

Gas chromatography of Titan's atmosphere

IV. Analysis of permanent gases in the presence of hydrocarbons and nitriles with a Molsieve PLOT capillary column

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ABSTRACT

A Molsieve 5A wide-bore capillary column was systematically studied for the separation of CO and N₂ in the presence of other permanent gases, including noble gases, light hydrocarbons and nitriles, which are all plausible constituents of Titan's atmosphere. This column has a chromatographic behaviour similar to that of a molecular sieve 5A packed column. The efficiency of the column, the detection limit of CO in N₂ and the effect of the presence of nitriles in the injected samples on the chromatographic performance of the column were characterized by determining Van Deemter curves for CO, N₂ and noble gases at different temperatures. This column offers a rapid separation of the selected solutes under isothermal conditions, with about 1000 theoretical plates/m at 60°C for most of the solutes.

INTRODUCTION

As reported in previous papers in this series [1–3], we are systematically studying GC columns that could provide the separation of most of the constituents of Titan's atmosphere and of the pyrolytic products of its organic aerosols, for integration in the GC–MS instrument of the Cassini–Huygens mission. One of the objectives with this instrument is to determine the vertical concentration profile of several of the organic and inorganic species present in the atmosphere, including hydrocarbons, nitriles, CO, N₂, CH₄, Ar and other noble gases. The GC subsystem should be able to achieve the

separation of these compounds in a relatively short time (*i.e.*, within less than, say, 10 min), under conditions fully compatible with the constraints of space instrumentation. These include the constraints induced by GC–MS coupling such as low carrier gas inlet pressure, low flow-rate and simple column temperature cycle (the easiest being isothermal conditions). The previous papers reported studies of GC columns for analysing organic compounds. This present paper deals with the analysis of CO and permanent gases. Such an analysis is of paramount importance, as the GC–MS instrument will have to confirm and determine the depletion of CO in Titan's stratosphere, relative to the troposphere [4], the origin of which is still not clearly understood [5]. To achieve such an objective, it is crucial that the GC stage provides a good separa-

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tion of CO from N₂, as the MS subsystem will not be able to perform direct determination of CO because of the presence of large amounts of N₂, the main atmospheric component, and because of the limited mass resolution of the instrument.

To achieve such a separation, we have carried out studies in two complementary directions: small and short columns packed with microparticles and wide-bore capillary columns, both using a molecular sieve. This packing material has been widely used in the GC analysis of permanent gases with conventional packed columns, including GC devoted to space instrumentation [6,7]. A molecular sieve has also been used recently as a coating material in wide-bore fused-silica capillary columns, such as the Molsieve 5A column (Chrompack, Middelburg, Netherlands). The characteristics and chromatographic performance of this capillary column have already been published [8].

A wide-bore Molsieve 5A column seems to offer the advantages of both capillary columns, *i.e.*, combining the possibility of high resolution and relatively fast analysis, and those of conventional packed columns, with a high charge capacity [8]. However, no detailed studies of this column, including Van Deemter curves, have been reported. In addition, no data were available on the separation limit of CO in N₂ or on the possible effect of the injection of non-eluted compounds such as nitriles on the behaviour of this column. To obtain such crucial information (in particular in terms of reproducibility of the chromatograms, and eventual degradation of its performance due to the injection of compounds of high polarity), we have systematically studied a Molsieve 5A capillary column and the results are reported in this paper.

EXPERIMENTAL

Column and gas chromatograph

The Molsieve 5A column was a 10 m × 0.53 mm I.D. PLOT fused-silica capillary column coated with a 50- μ m film of molecular sieve 5A. It was mounted on a Hewlett-Packard Model HP 5890 Series II gas chromatograph equipped with a micro thermal conductivity detector, an elec-

tro-pneumatic six-port gas sampling valve (Valco) with a 0.25- or 2-ml sample loop and a Spectra-Physics Model SP 4100 integrator-recorder.

The GC column was operated isothermally at temperatures in the range 30–130°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 equivalent HETP values it can provide faster analyses. In addition, it is more convenient for GC-MS instrumentation in space, as it is much more easily pumped out than other carrier gases. Its flow-rate was adjusted around 2 ml/min (except when determining HETP values).

