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GAS CHROMATOGRAPHY OF TITAN'S ATMOSPHERE

I. ANALYSIS OF LOW-MOLECULAR-WEIGHT HYDROCARBONS AND NITRILES WITH A PORAPLOT Q POROUS POLYMER COATED OPEN-TUBULAR CAPILLARY COLUMN

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SUMMARY

A PoraPLOT Q column was utilized for gas chromatographic analyses of various mixtures of low-molecular-weight saturated and unsaturated hydrocarbons and nitriles, which are plausible constituents of the atmosphere of Titan, the largest satellite of Saturn. This capillary column coated with styrene–divinylbenzene copolymer has a chromatographic behaviour similar to that of a Porapak Q packed column when analyzing these compounds. Its chromatographic behaviour however, is drastically improved by its much higher resolving power. With more than 1000 theoretical plates per metre for nitriles, this column offers a rapid separation of these compounds from C_1–C_8 hydrocarbons, even under isothermal conditions. It appears to be a viable choice for the gas chromatograph–mass spectrometer aboard the Huygens probe of the Cassini mission which is planned to explore Titan's atmosphere.

INTRODUCTION

For the development of space missions involving gas chromatography (GC), rapid GC analyses with good resolution and compatible with the requirements of space instrumentation and planetary missions are now needed. This is the case in particular with the joint NASA-ESA Cassini mission to the Saturn system, planned to be launched in 1996[1].

Cassini and the in situ analysis of Titan's atmosphere

One of the main objectives of the Cassini mission is to explore the atmosphere of Titan, the largest satellite of Saturn, from an atmospheric probe called Huygens. Several of the nine scientific instruments aboard will allow the *in situ* analysis of Titan's atmosphere during the 3-h descent of the probe. These include a gas chromatograph operating in two possible modes: not coupled or coupled to a mass spectrometer. It will be able to analyze gases either directly sampled from the atmosphere, or provided after pyrolysis by an aerosol collector-pyrolyzer experiment[1].

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Titan's atmosphere is mainly composed of nitrogen with a noticeable mole fraction of methane and the likely presence of argon. Several minor constituents have already been detected: at the 1000–10 ppmv level, H_2, CO and C_2H_6; below 10 ppmv, saturated C_2–C_3 hydrocarbons, ethylene, acetylene, propyne and diacetylene, HCN, C_2N_2, HC_3N and CO_2. Several other hydrocarbons and nitriles are expected to be present in this environment[2].

GC requirements

The GC experiment aboard Huygens must be able to analyze simultaneously C_1–C_8 hydrocarbons, C_1–C_4 nitriles and dinitriles, CO, H_2 and CO_2, in the presence of large amounts of N_2 and Ar, within a short enough time frame (less than about 15 min) necessary for several analyses.

However, it must offer a resolution high enough to allow the separation of most of these expected atmospheric constituents, with a column capacity allowing their quantitative analysis in an high dynamic range of concentration.

In order to solve this problem, we are currently developing chromatographic studies in two directions: the use of small and short columns packed with microparticles, and the use of capillary columns. We plan to present the different results of such studies in a series of articles. This article, the first in the series, is devoted to the study of a PLOT (porous-layer open-tubular) capillary column[3].

Capillary GC columns have not yet been used in space instrumentation. However, they can offer a good resolution within a relatively short time of analysis, if they are not too long, and their use simplifies the coupling of the gas chromatograph with a mass spectrometer. With PLOT capillary columns one can combine these advantages with the chromatographic capabilities of adsorption materials such as porous polymers, which can be used as column coatings.

Porous polymers have been largely utilized as packing materials in GC. In particular, styrene polymers or styrene–divinylbenzene or ethylvinylbenzene copolymer packings such as Chromosorb 103 (Manville, Lompoc, CA, U.S.A.) or Porapak Q (Waters, Milford, MA, U.S.A.) have been used intensively in packed GC columns to analyze gaseous mixtures including hydrocarbons and nitriles[4–7]. This type of adsorbent has also been used as a packing material in space gas chromatographs, such as that of the "gas exchange" experiment of the Viking Mission to Mars[8] and the Pioneer-Venus sounder probe gas chromatograph[9,10].

