ELSEVIER

Journal of Chromatography A, 688 (1994) 161–170

JOURNAL OF CHROMATOGRAPHY A

Gas chromatography of Titan's atmosphere
V. Determination of permanent gases in the presence of hydrocarbons and nitriles with a molecular sieve micropacked column and optimization of the GC parameters using a Doehlert experimental design

E. de Vanssay[a], S. Zubrzycki[a], R. Sternberg[a,*], F. Raulin[a], M. Sergent[b],
R. Phan-Tan-Luu[b]

[a]*LISA, Centre Multidisciplinaire de l'Université Paris 12-Val de Marne, Avenue du Général de Gaulle, 94010 Créteil Cedex, France*

[b]*Laboratoire de Méthodologie de la Recherche Expérimentale, Centre de St Jérôme, Avenue Escadrille Normandie Niémen, 13397 Marseille Cedex 20, France*

First received 29 June 1994; revised manuscript received 18 August 1994

Abstract

An alternative for the GC determination of permanent gases in Titan's atmosphere, given the severe constraints of space instrumentation, is the use of a 100–120-mesh molecular sieve 5A micropacked column. Because of its high efficiency, small pressure drop and short analysis time, such a column is fully compatible with the experimental constraints of the Cassini–Huygens mission. In order to optimize the GC conditions associated with this column, a methodological approach was supported by a Doehlert experimental design. With such optimized conditions, the column provides a rapid separation of the selected products under isothermal conditions, with about 900 theoretical plates per metre at 70°C for most of the solutes studied.

1. Introduction

The composition and structure of the atmosphere of Titan, the largest satellite of Saturn, will be studied in detail by the Cassini–Huygens mission. The Huygens probe will carry a GC–MS experiment for analysing the chemical structure of Titan's atmosphere. As reported in previous papers [1–4], we are systematically studying GC columns that could provide the separation of most of the chemical constituents of Titan's atmosphere and of the pyrolysis products of its organic aerosols. We have shown that a Chrompack Molsieve 5A PLOT capillary column provides very good results for the separation of permanent gases, even in the presence of hydrocarbons and nitriles [4]. However, its mechanical strength seems too weak for space applications.

A literature survey indicated that molecular sieve 5A is one of the best materials for analyses for permanent gases. Because of the low head

---

* Corresponding author.

SSDI 0021-9673(94)00796-9

pressure and low flow-rate imposed by space instrumentation, we chose the smallest internal diameter tubing compatible with the smallest particle size commercially available. We studied columns made of 0.8 mm I.D. stainless-steel tubing packed with 100–120-mesh (150–125-μm particle diameter) molecular sieve 5A.

In such a configuration, we assume that column temperature, column length and carrier gas column head pressure are the three main parameters that can affect the chromatographic performances. For this reason, to optimize these GC parameters, we applied a methodological approach, supported by a Doehlert experimental design [5,6], which takes into account the possible interactions between parameters. The studied response functions include both classical GC performance functions and space instrumentation constraints. In the case of the Huygens GC–MS instrument, the main chromatographic constraints are as follows: (i) low inlet pressure (i.e., about 0.5 bar), for efficient sampling; (ii) low outlet flow-rate (i.e., about 1 ml/min), for efficient GC–MS coupling; and (iii) column temperature between 30 and 100°C, at least slightly above ambient (about 30°C) but not exceeding 100°C, because of the limited power available on the probe.

The aim of this work was the development of a GC column able to determine the vertical profile of CO concentration in the atmosphere of Titan where N_2 is the major component. We therefore focused our attention on the determination of N_2 and CO, including the detection limit of CO in N_2 gas mixtures. We also studied the chromatographic behaviour of C_1–C_2 hydrocarbons and the effect of nitrile injection on the column efficiency.

2. Optimization

The joint action of column temperature, column length and carrier gas pressure on column performance can be studied through theoretical approaches [7]. However, this approach is generally very complex and often requires the use of parameters the values of which are not available. We propose here a multivariate experimental approach. The overall strategy is (i) definition of the most important experimental factors, (ii) choice of the experimental domain and (iii) adjustment of these factors, by a response surface technique, to an optimum chromatographic separation taking into account the range of parameters values imposed by space instrumentation. For analysing the results we consider both chromatographic separation and the constraints of space instrumentation.