In most of the studies, the gas chromatograph was used in the split mode (splitting ratio from 10:1 to 100:1). For studying the effect of the dilution of CO in N₂, the splitless mode was chosen. In that case, to obviate any effect of the injector dead volume, a purge septum flow of hydrogen was maintained at 1 ml/min.

Sampling

Standard gas mixtures of known composition, including CO, N₂, CH₄, C₂H₆ 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, then a commercial CH₄-Ar mixture and each component were successively introduced by expanding a known volume at a known and precalculated pressure, as described previously [1]. A similar method was used for preparing the samples used to study the effect of CO dilution. 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 contents of the reservoir to the loop, initially evacuated.

The vacuum line through the primary pump was able to reach a vacuum as good as 10⁻² mbar, checked with a Pirani vacuum gauge (MKS, Andover, MA, USA). Absolute pressures were measured with a pressure gauge (Schlumberger, Montrouge, France) with a relative precision of better than 1%.

Reagents

Cyanogen was obtained from Matheson (East Rutherford, NJ, USA) and helium (grade C) from 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 purchased from Alpagaz–L'Air Liquide (Bois d'Arcy, France).

Determination of Van Deemter curves

To determine experimentally the height equivalent to a theoretical plate (HETP), H , versus the mean linear velocity of the carrier gas, \bar{u} , the different selected solutes were injected with helium at different inlet pressures of the carrier gas and different column temperatures. The outlet flow-rate was measured with a bubble flow meter.

The value of \bar{u} was calculated from the relationship $\bar{u} = L/t_m$, where L is the length of the column and t_m is the retention time of helium. For the selected solutes, H was calculated from the classical relationship:

$$H = \frac{Lw_h^2}{5.54(t_r - t_m)^2} \quad (1)$$

where t_r is the retention time of the solute and w_h is the peak (assumed to be Gaussian) width at half-height.

The fitting of the Van Deemter curve with the experimental data was performed by using a polynomial regression program based on an extended Golay–Giddings equation:

$$H = B/\bar{u} + C\bar{u} + D\bar{u}^2 \quad (2)$$

where the term $D\bar{u}^2$ represents the apparatus contribution [9].

To verify the influence of these coefficients on the fitting, we studied two other polynomial regression programs. The first uses the classical Golay equation:

$$H = B/\bar{u} + C\bar{u} \quad (3)$$

and the second, because of the small effect of C , uses the equation

$$H = B/\bar{u} + D\bar{u}^2 \quad (4)$$

Optimization of detector response

In preliminary work, we studied and optimized the response of the thermal conductivity detector, particularly for CO. This response can be characterized by $R = (A/w)P$, where A is the integrated area of the chromatographic peak, w its half-width and P the pressure of the injected solute. R was studied as a function of the ratio of the detector to column temperature, T_d/T_c , and as a function of the duration of the splitless mode for various sample pressures. The highest responses were obtained for a splitless duration of about 30 s and a T_d/T_c value of about 2.

RESULTS AND DISCUSSION

The Molsieve column provides a good separation of most of the selected solutes within a relatively short time. For instance, at 90°C, as shown in Fig. 1, with the exception of He and Ne which are co-eluted, all the permanent gases and CH₄ are measured in about 8 min. Under these conditions, the higher molecular mass organic compounds are not eluted before 22 min (ethane).

In order to characterize quantitatively the performance of the column and its behaviour after injection of nitriles, we determined Van Deemter curves at different temperatures with and without injection of nitriles. Fig. 2 presents

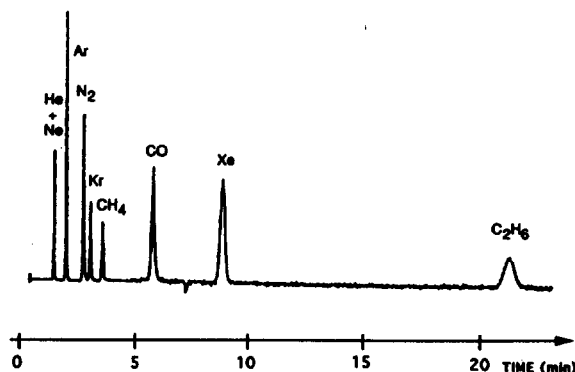


Fig. 1. Gas chromatogram of a gaseous mixture of He, Ne, Ar, N₂, Kr, CH₄, CO, Xe and C₂H₆ on a 10 m × 0.53 mm I.D. Molsieve 5A (film thickness 50 μm) fused-silica PLOT column at 90°C. Carrier gas, H₂; outlet flow-rate, 2 ml/min; amount injected, ca. 3 nmol of each constituent; splitting ratio, 40:1; thermal conductivity detector.