PoraPLOT Q

A fused-silica PLOT capillary column coated with the same kind of porous polymer (styrene–divinylbenzene) named PoraPLOT Q has recently been commercialized (Chrompack, The Netherlands). Detailed studies of the characteristics and chromatographic performances of this column, and comparisons with those of Porapak Q packed columns, have already been published[11,12]. PoraPLOT Q seems to offer the advantages of the Porapak Q column, such as the possibility of separation of permanent gases, and volatile polar and apolar organic compounds, with the high resolution of a capillary column. However, no data were available on the separation of nitriles and very few on that of alkynes with this PLOT column.

We found the close similarities between this capillary column and the column packed with Porapak Q to be particularly interesting. For this reason, we decided to test the capabilities of PoraPLOT Q in analyzing nitriles and mixtures of nitriles and hydrocarbons (alkanes, alkenes and alkynes). This first paper in the series presents the main results of the above-mentioned study. The next papers will be devoted to similar studies carried out with a Al_2O_3–KCl PLOT capillary column, and with short columns packed with micro-particles.

EXPERIMENTAL

Column and gas chromatograph

The PoraPLOT Q column (Chrompack, Netherlands) was a 10 m × 0.32 mm I.D. PLOT fused-silica capillary column coated with a 10-μm film of styrene–divinylbenzene copolymer. It was mounted in a split mode (splitter ratio: 100/1) on a Carlo Erba Model Fractovap 2150 gas chromatograph equipped with a linear temperature programmer Model LT 232, a flame ionization detector and a Shimadzu Model IRC-1B integrator recorder.

The following conditions were chosen for all the presented results: injector temperature = detector temperature = 225°C. The carrier gas was hydrogen.

Sampling

Both liquid and gas mixtures have been tested. The complex gas mixtures of standard volatile hydrocarbons and nitriles were prepared in a sampling glass reservoir equipped with a septum. This reservoir was connected to a glass vacuum line. It was initially evacuated and isolated from the line. Then constituents of the mixture were successively introduced in the reservoir. This was done by expanding a known and adequate pressure of a pure constituent from the known volume of the vacuum line into the additional known volume of the reservoir (where the pressure before this expansion was also known). Nitriles which are liquids at room temperature were added to the gaseous mixture (at a pressure lower than their saturation vapour pressure) by introducing a calculated volume of liquid in the sampling reservoir through its septum with an Hamilton liquid syringe. The final mixture was sampled from the reservoir with a 1-ml Hamilton gas syringe equipped with a gas-tight stopcock. The concentration of each constituent in the gaseous sample was decreased by a known factor by dilution in air in the syringe itself.

When using liquid mixtures the constituents were diluted in methanol. The final liquid mixture was sampled with a 0.5-μl Hamilton liquid syringe.

Reagents

Allene and cyanogen were from Matheson (East Rutherford, NJ, U.S.A.). Methylacetylene (propyne) and ethylacetylene (1-butyne) were from Baker (Phillipsburg, NJ, U.S.A.). 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.

Pentanes, 2-methyl-2-butene, 1-hexene, *n*-hexane, benzene, cyclohexane, cyclohexene, acetonitrile, acrylonitrile and propionitrile were obtained from Prolabo (Paris, France). 1-Pentene and 3-methylpentane were from Fluka (Buchs, Switzerland). Butyronitrile, isobutyronitrile, methacrylonitrile, cyclopropanecarbonitrile, crotononitrile (mixture of *cis* and *trans* isomers) and 3-butenenitrile were from Riedel-de-Haën (Hannover, F.R.G.).

Hydrogen cyanide was prepared by acidification of sodium cyanide with sulphuric acid[13]. Cyanoacetylene (propynenitrile) was synthesized by the dehydration of propynoic acid amide, and cyanopropyne (2-butynenitrile) was synthesized by the cyanidation of 3-chloropropyne. Details of these syntheses have been published elsewhere[14].