The chromatographic functions measured for given chromatographic parameter values are called responses. For many reasons (particularly since it induces a loss of information) the use of a global chromatographic response function was considered unsuitable. We preferred the use of several complementary specific response functions, namely the height equivalent to a theoretical plate (HETP) to characterize the column efficiency, the capacity factor (k') for measuring the retention and the valley height (P) to characterize the chromatographic resolution. In addition, this study also included the use of parameters (head column pressure of carrier gas and column temperature) and of response (outlet column flow-rate of carrier gas) imposed by space instrumentation. The flow-rate must be around 1 ml/min, for a head pressure drop lower than 0.5 bar and a temperature range of 30–100°C without temperature programming if possible.

3. Experimental

3.1. Column and gas chromatography

Columns packed with molecular sieve 5A were prepared with 0.8 mm I.D. stainless-steel tubing. The column length is one of the experimental parameters: three values were chosen (0.5, 0.75 and 1 m). Each column was mounted on a Hewlett-Packard HP 5890 Series II gas chromatograph, equipped with a micro thermal conductivity detector, an electro-pneumatic six-port gas sampling valve (Valco) with a 0.25-ml sample loop and a Nelson OMEGA data acquisition system. A laboratory-made adaptation of a back-pressure regulator (0–2 bar) helps to derive a stable pressure with good precision in the direct injection mode because the column is directly connected to the gas sampling valve by a zero-dead-volume adapter.It is connected to the detector by uncoated fused-silica capillary tubing about 15 cm long. In order to cover a large range of pressure (0–7 bar) we added a three-port switching valve (Valco) which allows one to switch the carrier gas from the capillary column (0–2 bar) to the packed column (0–7 bar) modified injector system (Fig. 1). In the present study, owing to the range of carrier gas pressure used (0–0.5 bar), and to the highest possible accuracy of the associated manometer (about 0.02 bar), we used only the capillary column system.

The GC column was operated isothermally in the range 30–100°C. The temperatures of the detector, injector and gas sample valve were chosen as a function of the column temperature. Hydrogen was used as the carrier gas because for an equivalent column efficiency it can provide faster analyses. In addition, it is much more convenient for GC–MS space instrumentation,

