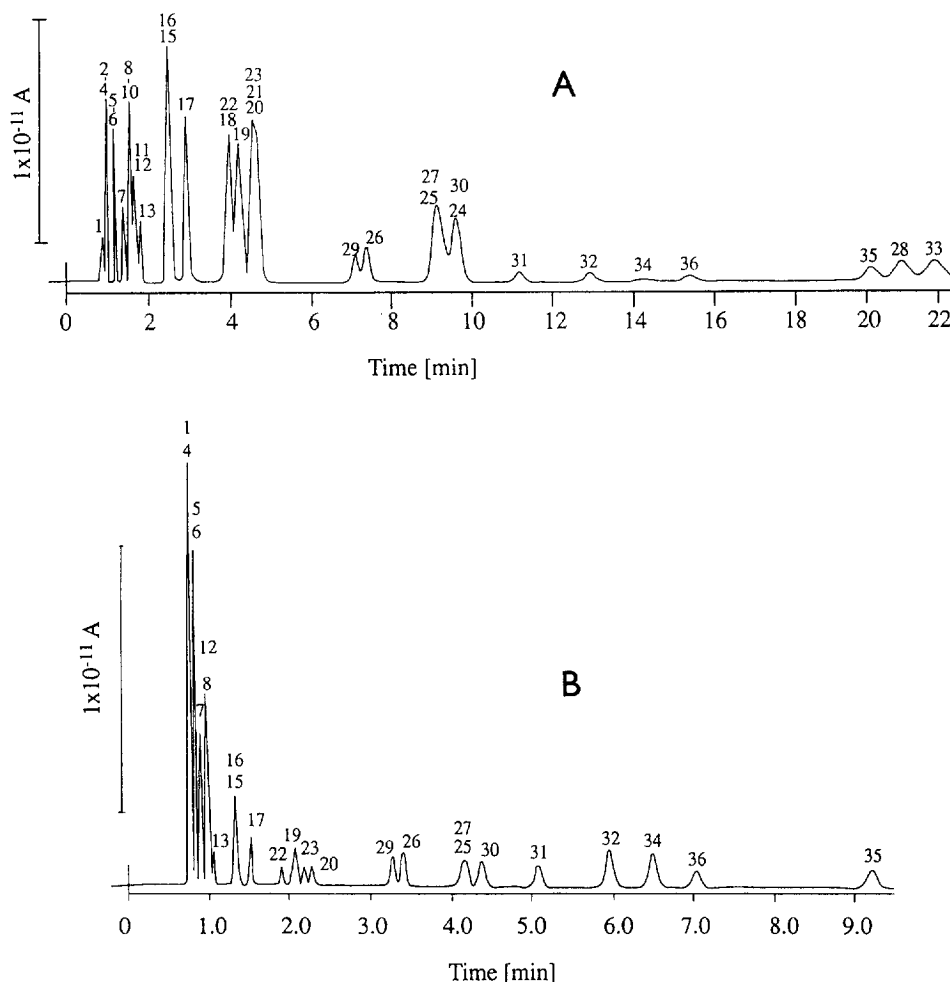


Fig. 3. (continued on p. 68)

