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Gas chromatography for in situ analysis of a cometary nucleus II. Analysis of permanent gases and light hydrocarbons with a carbon molecular sieve porous layer open tubular column

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Abstract

Considering the severe constraints of space instrumentation, a great improvement for the in situ gas chromatographic (GC) determination of permanent and noble gases in a cometary nucleus is the use of a new carbon molecular sieve porous layer open tubular (PLOT) column called Carbobond. No exhaustive data dealing with this column being available, studies were carried out to entirely characterize its analytical performances, especially when used under the operating conditions of the cometary sampling and composition (COSAC) experiment of the European Space Agency (ESA) Rosetta space mission to be launched in 2003 for a rendezvous with comet 46 P/Wirtanen in 2011. The high efficiency and speed of analysis of this column at both atmospheric and vacuum outlet column pressure is demonstrated, and the kinetic mass transfer contribution of this carbon molecular sieve adsorbent is calculated. Besides, differential adsorption enthalpies of several gases and light hydrocarbons were determined from the variation of retention volume with temperature. The data indicate close adsorption behaviors on the Carbobond porous layer adsorbent and on the carbon molecular sieve Carboxen support used to prepare the packed columns. Moreover, taking into account the in situ operating conditions of the experiment, a study of two columns with different porous layer thicknesses allowed one to optimize the separation of the target components and to select the column parameters compatible with the instrument constraints. Comparison with columns of similar selectivity shows that these capillary columns are the first ones able to perform the same work as the packed and micro-packed columns dedicated to the separation of this range of compounds in GC space exploration. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the last improvements in gas chromatography (GC) for space exploration was the use of capillary columns, for the first time, in the gas

chromatography–mass spectrometry (GC–MS) experiment of the Huygens Probe [1] of the US National Aeronautics and Space Administration (NASA)–European Space Agency (ESA) Cassini–Huygens mission launched in October 1997 [2,3]. Compared with the packed columns previously used [4], such capillary columns are better suited within the technical requirements of the space missions

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(mainly low carrier gas and energy consumption), and allow one to especially improve the analytical performances of the GC instrument (better efficiency, shorter analysis time). However, a micro-packed column [3] was used for the permanent and noble gases separation by the GC–MS experiment because no capillary column that could fit the space constraints was available.

As part of the development of the GC subsystem of the COmetary Sampling And Composition (COSAC) experiment [5] on board the cometary nucleus lander of the ESA Rosetta mission [6], in the continuity of the work on the diphenyl–dimethylpolysiloxanes (DP–DMPS) liquid capillary columns [7], a new bonded carbon molecular sieve porous layer open tubular (PLOT) capillary column, called Carbobond, was studied with the aim to replace packed or micro-packed columns for permanent and noble gases analyses. The main difference with similar PLOT columns is the stationary phase which is made of a new type of carbon adsorbent, forming a porous layer on the internal capillary wall by the mean of an in situ growing process. Thus, this prevents from significant stationary phase bleeding when using high operating temperatures or valve switching, and increases the mechanical stability [8]. Moreover, bonding the carbon layer to the internal capillary wall increases its robustness. Finally, the carbon layer is deactivated in order to prevent irreversible adsorption of species such as unsaturated hydrocarbons or polar oxygenated compounds.

As no exhaustive data were available for this type of column, a complete characterization was carried out in order to evaluate their ability to replace the packed ones dedicated to the light compounds analysis in GC space exploration. With the aim of its use in the COSAC experiment, selectivity and efficiency of the column were investigated at both laboratory and in situ experimental operating conditions, and especially at vacuum outlet pressure. Moreover, the thermodynamic adsorption parameters of the carbon adsorbent used were characterized and an optimization of the column geometry was operated to improve the separation in view of the space instrument requirements. Finally, these data were compared with those previously obtained with packed columns having similar selectivity.

2. Experimental

2.1. Columns

Two Carbobond PLOT columns having the same internal diameter (0.25 mm) and the same length (15 m) were used in this study, all provided by Varian–Chrompack (Middleburg, The Netherlands). Their carbon layer thickness are, respectively, 6 μm (column No. 1) and 10 μm (column No. 2). It must be pointed out that they have a metallic external wall in order to improve their robustness (especially during the launch phase which generates vibrations) and the carbon layer is bonded to the internal capillary wall according to the Ultimetal technique.

2.2. Gas chromatograph

GC measurements were carried out on a Varian CP-3800 GC system, equipped with thermal conductivity detection (TCD) systems and a linear temperature programmer. During the measurements, the TCD systems were heated at 110°C and their signals were connected to a Varian Star data acquisition system. The injection system is composed of two electro-pneumatic gas sampling valves (Valco), with 0.2 and 2 μl sampling loops, heated at 120°C. All the measurements were performed in the splitless mode and the GC columns were operated isothermally at temperatures in the range 20–80°C.

The carrier gas was helium (grade C), the same as for the COSAC experiment. A series of three filters removing water, hydrocarbons and oxygen traces was used to improve its purity. Hydrogen was also used as carrier gas for the experiments required for the determination of the coefficients of the plate height equation.

2.3. Reagents and sampling

All the compounds used (except water and hydrogen cyanide) were obtained in gaseous state from Linde (Lyon, France) and Air Liquide (Moissy Cramayel, France). These gases are of analytical grade. The distilled water used was vaporized under vacuum at room temperature, and hydrogen cyanide was prepared by acidification of sodium cyanide with

sulfuric acid. Gas mixtures were obtained as previously described for Huygens GC studies [9].

3. Results and discussion

Analysis of mixtures of the target compounds was studied and Fig. 1 illustrates the separation of the inorganic compounds and methane on the PLOT columns No. 1 and No. 2.

