Gas chromatography of Titan's atmosphere
VIII. Analysis of permanent gases with carbon molecular sieve packed capillary columns

A. Aflalaye[a], R. Sternberg[a,*], D. Coscia[b], F. Raulin[a], C. Vidal-Madjar[c]

[a]LISA, Université Paris 7 et 12 - URA 1404 du CNRS, Centre Multidisciplinaire, 61 Avenue du Général de Gaulle,
F. 94010 Créteil Cedex, France
[b]LISA and Service d'Aéronomie, B.P.3, 91371 Verrières le Buisson Cedex, France
[c]Laboratoire de Physico-Chimie des Biopolymères, UMR 27 CNRS-Université Paris 12, 2 Rue Henri Dunant, 94320 Thiais, France

Abstract

An alternative for an in situ GC analysis of permanent gases in Titan's atmosphere, given the severe constraints on space instrumentation, is the use of microcolumns packed with carbon molecular sieve. The differential adsorption enthalpies are determined from the variation of retention volume with temperature. A linear variation with the polarisability of solutes is obtained and the relative retentions are similar to the adsorptions observed on graphitized carbon black. Two columns having different porosities are compared with respect to efficiency, resolution and detection limit. They all provide high efficiency, fast analysis and a detection limit of CO in N_2 suitable for the quantification of Titan's atmosphere composition. This detection limit is also studied with a vacuum column outlet using a mass spectrometer under conditions close to those of the flight instrument of the Huygens probe.

Keywords: Titan's atmosphere; Stationary phase, GC; Carbon molecular sieve; Carbon monoxide; Nitrogen; Permanent gases

1. Introduction

With a view to preparing the Cassini–Huygens mission [1] we are systematically studying GC columns suitable for in situ analysis of Titan's atmosphere (see Refs. [2–4] and references therein). In particular we have shown that a Molsieve 5A porous layer open tubular (PLOT) column can achieve a good separation of permanent gases, such as Ar, other noble gases, CH_4, and primarily, CO at very low concentrations in N_2. However, PLOT columns are not adequate for this type of space application. The film of adsorbent material coated on the wall of the capillary tubing is not strongly bound. Consequently, the coating is not mechanically stable enough for use on an atmospheric probe, considering the high level of vibration on the probe during several phases of the mission (launch and probe entry).

Previous studies have shown that packed capillary columns can serve as suitable alternatives to PLOT columns. For example, columns packed with molecular sieve 5A [3] produced a good separation of the test solutes including CO highly diluted with N_2.

*Corresponding author.

However, its hydrophilic behaviour leads to non-desirable chromatographic consequences, particularly for CO retention and band broadening [5,6]. Moreover it elutes methane, one of the main components of Titan's atmosphere, between N_2 and CO which may complicate CO discrimination and detection. These problems could be solved by using a non specific adsorbent. The present paper therefore, describes the results of similar studies with carbon molecular sieve columns. Using different pore sizes and thus different specific areas, we have studied the influence of these parameters upon chromatographic separations and efficiencies. The performance of each column was characterized by determining Van Deemter curves for CO and N_2, and by studying the separation of a mixture of permanent gases, in particular of small concentrations of CO diluted in N_2. Moreover the thermodynamics of adsorption of various light gases on carbon molecular sieve have been determined.

2. Experimental

2.1. Columns

The carbon molecular sieve adsorbents were from Supelco (Bellefonte, PA, USA). Table 1 lists the characteristics of the columns used in this work. Two different 2 m×0.76 mm I.D. packed columns made from Silcosteel tubing (Restek, Bellefonte, PA, USA) were studied: the first (column A) packed with Carboxen 1000 (175/250 μm) and the second (column B) packed with Carboxen 1004 (150/175 μm).