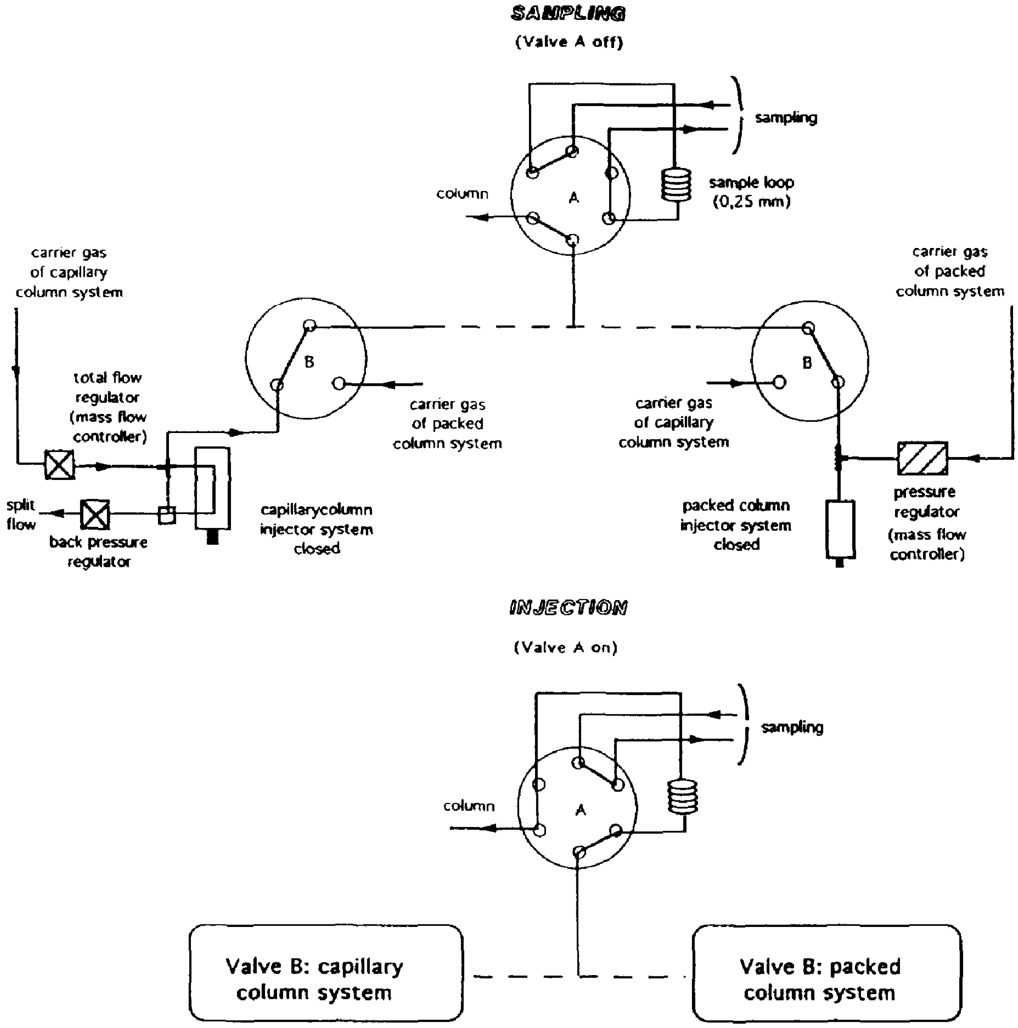

Fig. 1. Schematic representation of the laboratory-made injector adaptation with a gas sampling valve.

as it is much more easily pumped out than other carrier gases.

3.2. *Sampling*

Standard gas mixtures of known composition including CO, N_2, CH_4, C_2H_6 (with eventually other C_2 hydrocarbons) and noble gases (He, Ne, Ar, Kr and Xe) were prepared and stored in a sampling glass reservoir connected to a vacuum line and equipped with a high-vacuum stopcock (SVT, Ris Orangis, France). This reservoir was initially evacuated and then, except for CH_4 and Ar, each individual component was successively introduced by expanding a known volume of each gas at a known and precalculated pressure, as described previously [1]. CH_4 and Ar were introduced simultaneously by using a commercially available CH_4–Ar gas mixture (90:10). A similar method was followed to prepare the samples used to study the effect of CO dilution in N_2. The loop of the gas sampling valve was also connected to the vacuum line. It was directly sampled, at a known pressure, by expanding the content of the reservoir to the loop, initially evacuated.

The vacuum line, connected to a primary pump, was able to reach a vacuum as good as 10^{-2} mbar, checked with a Pirani vacuum gauge (MKS, Andover, MA, USA). Sample absolute pressures were measured with a manometer (Schlumberger, Montrouge, France) with a relative precision of better than 1%.

3.3. *Reagents*

Helium (grade C) was supplied by AGA (Toulouse, France). All other gases, i.e., argon–methane mixture (90:10, pure), nitrogen, neon and ethane (grade N30), krypton (grade N35), xenon, carbon monoxide and methane (grade N45) were supplied by Alphagaz–L'Air Liquide (Bois d'Arcy, France).

3.4. *Selection of experimental factors and studied responses*

The aim of this work was the GC study of CO when diluted in N_2. The effect of the column diameter and particle size on the detection limit are well known: the detection limit increases when these factors decrease. We therefore fixed the particle diameter at the lowest commercially available size, i.e., 100–120 mesh, corresponding to 150–125 μm mean particle diameter (d_p). We also used an optimum column diameter ($d_c = 0.8$ mm I.D.) corresponding to this particle diameter ($dc/dp \approx 5$) [7].

Table 1
Experimental domain

Real factor (natural variable)	Coded variable	Units	Centre	Step
U_1 = column temperature	*X1*	°C	75.00	50
U_2 = column pressure	*X2*	bar	0.40	0.69
U_3 = column length	*X3*	m	0.75	0.306

For each response, one can derive a model, and each response model is expressed using coded variables. In the following, *Xi* stands for the coded setting of real variable U_i. The column parameters, carrier gas head pressure, temperature and column length, which all have an effect on retention time and on chromatographic efficiency, were studied. The variation steps (ΔU_i) and centre values (U_i^0) of these experimental factors are specified in Table 1. The use of coded factor settings instead of the natural values (U_i) allows a quantitative comparison of the relative importance of each variable directly from the model.