3.1. Thermodynamic adsorption results

For an ideal gas, in the linear range of the adsorption isotherm (small amount injected), the

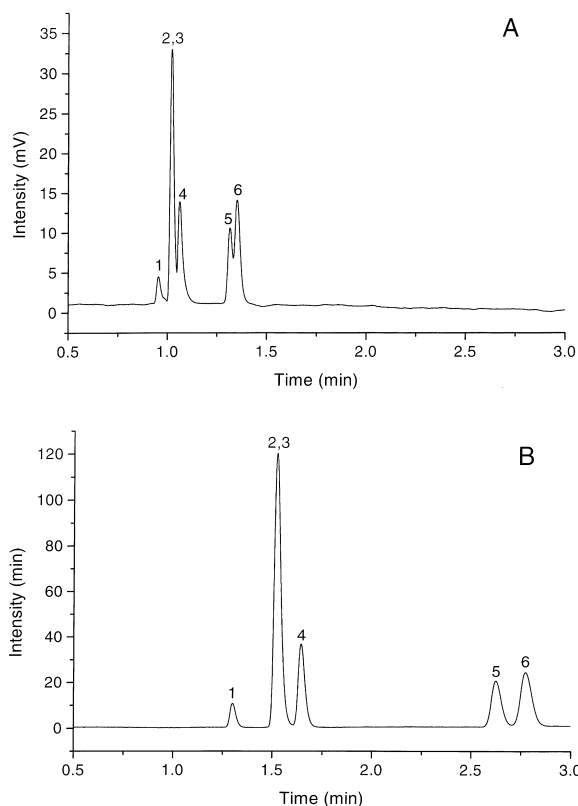


Fig. 1. Comparison of the separation of the inorganic gases and methane on columns (A) No. 1 and (B) No. 2 at 30°C and 150 kPa absolute head pressure under atmospheric column outlet pressure. Peaks: 1 = neon, 2 = nitrogen, 3 = argon, 4 = carbon monoxide, 5 = methane, 6 = krypton.

adsorption equilibrium constant K [10] is related to k' by $K = k'V_0/A_sRT$ where R is the gas constant and A_s is the total surface area of the adsorbent in the column. The capacity factor for a compound, k' , is calculated by $k' = (t_r - t_0)/t_0$. t_r is the retention time of the considered compound and t_0 the retention time of a non adsorbed compound. t_0 was determined from the elution time of neon. The void volume of the capillary column was measured from t_0 value with $V_0 = t_0jFT/T_f$, where F is the flow-rate, j is the James–Martin pressure correction factor, T is the column temperature and T_f is the temperature of the flow meter. $V_0 = 0.80 \text{ cm}^3$ for column No. 1 and $V_0 = 0.95 \text{ cm}^3$ for column No. 2.

The variation of K with temperature gives the differential change in the adsorbate enthalpy, ΔH , or the isosteric heat of adsorption $Q_{st} = -\Delta H = RT^2\partial \ln K/\partial T$. Studies carried out at different temperatures enabled one to determine the isosteric heat of adsorption of the solutes eluted on the Carbobond capillary columns, with $Q_{st} = RT^2\partial \ln k'/\partial T + RT$. A linear variation of $\ln k'$ versus the reciprocal absolute temperature T (Fig. 2), was observed (linear regression factor of the plotted curves are greater than 0.99 for all the compounds). Q_{st} was calculated from the slope of the straight line α with $Q_{st} = R\alpha + RT$. These values are listed in Table 1 where are also given the net retention volumes measured at 30°C, V'_R , with $V'_R = k'V_0$.

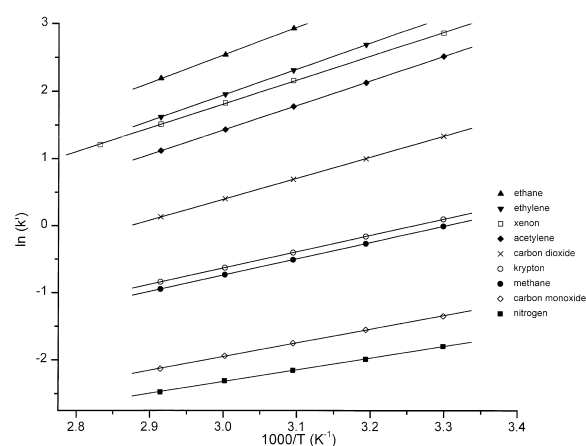


Fig. 2. Variation of $\ln k'$ with temperature on column No. 2 for all the targeted compounds.

Table 1
Comparison of the adsorption thermodynamics on different types of carbon columns at 30°C

Compound	Capillary column No. 1, $V_0 = 0.80 \text{ cm}^3$		Capillary column No. 2, $V_0 = 0.95 \text{ cm}^3$		Packed column Carboxen 1004 ^a $V_0 = 1.05 \text{ cm}^3$		GCB, 7.6 m ² /g	
	V'_R (ml)	Q_{st} (kJ/mol)	V'_R (ml)	Q_{st} (kJ/mol)	V'_R (ml)	Q_{st} (kJ/mol)	V'_R (ml)	Q_{st} (kJ/mol)
Ne	–	–	–	–	–	–	0.5 ^b	3.5 ^b
N ₂	0.0050	10.9	0.16	14.4	2.4	16.1	3.1 ^b	9.5 ^b
CO	0.0078	16.5	0.25	16.9	4.6	18.8	–	–
CH ₄	0.28	16.7	0.94	20.2	14.7	23.0	7.6 ^c	12.9 ^c
Kr	0.31	19.1	1.05	20.2	17.6	23.0	8.0 ^b	12.0 ^b
CO ₂	1.6	26.2	3.6	26.0	–	–	10.2 ^b	16.9 ^b
C ₂ H ₂	6.6	31.9	11.8	30.1	–	–	14.4 ^c	17.6 ^c
Xe	4.5	29.7	16.6	29.3	–	–	32.7 ^b	16.0 ^b
C ₂ H ₄	6.4	31.9	21.1	31.7	–	–	28.0 ^c	17.9 ^c
C ₂ H ₆	10.4	33.8	41.3	34.0	–	–	39.6 ^c	18.9 ^c

^a From Ref. [11].