The columns were prepared as follows: a small conic reservoir, connected to the inlet end of the column, containing carboxen continuously feeds the column which is fixed in vertical position on a

Table 1
Characteristics of the columns[a]

Characteristics	Column A	Column B
Packing material	Carboxen 100	Carboxen 1004
Particule size (mesh)	60/80	80/100
Mean diameter (μm)	250–175	175–150
d_c/d_p	3.6	4.7
Surface area (m^2/g)	≥1200	700

[a] Values given by Supelco (Bellefonte, PA, USA).

vibrating system. Vacuum is applied at the exit of the column to optimize the filling. The column is considered to be filled when there is no change in the volume of the packing material in the conic reservoir. Then the column is gently coiled and conditioned overnight at 180°C in the gas chromatograph. The quality and repeatability of the packing procedure is controlled by weighting the exact mass of carboxen introduced into the column. It must be noted that carboxen is a spherical and hydrophobic material and that the columns are easily filled.

2.2. Gas chromatographs

Gas chromatographic measurements were carried out on a Perkin-Elmer Autosystem (Norwalk, CT, USA) gas chromatograph, equipped with a flame ionisation detector (FID), a thermal conductivity detector (TCD), an electro-pneumatic ten-port gas sampling valve with a 100-μl sample loop. Data acquisition, quantitation and chromatogram re-plotting were done with a PE-NELSON Turbochrom 3 data system.

The GC columns were operated isothermally, in the 30–100°C temperature range. Temperatures of the detector, injector and gas sampling valve were 20°C higher than column temperature. Hydrogen was used as carrier gas, since for a given efficiency a faster separation is achieved. Moreover it is convenient for GC–MS space instrumentation because it is much easier stored and pumped out than other gases. The hold-up volume of the columns was determined from the retention time of helium, an unretained compound since it is coeluted with neon.

2.3. Samples

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

Standard gas mixtures of known composition including CO, N_2, CH_4, C_2H_6 (with possibly other C_2 hydrocarbons) and noble gases (He, Ne, Ar and Kr) 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 connected to a glass vacuum line. The mixed compounds were successively introduced into the reservoir. This was done by expanding a known and adequate pressure of a pure constituent from a known volume of the vacuum line into an additional known volume of the reservoir, where the pressure before this expansion was also known. The same method was used for preparing the samples for studying the effect of CO dilution in N_2. The loop of the gas sampling valve (100 µl) was connected to the vacuum line. Vacuum was provided by means of a primary pump (ALCATEL CIT, Annecy, France), capable of reaching a vacuum as good as 10^{-2} mbar, checked with a Pirani vacuum gauge (MKS, Andover, MA, USA). The sample absolute pressures were measured with a manometer (Schlumberger, Montrouge, France) with a relative precision better than 1%. Inlet pressure of the carrier gas was measured with the gas chromatograph manometer with a relative precision of about 5%.

2.4. GC–MS tests

The GC–MS detection limit measurements of CO diluted in N_2 were carried out on a Varian SATURN II GC–MS instrument equipped with a six-port gas sampling valve including a 100-µl sampling loop. The GC–MS uses an ion trap system with a mass range from 10 to 650 amu. The carrier gas is hydrogen and the inlet flow-rate is measured with a massic flow meter (MKS type 258C, USA).

3. Results and discussion

The separation of mixtures of He, Ne, CO, N_2, Ar, CH_4 and Kr was studied on both carbon molecular sieve packed columns. Fig. 1 shows the results obtained with column A and B at 50°C. At their optimal absolute inlet pressure conditions which are 1.45 and 1.8 bar for columns A and B, respectively, the total separation time is less than 8 min for column A and 5 min for column B. Unlike on molecular sieve 5A columns [2,3] CO is less retained than methane leading to a faster separation and a sharper peak.

3.1. Column efficiencies

Fig. 2 shows the plot of H, the height equivalent to a theoretical plate (HETP), vs. $\bar{u}$, the linear velocity of the carrier gas. The experiments for both columns were performed at 50°C for a sample injection volume containing an equimolar gas mixture of CO and N_2 and He at a pressure of 50 mbar. It is clear that the best results, in term of separation efficiency, are obtained with column B. The minimum HETP on this column is around 0.65 and 0.80 mm compared to 1.15 and 1.30 mm with column A, for CO and N_2, respectively. Compared to the results with column B packed with carboxen 1004, the lower efficiency observed with column A is probably due to the larger particle size of the carboxen 1000 support (Table 1). Moreover, it must be emphasized that the slopes of the plate height curve are quite different with both columns. The increase in HETP at high carrier gas velocities is larger on column A. The consequence is a relatively flat minimum, allowing the use of the carboxen 1004 column within conditions of high $\bar{u}$ far from optimal values, without losing too much efficiency. Thus, by operating the column at twice the optimum flow-rate, the efficiency is decreased for both compounds (Fig. 2a,b) by less than 15%.