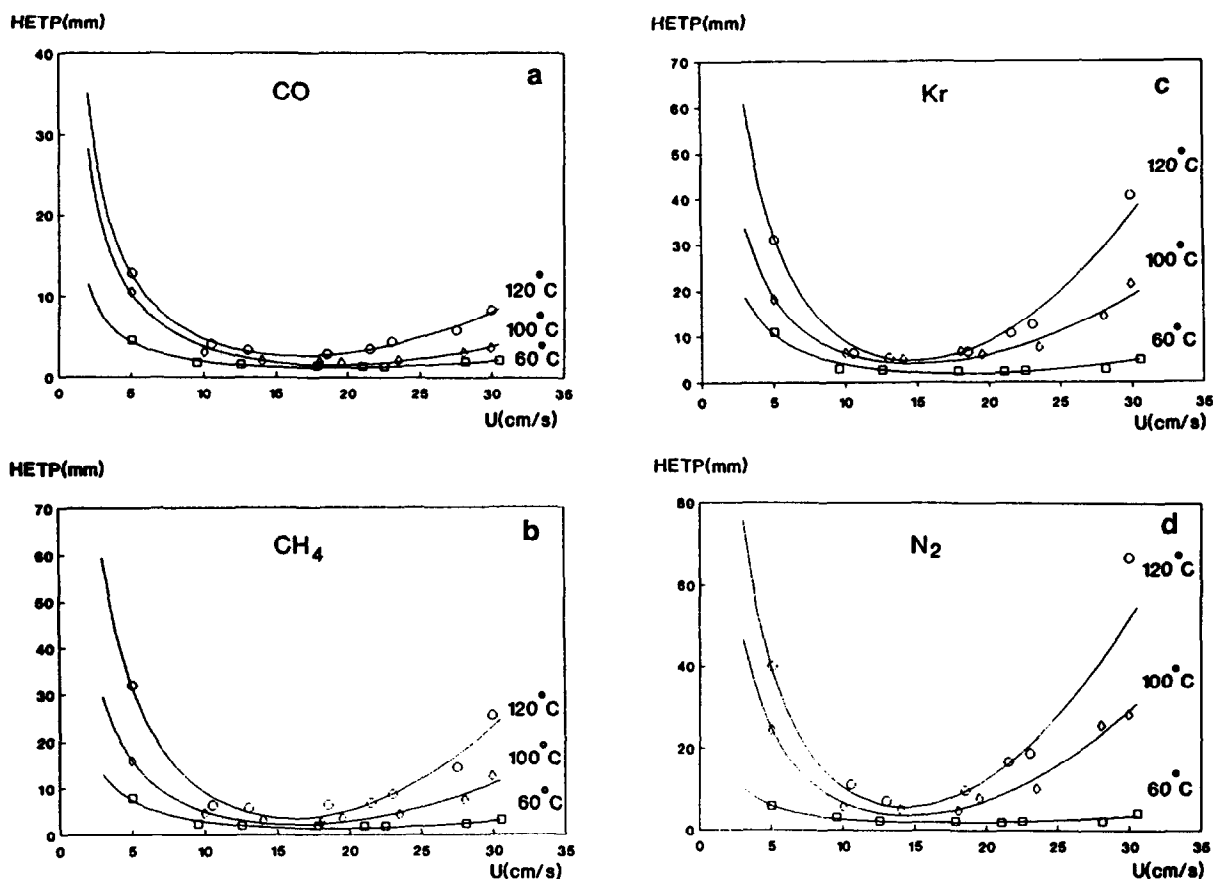


Fig. 2. Plots for (a) CO, (b) CH₄, (c) Kr and (d) N₂ of the height equivalent to a theoretical plate (HETP) versus the mean linear velocity (\bar{u}) of the carrier gas (H₂) at 60, 100 and 120°C on a 10 m × 0.53 mm I.D. Molsieve 5A (film thickness 50 μm) fused-silica PLOT column. The points correspond to experimental data and the curves to the best theoretical fit based on the extended Golay–Giddings' equation: $H = B/\bar{u} + C\bar{u} + D\bar{u}^2$.