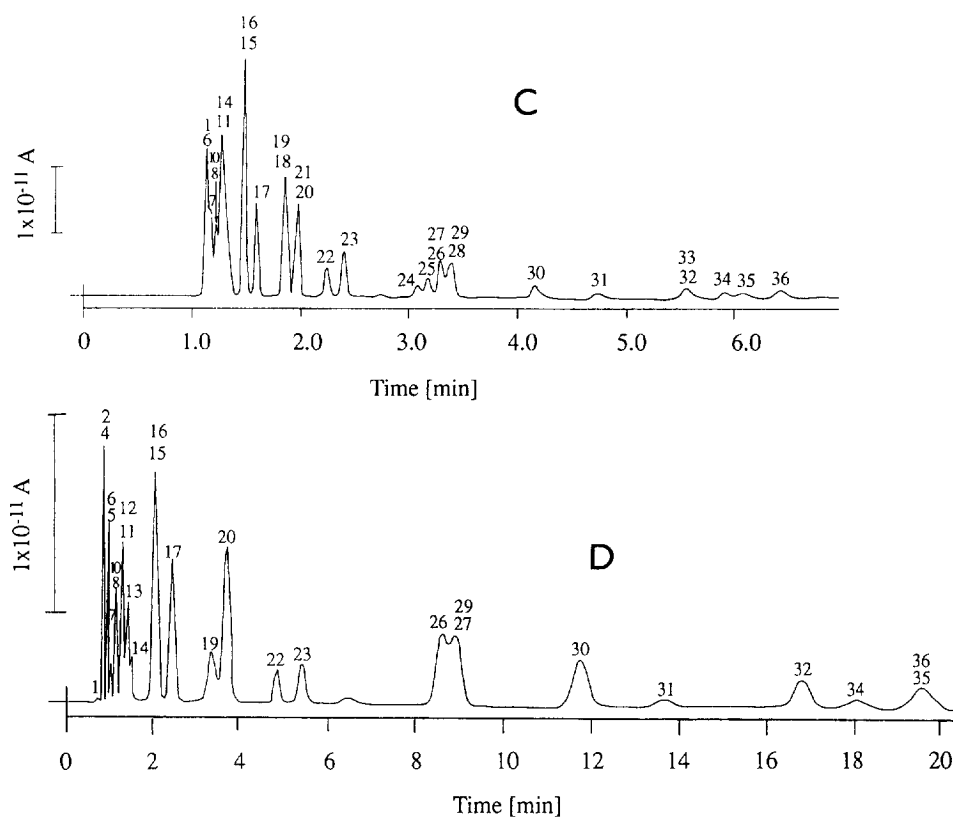


Fig. 3. GC analysis (isothermal 60°C; carrier gas H₂) of a gaseous mixture of C₁–C₈ hydrocarbons, PAH and C₁–C₄ nitriles. (A) Column XT1301A; outlet flow-rate, 0.33 ml/min; inlet pressure, 0.2 bar; split mode (400:1). (B) Column MXT 1301B; outlet flow-rate, 1.59 ml/min; inlet pressure, 0.2 bar; split mode (110:1). (C) Column MXT 1701A; outlet flow-rate, 0.33 ml/min; inlet pressure, 0.2 bar; split mode (400:1). (D) Column MXT 1701C; outlet flow-rate, 1.33 ml/min; inlet pressure, 0.2 bar; split mode (110:1). Peaks: 1=methane, 2=ethene, 3=ethane, 4=ethyne, 5=propene, 6=propane, 7=isobutane, 8=isobutene, 9=butane, 10=1-butene, 11=*trans*-2-butene, 12=butadiene, 13=*cis*-2-butene, 14=butyne, 15=pentane, 16=1-pentene, 17=2-methyl-2-butene, 18=cyclopentane, 19=3-methylpentane, 20=hexane, 21=1-hexene, 22=acetonitrile, 23=acrylonitrile, 24=*n*-heptane, 25=cyclohexene, 26=methacrylonitrile, 27=benzene, 28=cycloheptane, 29=propionitrile, 30=isobutyronitrile, 31=*cis*- or *trans*-crotononitrile, 32=3-butenitrile, 33=octane, 34=butyronitrile, 35=toluene, 36=*trans*- or *cis*-crotononitrile.

MXT1301A and MXT1301B show that the retention times of hydrocarbons correspond roughly to their boiling points and increase with the number of carbon atoms in their structure. Apolar hydrocarbons were less retained on the columns coated with the stationary phase (1701) than on the columns coated with (1301). The chromatographic behaviour of nitriles is somewhat similar in spite of the polarity of the CN group. The retention times of all the studied nitriles increase with the number of carbon atoms, whatever the nature of the carbon chain (saturated, ethylenic or acetylenic). With the columns MXT1701A and MXT1701C, there is an exception since methacrylonitrile is eluted before propionitrile

(Fig. 3C and D). It should be emphasized that the whole analysis takes only 10 min with columns MXT1701A and MXT1301B with larger β values (46.7–62.7). For the same test mixture, columns were less retained on the columns coated with the stationary phase having smaller β values (12.7–12.9) (MXT1301A, 1301C and MXT 1701C) or larger film thickness provide an analysis time of more than 15 min.

4. Conclusion

The cyanopropylphenyl dimethyl polysiloxane columns of medium polarity can be used to analyse nitrile compounds with a good selectivity while

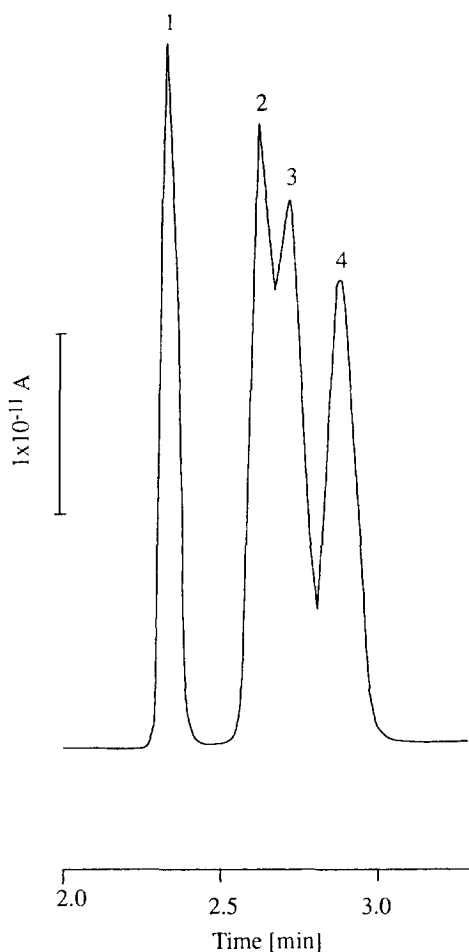


Fig. 4. GC analysis of gaseous mixture of methane (1), ethene (2), ethane (3), and ethyne (4) on a $15 \text{ m} \times 0.28 \text{ mm}$ I.D. MXT 1701 ($d_f = 5.5 \text{ } \mu\text{m}$) WCOT column. Temperature, isothermal at 20°C ; carrier gas, H_2 ; inlet pressure, 0.05 bar.

offering a good separation of the saturated and unsaturated hydrocarbons. The MXT capillary columns can be used advantageously for analysing in a relatively short time mixtures of both low molecular weight hydrocarbons and nitriles. Only the separation of C_2 hydrocarbons is difficult and requires sub-ambient temperature.

The data presented in this work showed that the

columns with lowest film thickness and smallest column diameter provide the best efficiencies in the shortest analysis time: there is no significant loss of efficiency when operated at high velocities. Except for the lighter hydrocarbons, such conditions are convenient for space instrumentation, considering the constraints imposed by the specification of Cassini-Huygens mission, specially those of temperature and pressure: the GC column temperature in the range 30°C – 70°C , no temperature programming because of the limited energy resources, a carrier gas flow-rate smaller than 1 ml/min , and inlet relative pressure between 0.6 and 0.9 bar. The 1701 type column of low film thickness and small internal diameter seems the most appropriate for the analysis of Titan's atmosphere.

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