In addition, Fig. 2 shows that the optimal linear velocity $\bar{u}_{min}$, is about twice as large with column B, in the range 10–18 cm s^{-1} for column B and 7–9 cm s^{-1} for column A, allowing faster analysis with column B (but in that case a higher pressure drop is required).

Plate height experiments were carried out at different temperatures (30 to 90°C) and very similar behaviours were also observed. Thus, the phenomenological description, discussed above is still valid at these two other temperatures.

3.2. Thermodynamic adsorption results

From the variation of k' with temperature the adsorption enthalpies were determined. A linear variation of ln k' versus the reciprocal absolute temperature was observed and the differential adsorption enthalpy $\overline{\Delta H}$ was calculated from the slope of the straight line (Fig. 3). For column B the results for all solutes are listed in Table 2, only the data for
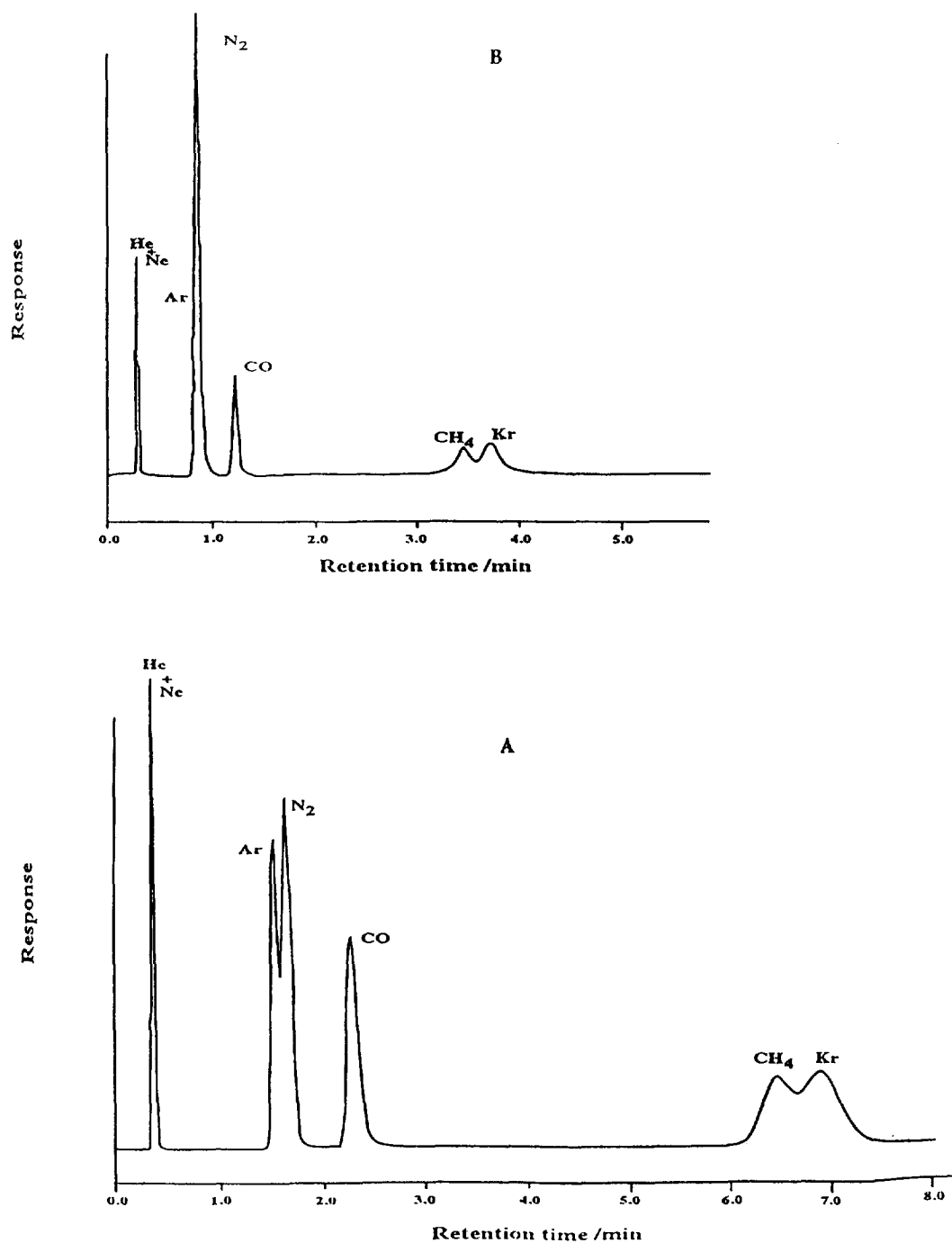
Fig. 1. Gas chromatogram of a seven-component gas mixture on carbon molecular sieve columns: (A) column A [2 m×0.76 mm I.D., carboxen 1000 (175/250 µm)]; conditions: temperature, 50°C; carrier gas, H_2; outlet flow-rate, 3.3 ml/min; absolute inlet pressure, 1.45 bar; thermal conductivity detector. (B) column B [2 m×0.76 mm I.D., carboxen 1004 (150/175 µm)]; conditions: temperature, 50°C; carrier gas, H_2; outlet flow-rate, 4.3 ml/min; absolute inlet pressure, 1.8 bar; thermal conductivity detector.
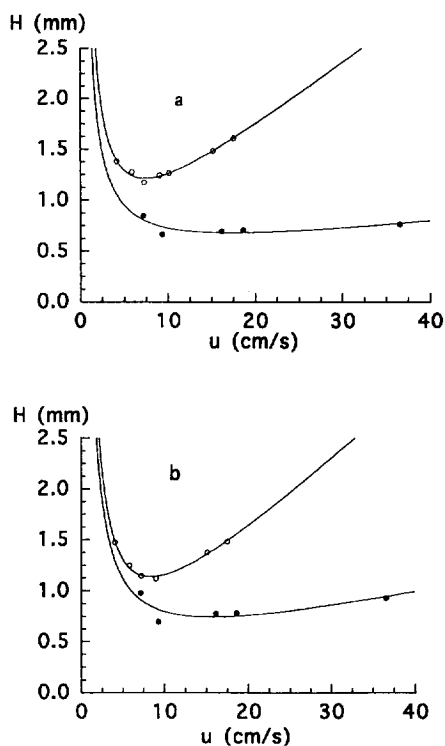
Fig. 2. Plot of the height equivalent to a theoretical plate (H) versus the mean linear velocity $(\bar{u})$ of the carrier gas (H_2) at 50°C on solutes: (a) CO and (b) N_2: ($\bigcirc$) column A, ($\bullet$) column B.