Determination of Van Deemter curves

To determine experimentally the dependence of the height equivalent to a theoretical plate, H, for selected solutes on the linear velocity of the carrier gas, u, we injected the selected solutes and methane at different inlet pressures of the carrier gas. The outlet flow-rate was measured with a soap flow meter.

The value of u was calculated from the relationship $u = L/t_m$, where L is the length of the column and t_m is the retention time of methane.

For the solute selected, H was calculated from the classical relationship

$$H = \frac{L}{5.54} \frac{\omega^2}{(t_R - t_m)^2}$$

where t_R is the retention time of the solute and ω is the half width of its chromatographic peak assumed to be gaussian.

RESULTS AND DISCUSSION

In order to characterize quantitatively the performances of the column and to use optimized flow-rate conditions for analyzing mixtures of hydrocarbons and nitriles, we have determined Van Deemter curves at different temperatures. In the

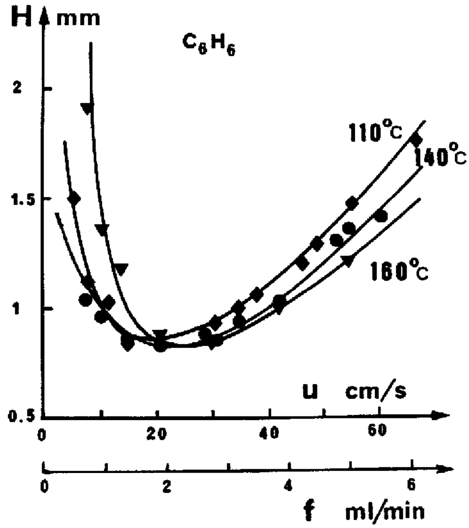

Fig. 1. Benzene: variation of H with the mean linear velocity, u, and outlet flow-rate, f, of the carrier gas (H_2) at 110, 140 and 160°C on a 0.32 mm I.D. PoraPLOT Q fused-silica column (thickness 10 μm). Total quantity injected: 2.2 (110°C) or 1.1 nmol (140 and 160°C). Split mode (100/1).

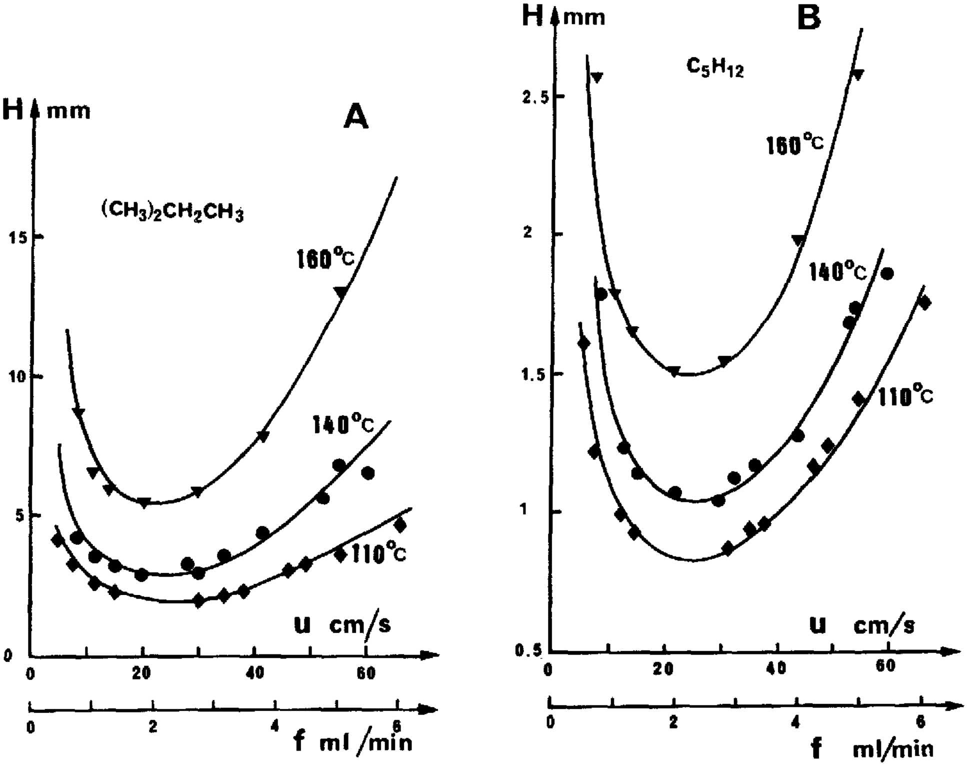

Fig. 2. Isobutane (A) and *n*-pentane (B): variation of *H* with *u* and *f* as in Fig. 1. Total quantity injected: isobutane, 0.9 nmol; *n*-pentane, 0.6 nmol.