^b From Ref. [12].

^c From Ref. [13].

Table 1 presents values previously obtained with a 2 m long column packed with Carboxen 1004 adsorbent [11]. The values of the isosteric heat of adsorption are close for both PLOT capillary columns, but slightly lower than the data obtained previously with the packed column [11]. However, the relative retention of the low-molecular-mass gases are very similar with PLOT and packed columns. Column No. 2 having a 10 μm thickness film coating has retention volumes three- to four-times larger than column No. 1. Moreover, one can notice that the retention volumes are 60-times lower with the PLOT column No. 1 (15 m long) than with the packed column (2 m long). This retention volume is directly proportional to the amount of adsorbent in the column. Considering that carbon molecular sieves have similar adsorption properties in terms of surface area, the amount of adsorbent per column length unit is 450-times larger with the packed column. That is the reason why PLOT columns enable to elute compounds of higher boiling point within short time at lower temperatures compared with packed columns.

It is interesting to compare the adsorption characteristics on the carbon porous layer with the data already published by Kiselev and co-workers [12,13] for the adsorption on graphitized carbon black (GCB). In Table 1 are given the net retention volume per gram of adsorbent on GCB. For alkanes, the data

on GCB are those measured by GC on a GCB of surface area of 7.6 m²/g [13]. The data for permanent gases were extrapolated at 30°C from adsorption equilibrium measurements [12].

In this work, neon was considered as a non retained compound. This approximation is valid as the retention of neon is about six-times as low as that of nitrogen on GCB. As a consequence, if one assumes the same ratio in the present experiment with Carbobond columns, the error made on t_0 approximation by considering neon as the non retained compound, is roughly 3% (at 30°C, $k' = 0.03$ with column No. 2).

Comparing the relative retentions to nitrogen, one can notice that CO₂ is comparatively more retained on column No. 1, but compounds of higher molecular mass (Xe, C₂H₄ and C₂H₆) are less retained. As observed with GCB, acetylene is less retained than xenon on column No. 2 whereas the reverse order is observed on column No. 1. Such different behaviors are difficult to explain considering that the differential adsorption enthalpies are quite close on both PLOT columns. This may result from differences in the surface coating of the PLOT carbon layer.

3.2. Efficiency

The efficiencies of both Carbobond PLOT capillary columns were compared by studying the peak

broadening of two test compounds (CO₂ and CH₄) as a function of the carrier gas velocity, at 30°C (operating temperature planned aboard COSAC experiment).

The theoretical expression of the plate height equation in gas–solid chromatography is given by [14]:

$$H = \left(\frac{B}{u_0} + C_g u_0 \right) \cdot f + C_k \bar{u} \quad (1)$$

where: (i) \bar{u} is the average carrier gas velocity and u_0 the carrier gas velocity at the column outlet ($u_0 = \bar{u}/j$). The James and Martin correction factor j is related to the inlet and outlet pressure (p_i and p_o) by:

$$j = \frac{3}{2} \cdot \frac{p_o(p_i^2 - p_o^2)}{(p_i^3 - p_o^3)^2} \quad (2)$$

(ii) The effect of pressure gradient on the plate height is accounted for by the pressure correction factor f given by:

$$f = \frac{9}{8} \cdot \frac{(p_i^4 - p_o^4)(p_i^2 - p_o^2)}{(p_i^3 - p_o^3)^2} \quad (3)$$

The variation of this term with pressure drop is small (from 1 to 9/8) and is considered as negligible.

(iii) B , the longitudinal diffusion coefficient is proportional to $D_{g,o}$, the diffusion coefficient of the solute at the column outlet pressure, with $B = B'D_{g,o}$. For open tube capillary columns $B' = 2$.

(iv) C_g , the coefficient for resistance to mass transfer in the gaseous phase is inversely proportional to $D_{g,o}$, with $C_g = C'_g/D_{g,o}$.

(v) C_k , the kinetic mass transfer coefficient is related to the average time of desorption by the equation:

$$C_k = \frac{2k'}{(1 + k')^2} \cdot \bar{t}_d \quad (4)$$

The coefficients of the plate height equation (Table 2) were determined, as indicated by Giddings and Schettler [14], by performing measurements of H at atmospheric outlet pressure on column No. 2, using two different carrier gases. The carrier gases selected for this study are helium and hydrogen because they are not adsorbed on the Carbond

Table 2

Coefficients of the plate height equation determined at atmospheric outlet pressure with two carrier gases (H₂ and He) at 30°C on column No. 2

Compound	Carrier gas	D_g (cm ² /s)	B'	C_k (ms)	\bar{t}_d (ms)
CH ₄	He	0.70	1.8 (0.2) ^a	2.0 (0.1)	4
	H ₂	0.75			
CO ₂	He	0.62	1.7 (0.1)	0.9 (0.4)	3
	H ₂	0.67			

^a Values in parentheses correspond to the absolute error for 95% confidence interval.

stationary phase. Plots of H vs. $x = u_0/D_{g,o}$ enable one to isolate the C_k term from the overall mass transfer contributions [15]. The diffusion coefficients of the solutes in the carrier gas at atmospheric pressure, D_g , were calculated at 30°C from the experimental values published by Fuller et al. [16].

Fig. 3 shows the variation of H with x for CH₄ (A) and CO₂ (B) eluted on the column with a thick film coating (column No. 2). The difference between H values measured with the two carrier gases (He and H₂) is caused by an important contribution of the kinetic mass transfer term, C_k . A linear least-square fit program was used to fit Eq. (1) to the experimental data measured for both H₂ and He carrier gases. A preliminary regression linear analysis for the determination of the three coefficients of Eq. (1) has shown that C_g values are quite small (less than 0.1 C_k). Thus, the contribution for mass transfer in the gaseous phase was considered as negligible and the linear regression was made to determine B' and C_k with $C_g = 0$. A good agreement between the model and the experimental results is obtained. Table 2 lists the coefficients B' and C_k and the errors in parameters determination for a 95% confidence interval. The agreement between the experimentally determined values of B' and the theory is quite good. The large contribution from mass transfer kinetics (C_k term) is responsible for the loss of efficiency at high carrier gas velocities. From its value was calculated the average desorption time \bar{t}_d (Eq. (4)).