CO and N_2 were determined for column A. Within the margins of experimental errors (R.S.D.$\leq$0.05), the results for both columns are close. A straight line fits well the plot of $\overline{\Delta H}$ vs. the polarisability (α) [7] of the gaseous molecules with a r^2 (regression coefficient) value of 0.992. At a given temperature,
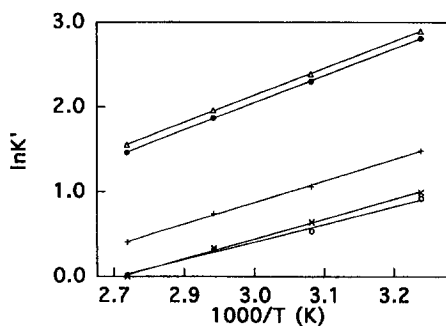

Fig. 3. Variation of ln k' with temperature on column B. Solutes: argon ($\bigcirc$), methane ($\bullet$), CO (+), N_2 ($\times$) and Kr ($\triangle$).

the k' values increase exponentially with $\overline{\Delta H}$. A linear plot is also found when ln k' is plotted as a function of α with a r^2 value of 0.988. These results agree with theory since both the dispersion and electrostatic contributions to the atom–atom adsorption potential are proportional to the polarisability of the adsorbate interacting groups [8]. One should note however, that the linearity of these plots do not permit us to distinguish between the non-polar Van de Waals forces and the electrostatic contributions.