following studies, hydrogen was used as a carrier gas, because for equivalent *H* values, it can provide faster analyses (the retention times are about two times smaller with H_2 as a carrier gas than with He). In addition, the use of H_2 facilitates the coupling with a mass spectrometer.

The results for benzene, isobutane, pentane, acetonitrile and acrylonitrile are given in Figs. 1, 2A, B, 3A and B respectively, for column temperatures of 110, 140 and 160°C. They have been obtained by injecting constant quantities of solute (0.6 to less than 4 nmol) in the injector of the gas chromatograph. In the case of benzene, the value of *H* is not very temperature dependent, at least for *u* values higher than about 10 cm/s (corresponding to an outlet flow-rate of about 1 ml/min). For a given flow-rate, a slight decrease in *H* is observed when the temperature is increased. The minimum of the curve is relatively flat. It is reached for linear velocities of about 20 cm/s (flow-rate of about 2 ml/min). Its value is 0.87 mm, corresponding to 1150 theoretical plates per metre.

The curves obtained with alkanes (Fig. 2A and B) differ significantly from that of benzene. First, *H* is temperature dependent: for the same carrier gas velocity, *H* markedly increases with temperature. It is at least two times higher at 160 than at 110°C. With butane, the minimum value of *H* is about 1.9 mm at 110°C. It is 2.8 mm at 140°C and more than 5 mm at 160°C. With pentane, the corresponding values are about three times smaller: 0.8, 0.9 and 1.5 mm at 110, 140 and 160°C respectively. For

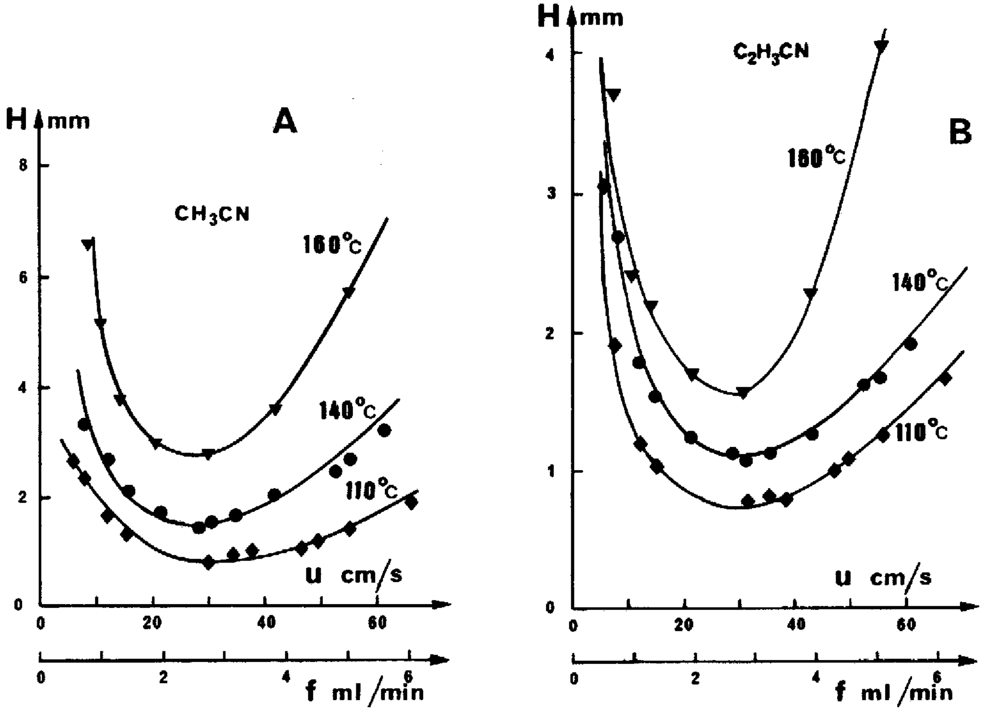

Fig. 3. Acetonitrile (A) and acrylonitrile (B): variation of H with u and f as in Fig. 1. Total quantity injected: acetonitrile, 3.8 nmol; acrylonitrile, 3 (110°C) or 1.5 nmol (140 and 160°C).