The different response functions (η_i) used in this work are summarized in Table 2. The column capacity factor (k') was measured for

Table 2
Response functions (η_i) selected in this study

η_1	Flow-rate (ml/min)
η_2	*trmax*: maximum retention time (min)
η_3	HETP CO (mm)
η_4	HETP Xe (mm)
η_5	k'Ar: capacity factor
η_6	$k'N_2$: capacity factor
η_7	k'CO: capacity factor
η_8	k'Xe: capacity factor
η_9	$P(N_2 - CH_4) = P1$: valley height
η_{10}	$P'1 + P2$

Table 3
Theoretical values of coded variables (reduced coordinates of cuboctahedron)

No.	Coded variable		
	X1	*X2*	*X3*
1	0	0	0
2	1	0	0
3	−1	0	0
4	0.5	0.866	0
5	−0.5	−0.866	0
6	0.5	−0.866	0
7	−0.5	0.866	0
8	0.5	0.2887	0.8165
9	−0.5	−0.2887	−0.8165
10	0.5	−0.2887	−0.8165
11	0	0.5774	−0.8165
12	−0.5	0.2887	0.8165
13	0	−0.5774	0.8165

Ar, N_2, CO and Xe. Calculations of HETP were done only for CO because of its importance in Titan's photochemical models and Xe because it is the last solute eluted. For N_2, Kr, CH_4 and CO the height of valley (*Pi*), which varies within the range 0–1, was estimated for N_2 and CH_4 (*P1*), N2 and Kr (*P'1*) and CO and Xe (*P2*) because these pairs of peaks may be co-eluted (the total resolution between the peaks related to these compounds is rare). The other responses studied were the duration of the analysis (*trmax*) and the flow-rate of the carrier gas (*Fc*). In fact, after data retriveal, the *P'1* and *P2* responses appeared not to be sufficiently explicit for a good optimization. Therefore, we finally considered the sum of these two responses; this is the η_{10} response and it varies within the range 0–2.

3.5. *Experimental design [5,6]*

We used a "Doehlert uniform shell design [5,6]". It is derived from the theoretical example described below, starting from the theoretical coefficients presented in Table 3. Let us consider that the twelve sets of coefficients of this table (Nos. 2–13) correspond the reduced coordinates of the twelve vertices of a regular cubooctahedron. Such a geometrical figure offers a spatial representation of an experimental domain (covering the range of selected experimental parameters). The first set of coefficients (No. 1) corresponds to the reduced coordinates of the central point of this figure. From this experimental design, one can deduce an experimental plan, by converting coded variables *Xi* into the real variable (to be experimentally used) U_i, using the relationship $U_i = U_i^0 + X_i \Delta U_i$. Table 4 sum-

Table 4
Doehlert design: natural and coded variables[a] for each experiment (test)

Test	Natural variable			Coded variable		
	U_1 (°C)	U_2 (bar)	U_3 (m)	*X1*	*X2*	*X3*
1	75	0.4	0.75	0	0	0
2	100	0.4	0.75	1	0	0
3	50	0.4	0.75	−1	0	0
4	87	0.6	0.75	0.48	1	0
5	62	0.2	0.75	−0.52	−1	0
6	87	0.2	0.75	0.48	−1	0
7	62	0.6	0.75	−0.52	1	0
8	87	0.45	1	0.48	0.25	1
9	62	0.35	0.5	−0.52	−0.25	−1
10	87	0.35	0.5	0.48	−0.25	−1
11	75	0.5	0.5	0	0.5	−1
12	62	0.45	1	−0.52	0.25	1
13	75	0.3	1	0	−0.5	1

[a] The equation $U_i = U_i^0 + X_i \Delta U_i$ allows one to switch from coded variables to natural variables; U_i^0 = value of the natural variable, *i*, at the centre of the experimental domain; ΔU_i = step of variation of the natural variable, *i*, for a unit variation of the coded variable *Xi*.

marizes the values of the real variables used in this study and the corresponding derived coded variables.

3.6. Mathematical methods

Principles of response surface methodology [8,9]

It is reasonable to assume that the variation of the observed responses Y is functionally related to the detailed settings of the experimental factors. However, as the responses are experimentally determined, there will always be an experimental error component. We therefore write the functional relationship between the observed response and the experimental factors as

$$Y = f(X1, X2, \ldots, Xn) + e$$

where Xi are the coded variables and e is the experimental error component. It is not possible to derive an analytical expression for f from purely theoretical considerations. However, if we try to estimate f through a Taylor expansion, it will take the form of a polynomial in the independent factors:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \sum \beta_{ij} x_i x_j + \sum \sum \sum \beta_{ijk} x_i x_j x_k + \cdots + e$$

A sufficiently good approximation can often be obtained if the Taylor development is truncated after the second-degree terms. The polynomial coefficients (which are in fact the model parameters) can be estimated by using the least-squares multiple regression of the polynomial to the observed response. The results (response surfaces) are obtained by the least-squares method. They are drawn up to 5% of the maximum experimental values, the lower variations being considered as non-significant.