In the case of the capillary column No. 1 with a

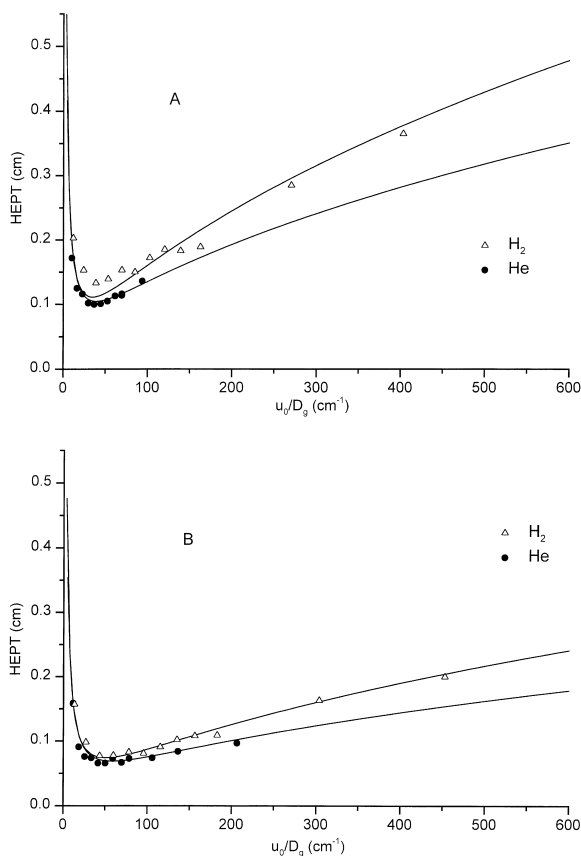


Fig. 3. Plot of H vs. x (u_0/D_g) for two carrier gases (H_2 and He) at atmospheric outlet pressure and 30°C for column No. 2: (A) CH_4 ($k' = 0.99$) and (B) CO_2 ($k' = 3.80$).

thin film coating, the C_k term is low and no significant difference exists between the plate height measured with He and H_2 as carrier gases in the H vs. x plot. Indeed, this work will show that it is possible to determine the C_k coefficient from studies at two different outlet pressures (atmospheric and 10 mbar). Moreover, the advantage of working at these sub-atmospheric outlet pressures is to operate at the experimental conditions of the COSAC experiment.

The plate height equation at sub-atmospheric outlet pressure [17] is useful for predicting the efficiencies with GC–MS systems (vacuum outlet mode of operation). For an ideal gas, $p_o u_o = p_i u_i$ and $p_a D_g = p_o D_{g,o}$, where u_i is the carrier gas velocity at column inlet and p_a is the atmospheric pressure. Then, the plate height equation (Eq. (1)) can be rearranged to:

$$H = \left(\frac{B' p_a D_g}{p_i u_i} + \frac{C'_g p_i u_i}{p_a D_g} \right) \cdot f + C_k \bar{u} \quad (5)$$

A linear regression was made on the experimental data obtained at two different outlet pressures with a single carrier gas to extract the three coefficients of the plate height equation B' , C_k and C'_g . The contribution for mass transfer in the gaseous phase is small compared to the kinetic mass transfer contribution. Large errors are thus made in C'_g determination and the values (either positives or negatives) obtained from curve fitting are not significant (small absolute value, about 0.1 ms). Therefore, the C'_g term was neglected and the coefficients B' and C_k (Table 3) were determined by linear regression with $C'_g = 0$. In this table are also given the errors in parameters determination, for a 95% confidence interval.

Fig. 4A and B illustrate the plot of H vs. \bar{u} (carrier gas He) for CO_2 eluted on columns No. 1 and 2. In both cases, the model fits well the experimental data measured at atmospheric outlet pressure ($p_o = 100$ kPa) and reduced outlet pressure ($p_o = 1$ kPa). The determination of the C_k term is now possible as experiments are performed in the high velocity range, when working at sub-atmospheric outlet pressures. In this case, the domain of low \bar{u} values is not reached because the inlet pressure controller was referenced to the atmospheric pressure and did not allow one to work below $p_i = 1$ bar at vacuum outlet pressure. Instead, the experiments performed at atmospheric outlet pressure allow the measurement of the B' coefficient. The combination of both experiments at atmospheric and sub-atmospheric outlet pressure gives a good estimation of the coefficients of the plate height equation.

Compared to the value determined for methane with column No. 1, the C_k term is about two-times larger with column No. 2. The comparison of the H vs. \bar{u} plot is illustrated in Fig. 5 when hydrogen is used as carrier gas. An important loss of efficiency is observed at high \bar{u} values with column No. 2: at $\bar{u} = 200$ cm/s, H is less than 0.2 cm with column No. 1 and about twice as large with column No. 2. As expected, a lower C_k coefficient is observed for CO_2 as this compound is more retained (larger k' value in Eq. (4)). Considering the confidence interval in parameters determination, the differences in C_k term obtained for CO_2 with both columns are not as

Table 3

Coefficients of the plate height equation obtained from measurements at both atmospheric and sub-atmospheric ($p_o=10$ mbar) outlet pressures on the two Carbobond PLOT columns

Compound	Carrier gas	Column No. 1			Column No. 2		
		B'	C_k (ms)	\bar{t}_d (ms)	B'	C_k (ms)	\bar{t}_d (ms)
CH ₄	He	2.7 (0.2) ^a	1.2 (0.2)	3	1.7 (0.1)	2.7 (0.1)	5
	H ₂	3.1 (0.4)	1.0 (0.1)	3	2.3 (0.1)	2.3 (0.3)	4
CO ₂	He	2.3 (0.2)	1.1 (0.1)	2	1.7 (0.1)	1.5 (0.2)	4
	H ₂	2.5 (0.6)	1.0 (0.1)	2	1.9 (0.4)	1.3 (0.2)	4

^a Values in parentheses correspond to the absolute error for 95% confidence interval.