For comparison with the present result, the data compiled from the literature [8] for the adsorption of several gaseous compounds on graphitized carbon black are listed in Table 3. Static methods were used to determine the differential adsorption enthalpies and the Henry adsorption constant K_H (at 273 K) or slope of the adsorption isotherm, extrapolated at zero surface coverage and given in volume per square meter. The absolute value of $\overline{\Delta H}$ on carboxen are about 30% larger than on graphitized carbon black. These carbon molecular sieves of large specific area (700–1200 m^2/g) have a microstructure with many active sites that interact strongly with the gaseous compounds.

Carbon molecular sieves are still non-specific type adsorbents according to Kiselev's classification [9] since the retention order of the inorganic gases and methane is similar to the relative adsorptions observed on graphitized carbon black: the adsorption data of CO are well located on the straight lines of Fig. 4 relating $\overline{\Delta H}$ and ln k' to the respective polarisability of the gaseous compounds. This compound is much more retained than methane on zeolite adsorbents [2,3]. One can notice that although having a larger polarisability, methane is less adsorbed than krypton on both carbon molecular sieve and graphitized carbon black.

3.3. CO, N_2 resolution

Before carrying out the study of the limit of CO detection, which means the determination of the smallest amount of CO detectable in CO–N_2 mixtures, a detailed study of CO, N_2 separation on both columns was performed. The peak resolution (R_s) for the two adjacent peaks of N_2 and CO was calculated using the equation [10]:

Table 2
Adsorption enthalpy, retention volume, polarisability, molecular mass and diameter of eluted solutes

Column	Solute	Mol. mass	Diameter (Å)	Polarisability (Å^3)	V'_r [a] (ml)	$\overline{\Delta H}$ (kJ/mol)
Column A	N$_2$	28	3.75	1.75	2.7	−14.2
	CO	28	3.71	1.95	4.0	−15.4
Column B	Ar	40	3.46	1.63	1.9	−13.60
	N$_2$	28	3.75	1.75	2.0	−15.00
	CO	28	3.71	1.95	3.1	−16.3
	CH$_4$	16	3.80	2.60	10.2	−20.5
	Kr	131	3.61	2.47	11.1	−20.5

[a] Adjusted retention volume $V'_r = V_r - V_o$ (V_o: hold-up volume).

Table 3
Adsorption on graphitized carbon black [8]: Henry constant and differential heat of adsorption

Solute	K_H^a (mm^3/m^2)	$\overline{\Delta H}$ (kJ/mol)
Ar	4.3	−9.6
N$_2$	–	−9.2
CH$_4$	11.9	−12.1
Kr	12.2	−13.2

[a] Extrapolated at 273 K.

$$R_s = \frac{2(t_{CO} - t_{N_2})}{\omega_{N_2} + \omega_{CO}} \qquad (1)$$

where t_{CO} and t_{N2} are the retentions for CO and N$_2$ from the injection instant and ω_{N2} and ω_{CO} are respectively the average peak width at base of N$_2$ and CO. Fig. 4 shows the plots of R_s calculated at 50°C vs. $\bar{u}$ for column A and column B. The
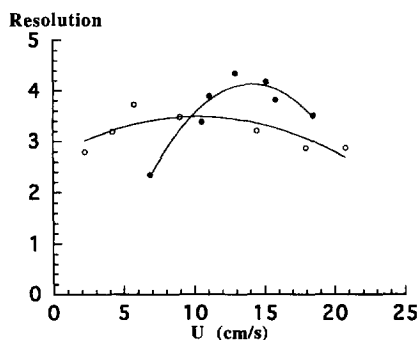

Fig. 4. Resolution of N$_2$–CO peak pair as a function of the average linear carrier gas (H$_2$) velocity. (○) column A, (●) column B.

resolution is larger for column B. For both columns the maximum resolution values established from the plots are 3.7 for column A and 4.3 for column B obtained from their optimal average linear velocity of the HETP curves respectively 6–10 cm/s for column A and 10–18 cm/s for column B.