these two solutes, the minimum of H is obtained for a u value of about 25 cm/s. In both cases, in the range of temperatures studied, the minimum corresponds to a linear velocity of about 30 cm/s (about 2.5 ml/min). A similar behaviour is observed in the case of nitriles (Fig. 3): H increases markedly with temperature. For acetonitrile, its minimum value is 0.8 mm at 110°C, 1.5 mm at 140°C and 2.7 mm at 160°C. For acrylonitrile, the values are 0.7, 1.1 and 1.6 mm respectively at the same temperatures. Again, the efficiency of the column seems to decrease when the temperature increases. In addition, for the two nitriles, the minimum of H is obtained for a u value of about 30 cm/s.

Thus, there is an observed increase in H with temperature for most solutes, either polar, such as nitriles, or apolar, such as alkanes. This suggests that the retention processes are mainly driven by gas–solid adsorption, and that there is a change in the physical structure of the organic polymer film in the range of temperatures. The particular behaviour of benzene seems to indicate that, for this compound, contrary to the other solutes for which H plots have been determined, the retention process involves mainly solubility phenomena. Effectively, this compound is less volatile than the other solutes considered above, and its chemical structure is very similar to that of the monomers constituting the organic polymer coating. From these results it also appears that with such a column, using H_2 as the carrier gas, the outlet flow-rate should be at least 2 ml/min. We have chosen this value for calibrating the column with hydrocarbons and nitriles.

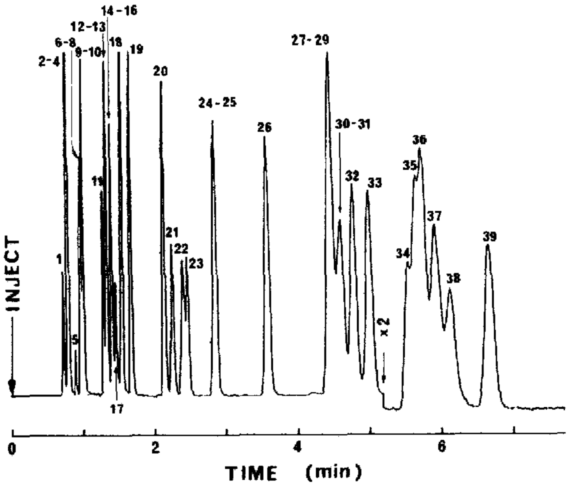

Fig. 4. Gas chromatogram of a gaseous mixture of C_1–C_6 hydrocarbons and C_1–C_4 nitriles on a 10 m × 0.32 mm I.D. PoraPLOT Q fused-silica column at 160°C. Carrier gas: H_2. Outlet flow-rate: 2 ml/min. Injected quantity: 1–3 nmol of each constituent; split mode (100/1). Flame ionization detector. Peaks: 1 = methane; 2 = ethene; 3 = ethyne; 4 = ethane; 5 = cyanogen; 6 = propene; 7 = hydrocyanic acid; 8 = propane; 9 = allene; 10 = propyne; 11 = isobutane; 12 = 1-butene; 13 = isobutene; 14 = butane; 15 = *trans*-2-butene; 16 = 1-butyne; 17 = *cis*-2-butene; 18 = cyanoacetylene; 19 = acetonitrile; 20 = acrylonitrile; 21 = 1-pentene; 22 = *n*-pentane; 23 = 2-methyl-2-butene; 24 = cyclopentane; 25 = propionitrile; 26 = methacrylonitrile; 27 = isobutyronitrile; 28 = 3-methylpentane; 29 = 1-hexene; 30 = cyanopropyne; 31 = *cis*- or *trans*-crotononitrile; 32 = *n*-hexane; 33 = 3-butenenitrile; 34 = benzene; 35 = butyronitrile; 36 = *trans*- or *cis*-crotononitrile; 37 = cyclohexane; 38 = cyclohexene; 39 = cyclopropanecarbonitrile.