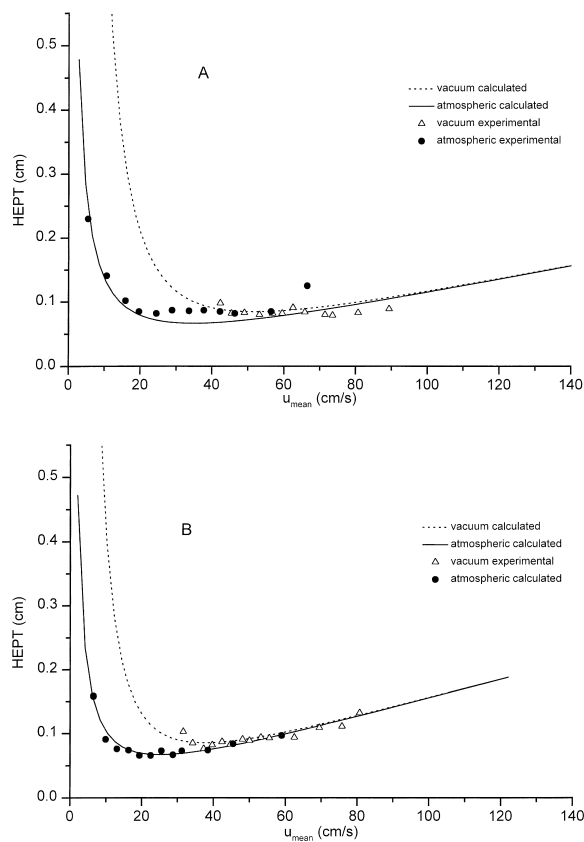


Fig. 4. Plot of H vs. \bar{u} for CO₂ with He as carrier gas on (A) column No. 1 and (B) column No. 2 at $T=30^\circ\text{C}$ under ambient and vacuum outlet pressure.

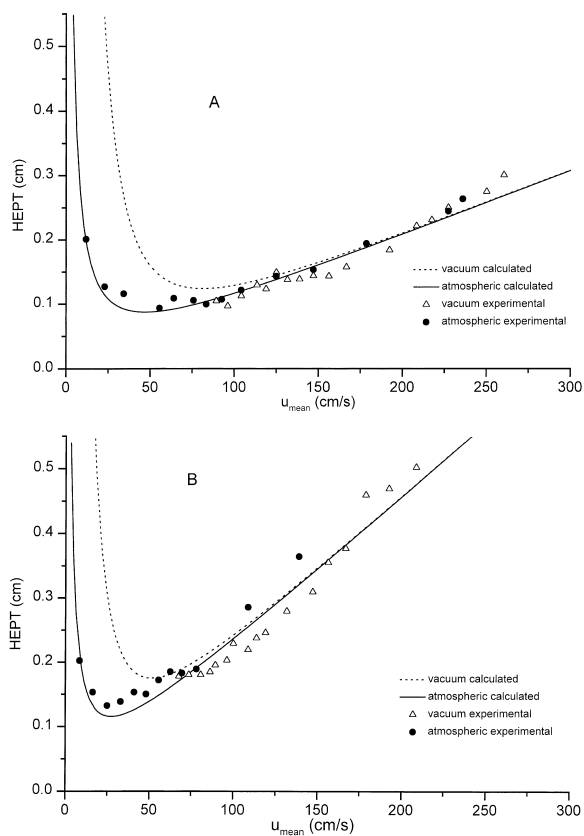


Fig. 5. Plot of H vs. \bar{u} for CH₄ with H₂ as carrier gas on (A) column No. 1 and (B) column No. 2 at $T=30^\circ\text{C}$ under ambient and vacuum outlet pressure.

important as found with CH₄, especially when He is used as carrier gas. Nevertheless, differences in the slopes of H vs. \bar{u} in the measurements at sub-atmospheric outlet pressure can be noticed when comparing Fig. 4A and B.

The mean time of desorption \bar{t}_d was determined from the C_k values; 3–5 ms for CH₄ and 2–4 ms for CO₂ (Table 3). Giddings [18] has estimated the mean desorption time for an adsorption on uniform surfaces. For a porous adsorbent as carbon molecular sieve (specific surface area of 1000 m²/g), the value expected for \bar{t}_d is 10⁻¹⁰ s and the C_k term is of the same magnitude. The large values of the C_k coefficient could be explained by the use of a non uniform porous adsorbent. A quite large value of C_k ($C_k = 0.18$ ms) was also observed when butane is eluted at 130°C on an aluminum oxide PLOT column [19].

If one considers the optimum efficiencies, they do not seem to be affected by the variation of the film thickness according to Fig. 4A and B thus allowing to use column No. 1 or No. 2 without a loss of efficiency. For both columns, the optimum efficiencies (≈ 0.09 and ≈ 0.07 cm, respectively at reduced and atmospheric outlet pressures) are obtained at inlet absolute pressures in the range 155–165 kPa. These values are slightly above the operating inlet pressure selected for the COSAC experiment, i.e., 150 kPa. However, according to the calculated plate height equations, the degradation of the efficiency remains smaller than 5% at this inlet absolute pressure (10% at 140 kPa), allowing the columns to work at conditions close to the optimum ones.