Fig. 5 presents chromatograms obtained at 50°C with column A and B for three different mixing ratios (5000, 500 and 50 ppm) of CO in N$_2$. The peak of CO is clearly visible for mixing ratios down to about 500 ppm. For column A, on the chromatogram corresponding to 50 ppm only a shoulder is visible for CO at the expected retention time which does not allow a quantitative analysis. Taking into account the injection (720 mbar) pressure and the sampling loop volume (100 μl), the amount of CO injected is about 4 ng (Fig. 5III). For column B we must point out that in spite of the better resolution for CO, N$_2$ separation, the shoulder at 50 ppm is hardly noticeable. This effect can be explained by a higher overloading of the carboxen 1004 adsorbent by the major product N$_2$, because of its lower specific area (700 m^2/g) and therefore its lower column capacity.

These limits of detectability are compatible with the amount of CO present in the atmosphere of Titan. However they are obtained under optimal experimental conditions i.e., atmospheric outlet carrier gas pressure with outlet flow-rates (about 3 ml min^{-1}) higher than the operational flow-rate of the flight GC–MS instrument and with a concentration sensitive detector (TCD) instead of a mass sensitive detector as the ion trap of the mass spectrometer.

In order to get closer to the conditions required by the flight instrument, the detection limit of CO
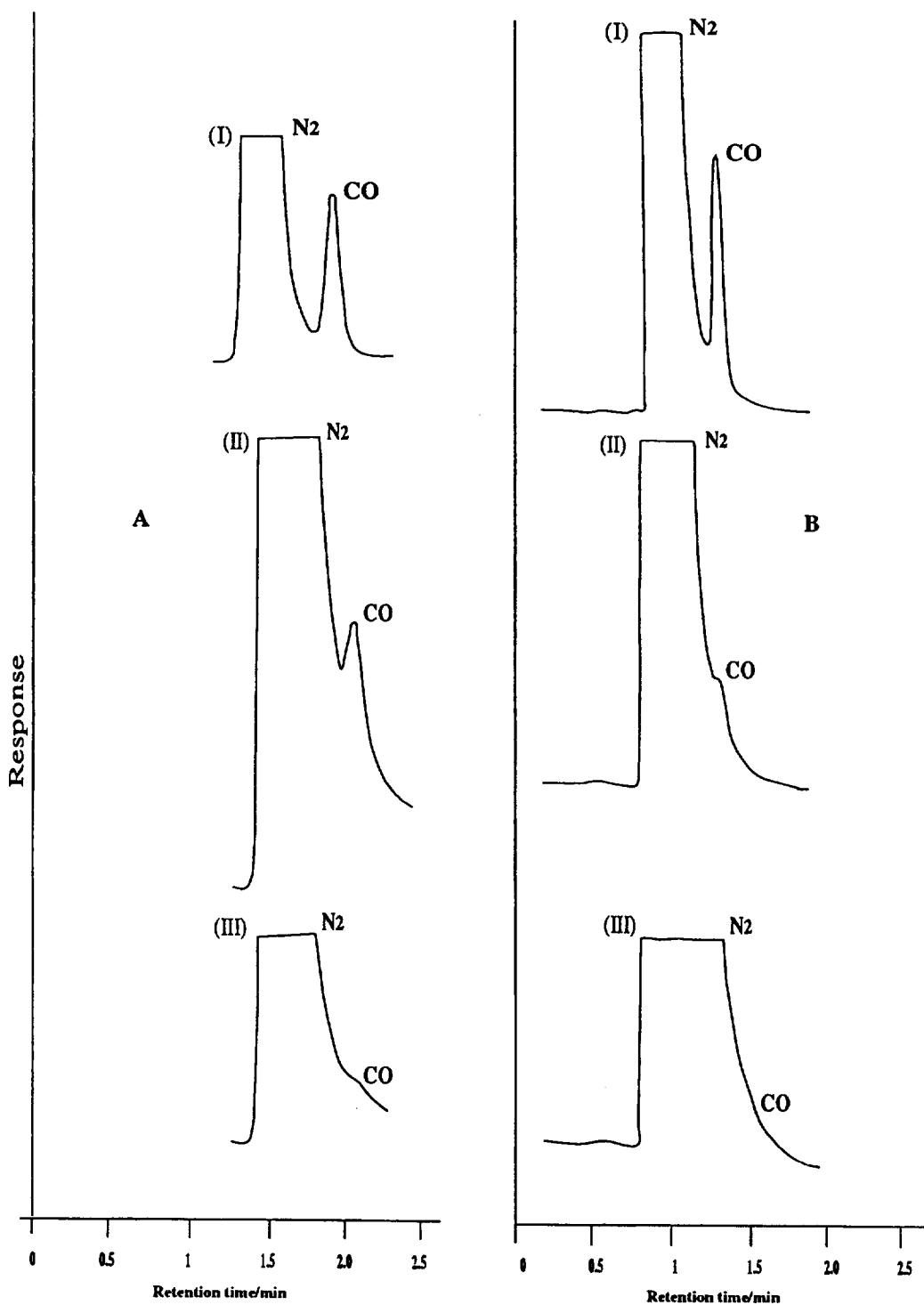
Fig. 5. Gas chromatographic separation of CO diluted with N_2 on carbon molecular sieve column: (A) column A; (B) column B; conditions: temperature, 50°C; carrier gas, H_2; pressure drop, 0.45 bar. (I) 5000 ppm of CO, (II) 500 ppm, (III) 50 ppm.