the results relating to N₂, CH₄, Kr and CO (Fig. 2A, B, C and D, respectively), for three column temperatures. They were obtained by injection of about 3 nmol of each solute in the injector. There is a satisfactory fit between the experimental results (points) and the extended theoretical fitting curves $H = B/\bar{u} + C\bar{u} + D\bar{u}^2$. For all these solutes, the minimum HETP (H_m) is reached for an optimum \bar{u} (\bar{u}_m) of about 20 cm/s at 60°C and 15 cm/s at 120°C, corresponding to 1.9 and 1.4 ml/min, respectively. This H_m ranges between 1 mm (CO at 60°C) and 8 mm (N₂ at 120°C) and it increases with temperature, as is usually observed. The part of the curve corresponding to \bar{u} values higher than \bar{u}_m has a slope that also increases with increasing temperature. This can

be easily explained by an increase in the diffusion coefficient of the solute with temperature.

The HETP values thus determined are of the same order of magnitude (1.4 mm at 60°C for methane) as those indicated by Chrompack, the column manufacturer (1.3 mm at 30°C for methane). These values are high probably because of the relatively large film thickness (50 μm).

The possible influence of the presence of nitriles in the injected samples on the behaviour of this column was studied by injecting various amounts of cyanogen, simultaneously with constant amounts (about 3 nmol) of CO and N₂, and by measuring the HETP for the two permanent gases. In each series of experiments, the amount

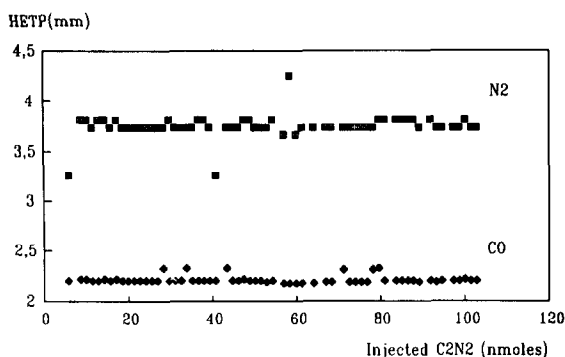


Fig. 3. Plot of the height equivalent to a theoretical plate (HETP) versus the amount of cyanogen (C_2N_2) injected for CO and N_2 at $100^\circ C$. Carrier gas, H_2 ; column, $10\text{ m} \times 0.53\text{ mm}$ I.D. Molsieve 5A (film thickness $50\ \mu\text{m}$) fused-silica PLOT.

of cyanogen was systematically increased from the first to the last injection. The column was then conditioned at $270^\circ C$ for 16 h, before carrying out a new series of experiments. The results show that the retention times of the eluted solutes are not modified by the presence of cyanogen in the sample, even after several injections of large amounts (several micromoles) of nitrile. Further, the HETP is not affected by the irreversible adsorption of these amounts in the column, as shown in Fig. 3.

CONCLUSIONS

The Molsieve 5A wide-bore capillary column allows a good and rapid separation of permanent gases, including CO, N_2 and noble gases, in the presence of hydrocarbons and nitriles. It is important to note that the injection of relatively large amounts (several micromoles) of cyanogen does not degrade or modify markedly the performance and behaviour of the column. The maximum mole fraction of nitriles in the low atmosphere of Titan is less than about 10^{-4} [10,11]. The sampling volume of the GC subsystem of the GC-MS set-up in the Cassini-Huygens mission will be less than 1 ml. Hence the absolute amount of nitrile in one sample (even at the maximum Titan atmosphere pressure of 1.5 bar) will be less than about 10^{-8} mol. Even after ten injections (which will peak during the descent of the probe), clearly the total

amount of nitrile adsorbed in the column will still be one to two orders of magnitude 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, in terms of temperature (about $100^\circ C$), flow-rate (less than about 2 ml/min) and inlet relative pressure (0.5 bar), are fully compatible with the constraints of MS coupling and space instrumentation.

However, the mechanical resistance of this column has not yet been tested under the acceleration and vibration conditions of a rocket launch. If such a test shows that it cannot withstand these intense vibrations, as has recently been observed for other PLOT columns [3], then one should consider the other option, viz., the use of a short capillary column packed with a molecular sieve. The study of such packed columns (similar to the present one) is in progress.

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