3.3. Separation power and column geometry optimization

The only information available about the cometary composition are provided by in situ or remote sensing analyses of the cometary atmosphere, but no direct data about the nucleus exist. Table 4 lists the compounds expected to be separated with the Carbond PLOT column and their abundance in the coma (relative to water). It must be pointed out that these relative abundance are probably not relevant from the nucleus ones because of the existence of extended sources, i.e., sources of molecules which are located in the cometary atmosphere and generated by secondary processes [20]. Nevertheless, these

Table 4

List of the lightest molecular species of the cometary atmosphere and their measured abundance relative to water [i.e., $Q(X)/Q(H_2O) \cdot 100$ with Q the production rate of the X compound in the coma]

Compound (adapted from Ref. [21])			
He < 3	0.02 < N ₂ < 0.2	0.7 < CH ₄ < 2	0.02 < HCN < 0.2
Ar < 17	2 < CO < 43	0.2 < C ₂ H ₂ < 0.9	HNC 0.007
Ne < 0.6	2.2 < CO ₂ < 13	C ₂ H ₄ n.d.	
Kr n.d. ^a	0.1 < NH ₃ < 1.4	0.4 < C ₂ H ₆ < 0.5	H ₂ O 100
Xe n.d.			

^a Non detected.

are the only quantitative data currently available [21].

Since HNC is unstable at room temperature and He is used as carrier gas, both compounds cannot be analyzed. The separation of all the other species was achieved and they were individually analyzed with the exception of HCN and NH₃ which do not elute from the column. This could be explained by an irreversible adsorption occurring in spite of the deactivation treatment of the carbon layer, or by a too long elution time considerably decreasing the signal-to-noise ratio of the nano-TCD systems, because of peak broadening.

In order to evaluate the separation power, equimolecular mixing of 11 species were analyzed on each column. A representative chromatogram obtained for a separation on column No. 2 is given in Fig. 6A and the data for both columns are presented in Tables 5 and 6. These analyses were performed at 30°C, the nominal temperature of the COSAC experiment.

One can observe that all the compounds are separated except Ar and N₂ which are totally co-eluted on both columns (Fig. 1). Moreover, the chromatogram can be divided into two parts: first the less retained compounds (from Ne to Kr) which have close retention times; then, peaks corresponding to compounds (mainly C₂ hydrocarbons) which have much longer retention times and are clearly well separated within the time scale. Therefore, the separation objective of the column is reached, but the main targeted compounds, i.e., permanent and noble gases, are not completely resolved even if separated. As a consequence, an optimization of the geometry

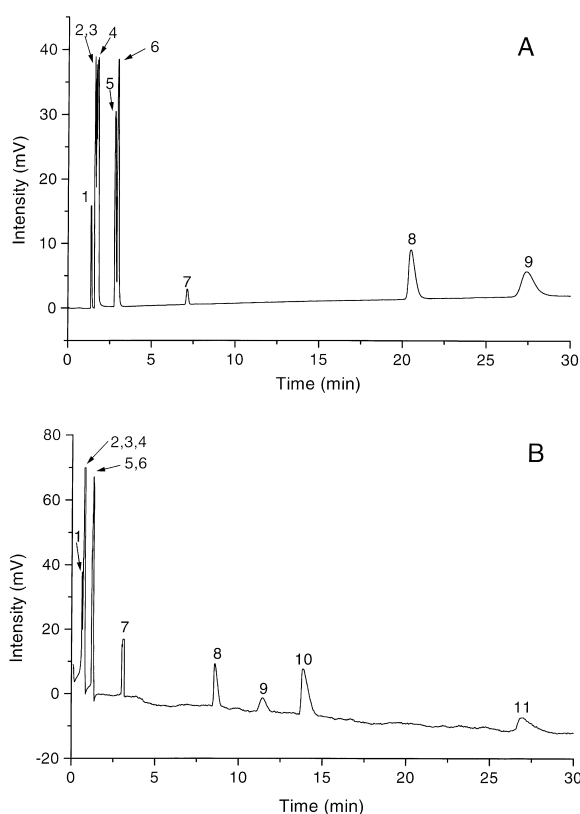


Fig. 6. Gas chromatographic separation of the targeted compounds with column No. 2 (15 m \times 0.25 mm, 10 μ m) at 30 $^{\circ}$ C and 150 kPa absolute head pressure: (A) under atmospheric column outlet pressure; (B) with 10 mbar of column outlet pressure. Peaks: 1=neon, 2=nitrogen, 3=argon, 4=carbon monoxide, 5=methane, 6=krypton, 7=carbon dioxide, 8=acetylene, 9=xenon, 10=ethylene, 11=ethane.

of the column was carried out in order to improve the resolving power of the less retained compounds.

To operate such an optimization, several restrictions were imposed by the column integration into the COSAC experiment: (1) limitation of the length at less than 15 m; (2) limited analysis time (17 min) [7]; (3) restricted carrier gas consumption which led us to select the minimum internal diameter compatible with a metallic tubing and the bonding technique of the manufacturer, i.e., 0.25 mm. As a consequence, only the film thickness and column length parameters have been investigated.

As expected, one can naturally observe an increase of the retention times (Table 5) from column No. 1 to No. 2 due to the increase of the film thickness. The worst case concerns ethane which is eluted after more than 30 min for the 10 μ m layer thickness column instead of the 17 min imposed for in situ experiment. Moreover, no C₂ hydrocarbons are eluted within this duration with column No. 2. Nevertheless, when focusing on the first six eluted compounds, the resolution is notably improved for all compounds (except Ar and N₂) (Table 6).

The column length parameter was also investigated by using a shorter column (10 m) similar to column No. 2. The total analysis time decreased to less than 17 min, thus allowing the elution of ethane from the column. However, a much lower resolution is observed for the less retained compounds (N₂, CO and CH₄, Kr).