diluted with N_2, was measured by using a laboratory GC–MS with the column outlet at very low pressure $(10^{-3}$ mbar).

3.4. GC–MS experiment

Column A has been selected because of its lower optimal gas velocity and also because of the higher sensitivity for CO detection in presence of N_2. The coupling between the column and the mass spectrometer is performed through a 22 cm long and 0.22 mm inner diameter fused-silica tubing which is connected to the outlet of the packed capillary column and directly inserted into the ion trap of the mass spectrometer, the pressure of which is fixed at a constant value of 10^{-3} mbar.
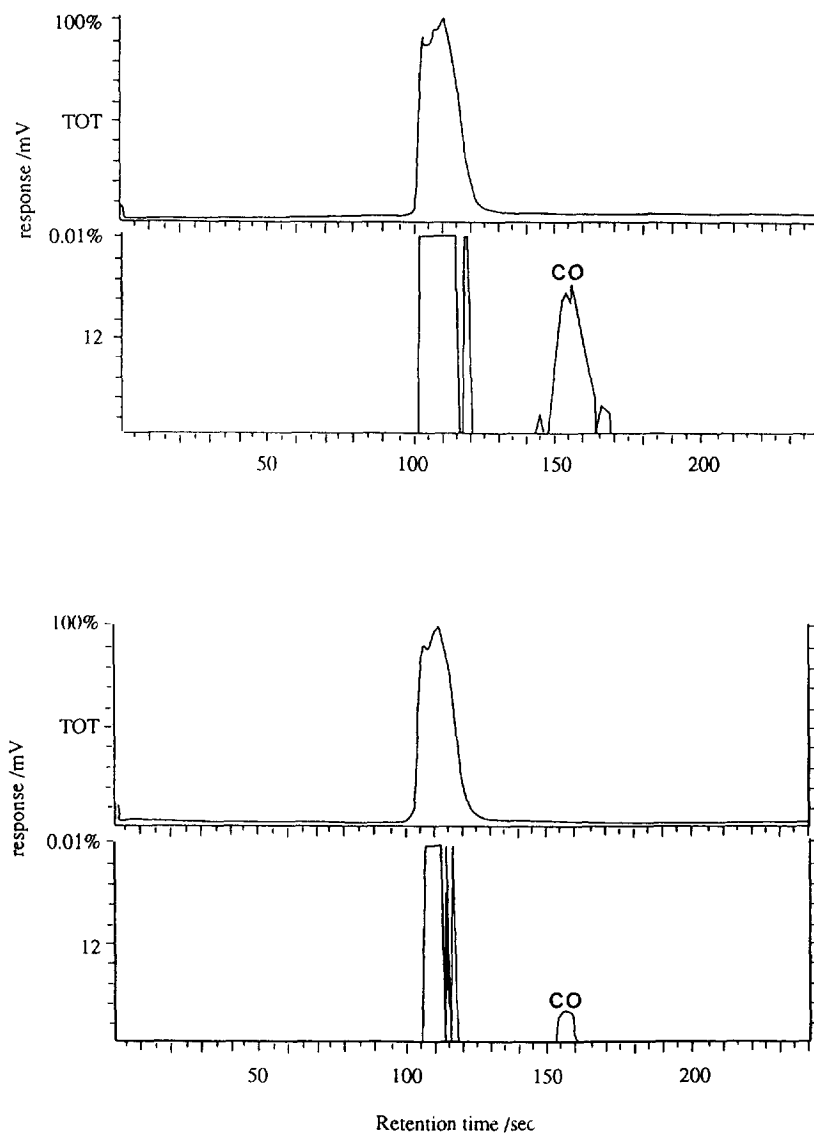