All analytical treatments were supported by a specific software named NEMROD [10]. The principal analysis of the main components is included in the software.

Desirability function

In order to quantify our "desire", we used a specified function defined between 0 and 1. The nature of this function is related to the type and range of variation of each response.

The principle of this function is based on the search for a global optimum. To obtain this optimum, we build a desirability function $D = f(Y1, Y2, \ldots, Yn)$ defined by

$$D = \left(\prod_j d_j^{w_j}\right)^{1/w}$$

with $w = \Sigma_j w_j$, where dj is a partial desire function of D defined for each response η_i and w is a balancing empirical factor which improves the specific weight of each dj function.

The last step is the search for the optimum of the D function. For that purpose, we plot the surface response of D versus the Xi parameter. If D is equal to zero, the corresponding values of Xi variables are not considered. The result of this computation is expressed on a response surface graph. In addition, the software gives the maximum value of D corresponding to the optimum set of values of the Xi variables.

4. Results and discussion

The responses observed in these experiments are summarized in Table 5. In Table 6, we have calculated the ten coefficients bi of the experimental model for each response Yi. First, a response surface study was carried out on all responses in order to visualize their behaviour. The results show that factor $X3$, which corresponds to the length of the column, is generally the most important and that the column head pressure ($X2$) generally exhibits a very small influence (except for the flow-rate $Y1$). However, this factor is one of the main parameters constrained by space instrumentation, so it is not possible to rule it out. We tried to optimize this experiment within the domain of parameter values compatible with such constraints.

Then, for optimizing the three parameters $X1$, $X2$ and $X3$, we determined the partial desire function dj for the ten responses (all responses except $P'1$ and $P2$). Four types of such a function are presented in Fig. 2. They corre-

Table 5
Values of each response for all experiments (test)

Test	Flow-rate (ml/min)	Analysis time (min)	HETP (mm)		Capacity factor				Valley height	
	Y1	Y2	Y3 (CO)	Y4 (Xe)	Y5 (Ar)	Y6 (N_2)	Y7 (CO)	Y8 (Xe)	P1 (Y9)	P'1 + P2 (Y10)
1	1.32	4.54	1.61	2.08	0.43	1.19	4.67	7.02	0.90	1.00
2	1.32	3.24	1.76	2.19	0.34	0.79	2.50	4.56	0.67	1.24
3	1.50	6.91	1.62	2.83	0.58	1.96	9.70	11.68	0.99	0.47
4	2.21	4.03	1.26	2.04	0.59	1.69	7.21	9.66	0.97	0.99
5	0.85	8.67	1.91	2.14	0.51	1.57	6.71	9.00	0.90	0.88
6	0.85	5.88	2.41	2.46	0.40	1.00	3.50	5.67	0.65	0.96
7	2.21	4.05	1.38	2.36	0.60	1.70	7.23	9.76	0.97	0.91
8	1.03	5.89	1.77	2.35	0.50	1.14	3.78	7.54	0.75	1.80
9	1.54	3.11	1.60	4.55	0.45	1.13	4.48	7.04	0.55	0.93
10	0.43	8.37	3.97	3.51	0.42	1.09	3.59	5.86	0.00	0.86
11	2.14	1.94	1.55	5.99	0.40	0.96	3.31	5.67	0.29	1.00
12	1.03	9.54	1.80	2.23	0.66	1.79	7.24	12.25	0.92	1.66
13	0.76	10.36	2.29	2.21	0.58	1.41	5.17	9.41	0.79	1.64