Fig. 4 shows a chromatogram of a mixture of C_1–C_6 hydrocarbons and C_1–C_4 nitriles at 160°C. The retention times of hydrocarbons are roughly in the order of their boiling points and increase with the number of carbon atoms in their structures. The chromatographic behaviour of nitriles is somewhat similar, in spite of the polarity of the CN group. With the exception of the non-polar compound C_2N_2 which is eluted very quickly, the retention times of all the nitriles studied increase with the number of carbon atoms, whatever the nature of the carbon chain (saturated, ethylenic or acetylenic). With this isothermal condition of relatively high temperature, many of the hydrocarbons are co-eluted, especially those with a small number of C atoms. There are also several interferences between hydrocarbons and nitriles. Hydrogen cyanide is co-eluted with propane and propene, propanenitrile with cyclopentane, 2-methylpropanenitrile with 3-methylpentane and with 1-hexene. A few nitriles, such as cyanopropyne and *cis*-crotononitrile are not separated. However, the separation is markedly better and faster than that obtained with a Porapak Q column using similar temperature conditions[4]. All the solutes injected are eluted in less than 7 min, and they exhibit symmetrical peaks.

Fig. 5 shows a chromatogram obtained under the same conditions, but at 100°C. Ethane is separated from the other C_2 hydrocarbons, propane from propene. Hydrogen cyanide is still co-eluted, but only with propene. Cyanopropyne and *cis*-crotononitrile again are co-eluted, butanenitrile and *trans*-crotononitrile are no

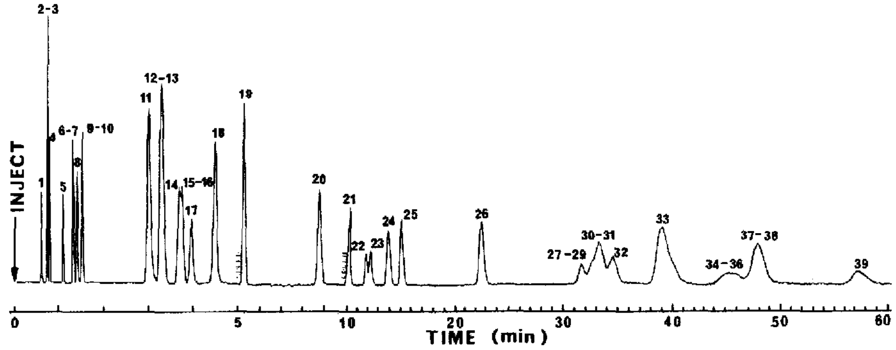

Fig. 5. Chromatogram obtained under the same conditions as in Fig. 4, but at 100°C. For peak identification see Fig. 4.

longer separated and are co-eluted with benzene. Elution of all the constituents of the mixture requires almost 1 h.

The separation can be improved by using programmed column temperatures. Fig. 6 shows as an example the analysis of a mixture of C_1–C_4 hydrocarbons and C_1–C_3 nitriles with a linearly programmed temperature starting from 40°C, isothermal for 2 min, then increased at 20°C/min to 115°C. The entire analysis takes 10 min and allows the separation of all the constituents, with the exception of ethylene and acetylene.