Therefore, the increase of carbon layer thickness (10 μ m being the thickest layer available) and

Table 5
Retention times (min) of the targeted compounds at 30 $^{\circ}$ C and p_i =150 kPa

Column	P_{out} (bar)	Retention time (min)										
		Ne	N ₂	Ar	CO	CH ₄	Kr	CO ₂	C ₂ H ₂	Xe	C ₂ H ₄	C ₂ H ₆
1	1	0.96	1.02	1.02	1.05	1.29	1.33	2.88	8.45	6.49	8.22	12.74
1	10 ⁻²	0.43	0.46	0.46	0.48	0.60	0.61	1.34	3.99	2.87	3.95	6.41
2	1	1.32	1.54	1.54	1.66	2.63	2.77	6.34	17.67	24.34	29.71	>30
2	10 ⁻²	0.57	0.67	0.67	0.73	1.17	1.22	2.79	7.75	11.21	14.02	24.00

Table 6
Resolution of pairs of inorganic compounds and methane at $p_i = 150$ kPa

Column	Resolution							
	Ne/N ₂		N ₂ /CO		CO/CH ₄		CH ₄ /Kr	
	$p_o = 1$ bar	$p_o = 10^{-2}$ bar	$p_o = 1$ bar	$p_o = 10^{-2}$ bar	$p_o = 1$ bar	$p_o = 10^{-2}$ bar	$p_o = 1$ bar	$p_o = 10^{-2}$ bar
1	1.85	2.23	1.16	1.22	6.38	5.82	0.76	0.68
2	4.63	4.69	2.29	2.25	14.79	11.95	1.83	1.23

column length greatly improves the resolving power of the column. For this reason, column No. 2 appears to be the most appropriate for the mission objectives but the total analysis time is quite long, largely above the time required for the in situ analysis.

3.4. Flight operating conditions

Low cometary surface pressures impose reduced pressure at the column outlet. Because of the higher pressure drop when applying such reduced pressures (Fig. 7), the analysis time is about half that observed at atmospheric outlet pressure. However, one can observe that resolutions (Table 6) are only slightly affected by the pressure drop increase. For an operating pressure of 1.5 bar, the mean velocities are, respectively, about 20 cm/s for atmospheric outlet pressure, and 45 cm/s for reduced outlet pressure. As shown in Fig. 4A and B, a loss of the efficiencies is observed when operating at reduced outlet pressure which explains the slightly lower resolution (Table 6). However, in spite of the lower efficiencies at the minimum of the height equivalent to a theoretical plate (HETP) and the larger C_k term, the best resolutions are obtained with column No. 2, that allows to achieve a baseline separation (corresponding to a resolution greater than 1.5) for all the couples of compounds considered. Therefore column No. 2 appears to be more suitable for the separation of the inorganic compounds, even if the analysis time is quite shorter with column No. 1.

Moreover, as shown in Fig. 6, the use of a reduced column outlet pressure allows the separation of all the compounds in less than 17 min (instead of 30 min with atmospheric pressure at the column outlet). Thus, the Carbobond columns allow one to separate low-molecular-mass hydrocarbons at the isothermal conditions of 30°C in an analysis time compatible

with the instrument requirements (except for ethane with column No. 2). The problem raised by the non elution of ethane within the constraints of the separation should be solved by the analysis of this compound with one of the other columns to be integrated in the experiment [5]. As a consequence, column No. 2 appears to be the most adapted

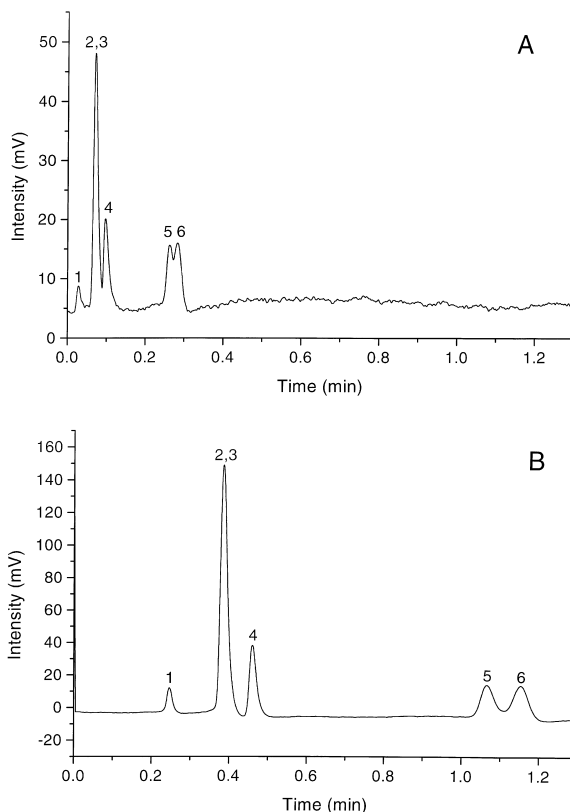


Fig. 7. Comparison of the separation of the inorganic gases and methane on columns (A) No. 1 and (B) No. 2 at 30°C and 150 kPa absolute head pressure under reduced column outlet pressure. Peaks: 1 = neon, 2 = nitrogen, 3 = argon, 4 = carbon monoxide, 5 = methane, 6 = krypton.

column, when used at in situ operating conditions, and therefore will be selected for the COSAC experiment.

Nevertheless, it must be pointed out that a slight programming temperature could solve this problem. This solution was tested by using a soft constant heating of the column during the total analysis time ($2^{\circ}\text{C}/\text{min}$), increasing the temperature from 30°C to 64°C . The programming temperature is obviously limited by the energy available, explaining the «unusual» slow heating of the column. It allowed one to elute all the compounds in less than 17 min (retention time of the last analyzed compound, C_2H_6 , being about 15.2 min) instead of 26 min under isothermal conditions. Moreover, the peak height of the C_2 hydrocarbons nearly doubled when using programming temperature whereas the noise level remained constant, thus showing the effective improvement of the sensibility that makes the analysis and identification of the compounds easier. Unfortunately, because of the power budget of the mission, such a programming temperature is not possible.

The only remaining problem concerns the Ar– N_2 coelution on all columns. In the case of the COSAC experiment, the only way to manage to separate these compounds would be to use lower temperatures. But even measurements performed at temperatures down to 0°C (far from the in situ operating temperature) did not allow to achieve such a separation. As a consequence, in the case of the COSAC experiment, only the coupling with the mass spectrometer could solve the problem of argon and nitrogen analysis during the mission.