spond to the type of variation of *dj* (between 0 and 1) versus the value of the following responses: (a) flow-rate (*Y1*), (b) *trmax* (*Y2*), (c) HETP (*Y3* and *Y4*) and (d) capacity factor and valley height (*Y5* to *Y10*). The observed curves exhibits non-linear variations. From this *dj* the global desire function *D* as a function of *Xi* is derived. Then, the variation of *D* can be plotted against the value of *Xi*, as shown in Fig. 3. Fig. 3a represents the variation of *D* of *X1* and *X2* for a given *X3* value ($X3 = 0.657$) fixed by the optimum *D* value. The projection of the volume thus defined on the *X1*, *X2* surface (along the *D* axis) is presented in Fig. 3b. The results of the computed optimization of the global *D* function allow one to define, in the first quadrant (Fig. 3b), a domain where the chromatographic parameters are optimum for the selected range of parameters values. In this domain, the point where the *D* function is optimum (top point) has the coordinates (0.223, 0.720, 0.657) corresponding to an 80°C column temperature (U_1), 0.55 bar column head pressure (U_2) and 0.9 m column length (U_3). To improve the reliability of these data, we studied the influence of small variations of the coordinates *Xi* on response *Yj*

Table 6
Coefficients *bi* of each experimental model response *Yi*

Coefficient	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10
b0	1.3200	4.540	1.6100	2.080	0.4300	1.9000	4.6700	7.020	0.9000	1.0000
b1	−0.1838	−0.065	0.3750	−0.275	−0.0984	−0.4510	−2.7468	−2.945	−0.2013	0.2213
b2	0.7946	−2.330	−0.6149	0.251	0.0558	0.1640	0.8607	0.986	0.0931	0.0411
b3	−0.2633	2.527	−0.2572	−1.482	0.0966	0.2372	0.9831	2.169	0.3307	0.4715
b11	0.0900	0.537	0.0800	0.430	0.0300	0.1850	1.4300	1.100	−0.0700	−0.1450
b22	0.2500	1.311	0.1467	0.083	0.1167	0.3384	1.5134	1.637	−0.0133	0.0383
b33	−0.3325	2.533	0.7733	1.962	0.0716	−0.0354	−0.8469	0.727	−0.5042	0.5183
b12	0.0000	1.599	−0.3580	−0.370	0.0577	0.3233	1.8418	1.865	0.1443	0.0000
b13	0.6797	−6.016	−1.3431	0.841	−0.0982	−0.4866	−2.2213	−2.823	0.1817	0.1286
b23	−0.5691	1.093	0.5397	−1.452	0.0565	0.1999	0.7847	1.083	0.0412	0.0271

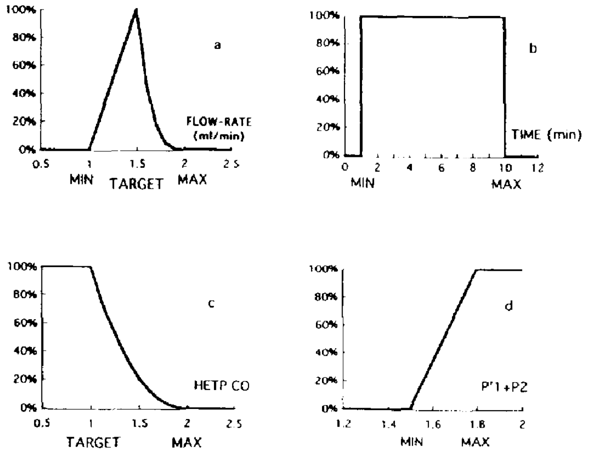

Fig. 2. Four typical partial desire function *dj* adapted for each experimental response function *Yi*: (a) represents flow-rate (*Y1*); (b) represents *trmax* (*Y2*); (c) represents HETP (*Y3* and *Y4*); (d) represents capacity factor and valley height (*Y5* to *Y10*).

and partial desire function *dj*. The results show only a slight variation of *Yj* and *dj* functions with *Xi*. This indicates that the range of parameter values corresponding to the optimum conditions is relatively wide.

A chromatogram obtained around the top point values is displayed in Fig. 4. Only one co-elution is observed, corresponding to He and Ne solute. This co-elution is also observed when a capillary column is used [4] excepted at low temperature (i.e., 20°C). The three solutes, N_2–Kr–CH_4, the GC resolution of which is characterized by the valley heights *P1* and *P'1*, are not fully separated, but this separation is sufficient for a quantitative GC–MS analysis.

4.1. CO dilution

Using the chromatographic values corresponding to the top point, we studied the limit of detection of CO in N_2 with a thermal conductivity detector. For 370 ppm of CO in N_2, the CO chromatographic peak is well separated from that of N_2 and its size and shape are compatible with a quantitative analysis. For 33 ppm of CO in N_2, the peak is still visible, but appears as a shoulder which does not allow a quantitative analysis.