In order to provide a more general view of the behaviour of this column, we have

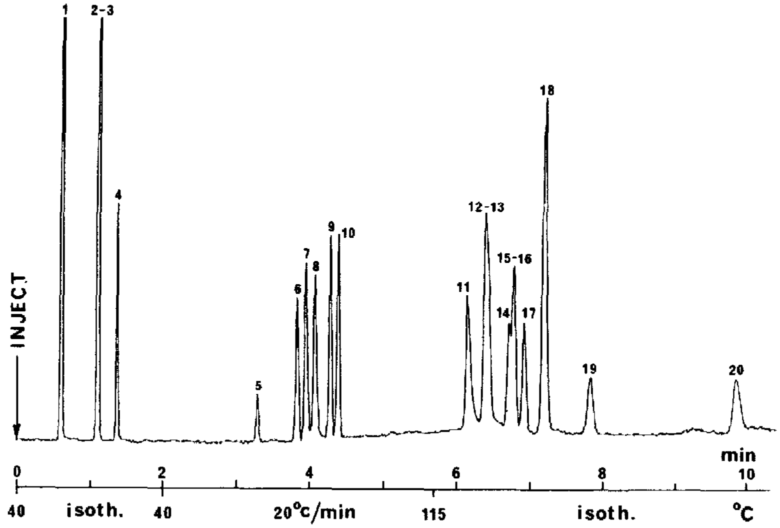

Fig. 6. Gas chromatogram of a gaseous mixture of C_1–C_4 hydrocarbons and C_1–C_3 nitriles. Conditions as in Fig. 4, but programmed temperature of the column: isothermal for 2 min at 40°C, then 20°C/min to 115°C. For peak identification see Fig. 4.

also determined the retention indices, I(i), of the solutes studied, using the Kováts system. The following equation was used

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

where t'_R is the relative retention time, P_z and P_{z+1} correspond to the paraffins with

TABLE I

RETENTION INDICES OF HYDROCARBONS AND NITRILES (*) ON PoraPLOT Q COLUMN AT 100 AND 160°C

Reference alkanes in brackets.

Solute	*Retention index*	
	100°C	*160°C*
(Ethane)	200	200
Cyanogen*	236.8	273
Propene	248.9	300
Hydrogen cyanide*	248.9	300
(Propane)	300	300
Allene	311	315.9
Propyne	311	315.9
Isobutane	380.5	384.7
1-Butene	389	390
Isobutene	389	390
(Butane)	400	400
trans-2-Butene	401.8	400
Butyne	401.8	400
cis-2-Butene	406.9	407.9
Cyanoacetylene*	420.9	423.5
Acetonitrile*	432.3	441.6
Acrylonitrile*	475.6	482.2
1-Pentene	489.2	490.8
(*n*-Pentane)	500	500
2-Methyl-2-butene	503.5	504.1
Cyclopentane	516.1	527
Propionitrile*	523.3	527
Methacrylonitrile*	560.5	559.6
Isobutyronitrile*	592.2	590.4
3-Methylpentane	592.2	590.4
1-Hexene	592.2	590.4
Cyanopropyne*	596.5	595
trans- or *cis*-Crotononitrile*	596.5	595
(*n*-Hexane)	600	600
Allyl cyanide*	611	605.8
Benzene	623.9	619.5
Butyronitrile*	623.9	622.2
cis- or *trans*-Crotononitrile*	623.9	624.0
Cyclohexane	628.8	628.2
Cyclohexene	628.8	628.2
Cyclopropyl cyanide*	645	643.6
(Heptane)	700	700

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}. The results are given on Table I, for two different temperatures: 100 and 160°C. It can be checked that, for a given chemical family, the retention index varies linearly with the number of carbon atoms in the solute.

CONCLUSIONS

The analogy between the PoraPLOT Q capillary column and a Porapak Q packed column, already reported for apolar and polar compounds other than nitriles, is also true for these organics. This PLOT column can be used advantageously for analyzing mixtures of hydrocarbons and nitriles, combining the advantages of the high resolution of a capillary column with the ability of styrene–divinylbenzene copolymer to allow the elution of polar and apolar compounds. A 10-m PoraPLOT Q column can provide a good separation of saturated and unsaturated low-molecular-weight hydrocarbons and nitriles, in a relatively short time. Only the separation of HCN and propene seems to be difficult and requires programmed temperature conditions. 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 existence of a coupling of GC with MS reduces the importance of the problem of co-elution, especially if the co-eluted compounds have well differentiated chemical properties and consequently mass fragmentation. This is the case of HCN–propene. Thus the PoraPLOT Q column may be a good choice for one of the chromatographic columns of the GC–MS instrument of the Titan probe.

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