Fig. 6. Total ion-mass and specific (m/z) ion-mass chromatogram of N_2/CO gas mixtures on column A. Column temperature, 50°C; carrier gas, H_2; absolute inlet pressure, 1.4 bar; MS (ion trap) detector; peak identification, MS (ion trap). (Top) 500 ppm of CO, (bottom) 50 ppm of CO.

Fig. 6 shows the chromatograms obtained with a mixture containing mixing ratios of 500 and 50 ppm of CO in N_2, respectively, at an absolute inlet pressure of 1.4 bar. The sampling injection pressures were, respectively, 56 and 40 mbar and the temperature was 50°C. Although the CO peak is not visible on the total ion-mass chromatogram we can detect and identify this trace component by using a "specific ion-mass chromatogram" which improves sensitivity by displaying the chromatogram corresponding to the fragmentation ion of mass 12. Thus, for a mixing ratio of 50 ppm we observe a small peak of CO, identifiable also by its retention time, allowing a quantitative analysis. As expected complementary studies with sampling loop volume and injection pressure variations show clearly that the detector response depends only on the total mass of CO injected whatever the sampling system and injection procedure, owing to the mass-sensitive nature of the ion trap detector. These conditions are now definitively ascertained: the collected sample whose pressure varies from 1 to 1500 mbars (depending upon the altitude of the probe during its descent), will be compressed to a value of 1.9 bar and introduced in the column through a sampling loop of 1 µl.

Since the flight mass spectrometer is a quadrupole mass filter [11] more convenient for the low masses (2 to 141 amu) with a sensitivity much higher (one or two orders of magnitude) than the laboratory GC–MS one, we can expect that the Carboxen-packed capillary column will permit an efficient separation of CO and a precise analysis of the concentration profile of its abundance in Titan's atmosphere.

4. Conclusion

Both chromatographic columns that were studied in this work are suitable for the analysis of low molecular mass compounds of Titan's atmosphere. A rapid separation of permanent gases, including CO, N_2 and noble gases is achieved with a separation time shorter than 8 min for both columns. The elution order is similar to the relative adsorptions observed on graphitized carbon black. A larger absolute value of the differential enthalpy of adsorption is found on carbon molecular sieve adsorbent which is proportional to the polarisability of the molecules. In spite of the column overloading by the major product N_2, more important with the lower specific area adsorbent (Carboxen 1004), they both exhibit a detection limit towards CO compatible with its abundance in the atmosphere of Titan. However, complementary studies, in particular on the effect of species like hydrocarbons (especially methane) and nitriles also present in Titan's environment, need to be carried out. Such investigations are in progress at the NASA/Goddard Space Flight Center's Atmospheric Experiment Branch using a GC–MS flight instrument.

Acknowledgments

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