4.2. Behaviour of light hydrocarbons and nitriles

Gas samples of Titan's atmosphere to be analysed will include light hydrocarbons and nitriles at noticeable concentrations. It is therefore of prime importance to know the chromatographic behaviour of these compounds on the GC columns which may be selected for the flight GC–MS instrument. If they are eluted with retention times short enough to be compatible with the GC analytical cycle, then the column dedicated to permanent gas analysis will also give information on these low-molecular-mass organics. If their retention time is longer than the duration of the GC analytical cycle, then it is important to know the shape of their GC peaks and to check whether there is any risk of interference between these "ghost" peaks and the others. Finally, if the compounds are not eluted at all, then it is necessary to check that their irreversible adsorption on the GC column does not induce any significant change in the chromatographic behaviour of the column.

The obtained results are the following. Hydrocarbons with more than two C atoms are not eluted from the molecular sieve 5A column at $T \leq 100°C$ (even after 2.5 h). C_2H_2 and C_2H_4 show very long retention times with broad and irreproducible GC peaks. Because of their low concentrations in Titan's atmosphere, the corresponding GC ghost peak expected from these compounds on the flight gas chromatograph should not interfere with the analysis of permanent gases. Only ethane gives a GC peak of noticeable intensity with the molecular sieve column, but with a retention time which is about twice that of CO (at 100°C). Its elution will have to be taken into consideration in interpreting Titan's gas chromatograms: the C_2H_6 peak may appear as a ghost peak eluted during the chromatographic cycle of a sample corresponding to a later injection. However, the shape of this peak, much broader than those of peaks corre-

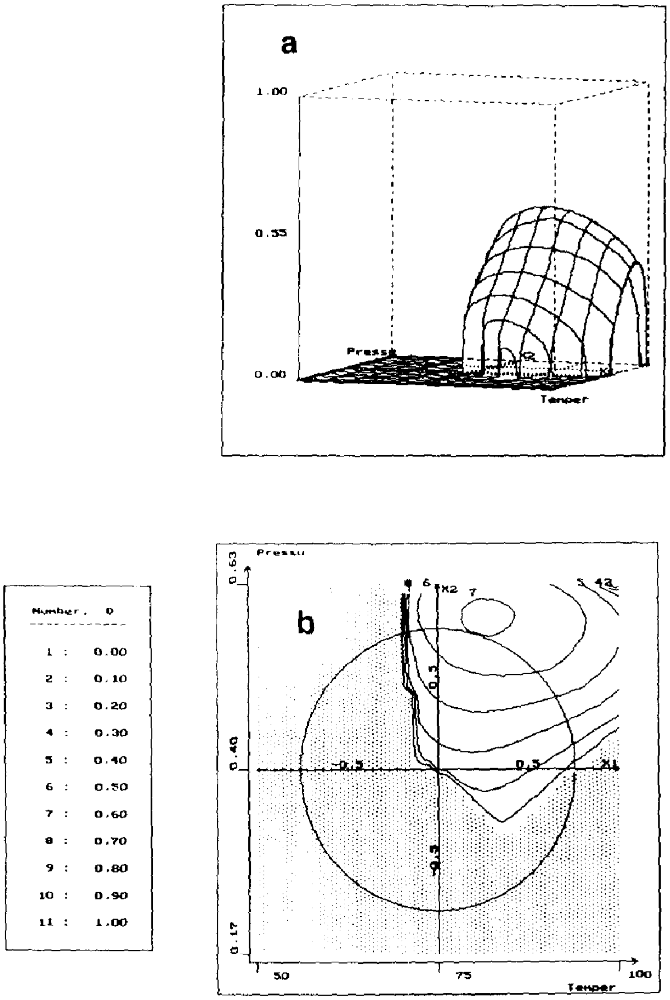

Fig. 3. (a) Response surface of the global desire function D versus $X1$ (temperature), $X2$ (pressure) and $X3 = 0.657$ (length). (b) Projection along the D axis of the surface defined in (a) on $X1$, $X2$ plan. Each curve represents an iso-D level. The values of each iso-D level are shown in the left column.

sponding to the last injection, may help to solve this problem.

Similar studies were carried out with nitriles (acetonitrile, cyanogen and butyronitrile). None of these compounds is eluted even at relatively high column temperatures (up to 100°C). The chromatographic behaviour of permanent gases was also studied after injecting various amounts of these nitriles (from 1 nmol to 2 μmol of each) into the molecular sieve 5A column. No significant changes in the retention times and peak shapes of the permanent gases were observed.