3.5. Influence of water

Water is the most abundant compound of the cometary nucleus and atmosphere (see Table 4). As a consequence, it could disturb the analysis by saturating the adsorption sites and thus could change the retention properties of the column. That is the reason why two types of analyses are expected to be performed with the COSAC experiment, one using a drying system allowing to remove water and the second being the direct analysis of the pure sample. Due to the deactivation of the carbon layer of the stationary phase and their hydrophobic behavior, the Carbobond columns do not adsorb water irreversibly

contrary to molecular sieves, such as Molsieve 5A type, which show their retention properties modified by such an adsorption [22,23]. Moreover, this property allows water to be eluted with the column.

With this aim, injections of water together with the previous mixing sample and massive injections of water alone have been performed on column No. 2. As expected [8], water is eluted from the column with a poor peak shape but it does not modify neither the retention times nor the peak shapes of the other species (Fig. 8). This is equally true when comparing chromatograms performed before and after several massive (typically $50\ \mu\text{l}$) injections of water. However, one can observe a partial coelution of water with ethane.

As a consequence, one can expect that Carbobond columns are able to elute water and keep their retention properties when analyzing cometary nucleus samples, dried or not.

3.6. Comparison with columns having similar selectivity

A series of columns aiming at the separation of the range of components targeted by the Carbobond columns have already been studied in the case of Titan's atmosphere exploration: molecular sieve 5A PLOT column [24], micro packed columns filled with Carboxen and molecular sieve 5A [11,25], and

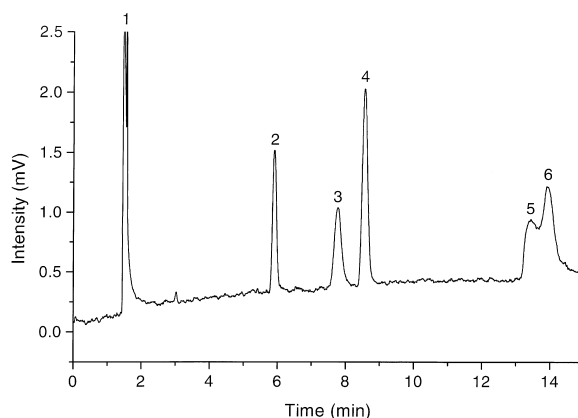


Fig. 8. Separation of N_2 , C_2H_2 , Xe, C_2H_4 and C_2H_6 with water on column No. 2. Absolute head pressure: 150 kPa. Temperature: 60°C . Absolute outlet pressure: 100 kPa. Peaks: 1=nitrogen, 2=acetylene, 3=xenon, 4=ethylene, 5=water and 6=ethane.

to a lesser extent, porous polymers (Hayesep A) [26] and molecular sieve 13X micro packed columns [26,27].

Among all the adsorbents studied for space application, it seems that molecular sieves 5A and 13X are the most adapted since all the selected compounds are separated except He and Ne. Molecular sieve 5A has also the advantage to exist under capillary PLOT column form, making it comparable, in terms of performance (efficiency, carrier gas consumption), to the Carbobond PLOT column. However, at the COSAC experimental operating conditions, the molecular sieve 13X adsorbent shows retention times too long to be compatible with the experiment constraints. Moreover, as for molecular sieve 5A, retention properties are disturbed by the presence of water in the sample (elution times inversion). Finally, the molecular sieve 5A PLOT column does not resist to the mechanical stress imposed by the vibrations generated during the rocket launch [28]. These are the main reasons why this column has not been selected for the GC–MS experiment of the Huygens probe. As a consequence, the only capillary column alternative to Carbobond cannot be used for space application, due to its poor robustness and its hydrophilic compartment.

Porous polymers supports are good packing material for the separation of gases and light hydrocarbons in presence of water. They were used in space studies for separating light gases in Viking and Pioneer Venus instruments [29,30]. Argon is well separated from nitrogen and elutes after this compound. However, CO coelutes with argon on the Porapak Q column [30]. A good resolution is achieved between Ar and CO with a Porapak N column. However, such results were obtained with a micro packed column at flow-rates larger than those used with the Carbobond PLOT column ones (several ml/min against less than one). Due to this reason (high carrier gas consumption), such column cannot be selected for space missions like Cassini–Huygens or Rosetta.

In the case of carboxen packing material, one can notice that the order of elution as well as differential adsorption enthalpies measured with Carbobond and Carboxen columns are quite close (see Table 1). As a consequence, the carbon molecular sieves used to make both types of columns should be of similar

nature. This comparison is interesting because Carboxen packing material showed good separation properties compared with other adsorbents, and has been selected for the Cassini–Huygens mission.

4. Conclusion

This work showed the suitability of the Carbobond PLOT column for in situ analysis of low-molecular-mass compounds present or expected to be found in the cometary nucleus, at the operating conditions of the COSAC experiment. An optimization study allowed to adjust the column parameters in order to improve the resolution of the eluted compounds and to select a column of 15 m×0.25 mm I.D. and 10 μm carbon film thickness. It equally proved the ability for a capillary column to replace the packed and micro-packed ones used in planetary exploration up today, thus allowing a drastic reduction of the carrier gas consumption. This conclusion is confirmed by the results of the environmental tests that reproduce the space and launch constraints: launch vibrations, radiations of the interplanetary medium and harsh cycles of temperatures that columns will be submitted during the cruise between the Earth and the comet. They show a good behavior of the stationary phase which is not damaged, at the opposite of conventional PLOT columns [28]. Such results are equally obtained with new PLOT columns having porous polymers as stationary phases, and that should be used to separate light targeted organic compounds (having typically one to three carbon atoms) heavier than the C₁ and C₂ hydrocarbons. The study of these columns should be the topic of a next article.

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