5. Conclusions

In this study, the experimental domain that we have defined a priori appears suitable for the space application we were looking for. However, we have not used the specific properties of the Doehlert experimental design. They consist in an easy displacement of the design into an unexplored portion of the experimental domain. Adding new variables that had not been previously studied is easy. Nevertheless, the small set of experiments that are derived from this method

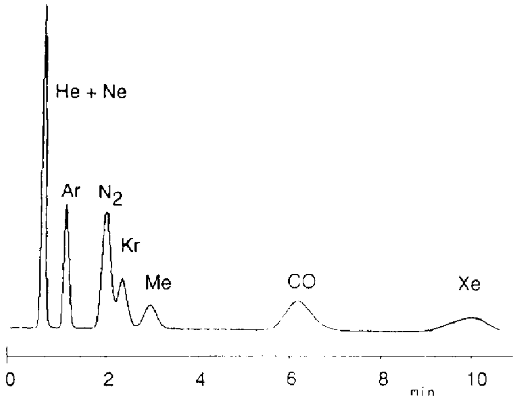

Fig. 4. GC analysis of a mixture of permanent and noble gases on a capillary column packed with molecular sieve 5A (1 m × 0.8 mm I.D.). Carrier gas, H_2; flow-rate, 1.3 ml/min; column head pressure, 0.45 bar; column temperature, 62°C.

allows a rapid overall study of the behaviour of the molecular sieve 5A packed column under relatively strong experimental constraints. With the optimum conditions obtained by this method (81°C, 0.55 bar and 0.91 m), which correspond to a flow-rate of 1.5 ml/min and an analysis time (*trmax*) shorter than 6 min, the molecular sieve 5A capillary column provides a sufficiently good separation of permanent and noble gases in the presence of hydrocarbons and nitriles for their determination in the atmosphere of Titan. The total amount of hydrocarbons and nitriles injected into the column during the descent of the Huygens probe in the atmosphere of Titan will still be one to two orders of magnitude [11,12] below the currently tested conditions. Hence it can be assumed that such a column will not be affected by the chemical conditions of Titan's environment. In addition, the chromatographic conditions are fully compatible with MS coupling and space instrumentation.

However, the determination of C_2 hydrocarbons does not seem possible with such a column. A study of capillary columns packed with other adsorbents such as molecular sieve 13X, Haysep A, carbon molecular sieve or mixed adsorbents is in progress. The experimental design used for these experiments will include new parameters such as the ratio of mixed adsorbents and CO concentration.

Acknowledgements

We thank E. Shiba for his help during the development of this work. This research was supported by a grant from the Centre National d'Etudes Spatiales.

References

[1] L. Do and F. Raulin, *J. Chromatogr.*, 481 (1989) 45.
[2] L. Do and F. Raulin, *J. Chromatogr.*, 514 (1990) 65.
[3] L. Do and F. Raulin, *J. Chromatogr.*, 591 (1992) 297.
[4] E. de Vanssay, P. Capilla, D. Coscia, L. Do, R. Sternberg and F. Raulin, *J. Chromatogr.*, 639 (1993) 255.
[5] D.H. Doehlert, *Appl. Statist.*, 19 (1970) 231.
[6] D.H. Doehlert and V.L. Klee, *Discrete Math.*, 2 (1972) 309.
[7] G. Guiochon and C.L. Guillemin, *Quantitative Gas Chromatography* (Journal of Chromatography Library, Vol. 42), Elsevier, Amsterdam, 1988.
[8] G.E.P. Box and N.R. Draper, *Empirical Model-Building and Response Surfaces*, Wiley, New York, 1987.
[9] A.L. Sunesson, C.A. Nilsson and B. Andersson, *J. Chromatogr.*, 623 (1992) 93.
[10] D. Mathieu and R. Phan-Tan-Luu, *NEMROD Software*, LPRAI, Marseille, France, 1978.
[11] A. Coustenis, in *Proceedings of Symposium on Titan*, ESA Spec. Publ., SP-338, Estec, Noordwÿk, Netherlands, 1992, p. 53.
[12] D. Toublanc, J.P. Parisot, J. Brillet, D. Gautier, F. Raulin and C.P. McKay, *Icarus*, in press.