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Short communication

# Gas chromatography for in situ analysis of a cometary nucleus IV. Study of capillary column robustness for space application

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## Abstract

As part of the development of the European Space Agency Rosetta space mission to investigate a cometary nucleus, the selection of columns dedicated to the gas chromatographic subsystem of the Cometary Sampling and Composition (COSAC) experiment was achieved. Once the space probe launched, these columns will be exposed to the harsh environmental constraints of space missions: vibrations, radiation (by photons or energetic particles), space vacuum, and large temperature range. In order to test the resistance of the flight columns and their stationary phases, the columns were exposed to these rough conditions reproduced in the laboratory. The comparison of the analytical performances of the columns, evaluated prior and after the environmental tests, demonstrated that all the columns withstand space constraints, and that their analytical properties were preserved. Therefore, all the selected capillary columns, even having porous layer or chiral stationary phases, were qualified for space exploration.
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*Keywords:* Capillary columns; Stationary phase, GC; Robustness

## 1. Introduction

Because of its robustness and its reliability, gas chromatography was and will be used as the main experiment for the in situ chemical analysis of extraterrestrial environments for planetary exploration [1]. However, it is only recently that improvements of capillary columns technology allowed their use for this type of analysis, with the Huygens probe of the NASA–ESA Cassini–Huygens mission [2]. The use of such columns is interesting since they generally have better analytical properties than packed ones, and they also better fulfill the increas-

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ing technical constraints imposed by more and more complex space exploration missions [3]. These are the main reasons why only capillary chromatographic columns were selected to be integrated in the GC subsystem of the Cometary Sampling and Composition (COSAC) experiment [4–6] of the ESA Rosetta mission [7], which aims at analysing the molecular composition of comet Wirtanen directly at the surface of its nucleus. However, whereas packed columns are known to be robust, very few data dealing with the resistance of the capillary columns and their stationary phases towards the rough conditions imposed by the rocket launch and space environment are available today.

During its journey to the comet, the spacecraft, and, therefore, the chromatographic columns, will be exposed to different sources of vibration, radiation, and also to variation of temperature under the vacuum pressure conditions of interplanetary space. Whereas a potential breaking of the columns can be prevented by using metal as the wall material (because the stationary phases properties can be kept safe today, considering different existing chemical treatments of the wall surface [8]), vibration, as the other constraints, can damage the stationary phases by: (i) altering the bonding of the stationary phases to the internal capillary wall (vibration, radiation and thermal variation) which can lead to an important bleeding; (ii) modifying the nature of the stationary phases (radiation and thermal variation for liquid stationary phases). Such phenomena could thus modify the analytical properties of the columns, or damage the system, either by obstructing the columns or by damaging the detectors for example. In all these cases, the interpretation of the data recovered from the space experiment would, therefore, be hazardous and not satisfying when considering the objective of the experiment.

That is the reason why, in order to test their resistance, all the columns used in the COSAC experiment were therefore subjected to a series of fundamental tests simulating the different types of constraints to be encountered during the flight of the probe. The aim of this paper is to report these different tests and to present the corresponding results which show the general robustness, and therefore the space compatibility, of the selected capillary columns.

## 2. Experimental

### 2.1. GC columns and stationary phases

The columns exposed to space environmental tests and their main characteristics are presented in Tables 1–3. Metal was selected as the external tube material for the general purpose columns whereas columns with chiral stationary phases are made of fused-silica because no metallic column of this type is commercially available.

All stationary phases, except the cyclodextrins of the Astec columns, are chemically bonded to the internal capillary wall in order to strengthen them and to try to prevent any bleeding effect. Two types of porous layer were used for the porous-layer open tubular (PLOT) columns: carbon molecular sieve (Carbobond) and divinylbenzene–ethylene glycol–dimethyl acrylate (MXT U). The stationary phases of the wall-coated open tubular (WCOT) columns are made of polydimethylsiloxane (PDMS) (MXT 1), 50% of PDMS and 50% of polydiphenylsiloxane (PDPS) (MXT 50), 35% of PDMS and 65% of PDPS (MXT 65), 86% of PDMS and 14% of cyanopropylphenyl (CNPP) (MXT 1701). Chiraldex columns have stationary phases made of trifluoroacetylated (G-TA), dipentylated (B-DA) and permethylated (B-PH) cyclodextrins. Finally, Chirasil-Dex column uses also cyclodextrin as stationary phase whereas Chirasil Val have $N$-propanoyl-L (or D) valine-*tert*.butyl-amide chemically bonded to dimethylpolysiloxane.

From the columns finally selected to be mounted in the COSAC experiment [6], only MXT 20 column was not exposed to these tests. However, its stationary phase is made of 80% of DMPS and 20% of PDPS. This composition is an intermediate one between those of the stationary phases of MXT 1 and MXT 65 columns, which include the least and the most important amount of DP groups of this family of columns. Therefore, if no influence of the space constraints is observed with these columns, one can reasonably extrapolate this conclusion to MXT 20 column, and to all columns of this family.

### 2.2. Chromatographs

For the general purpose columns with classical

Table 1
Chromatographic behavior of the selected columns before and after exposure to vibration (for separated enantiomers, the average values were calculated)

| Columns L (m)–I.D. (mm) –$d_f$ (μm) | T (°C)/ Δp (kPa) | Type and supplier | Test | Compounds and retention time (min)/peak width at half height (min) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Methane | | Ethyne | | Ethylene | | Ethane | | | | | |
| Carbobond | 80/50 | PLOT | Pre | 1.99 | 0.034 | 5.25 | 0.082 | 7.30 | 0.106 | 11.48 | 0.208 | | | | |
| 10–0.25–10 | | Varian | Post | 1.99 | 0.034 | 5.31 | 0.083 | 7.36 | 0.105 | 11.50 | 0.190 | | | | |
| | | | | Methane | | Pentane | | Ethanol | | Acetone | | Methyl acetate | | | |
| MXT U | 90/50 | PLOT | Pre | 0.46 | 0.010 | 3.82 | 0.175 | 3.19 | 0.081 | 4.75 | 0.149 | 5.86 | 0.148 | | |
| 10–0.25–5 | | Restek | Post | 0.46 | 0.010 | 3.82 | 0.166 | 3.24 | 0.094 | 4.87 | 0.160 | 5.93 | 0.161 | | |
| | | | | Methane | | Octane | | Pentanol | | Toluene | | Butanenitrile | | | |
| MXT 1 | 80/50 | WCOT | Pre | 1.09 | 0.012 | 3.58 | 0.049 | 2.96 | 0.057 | 2.80 | 0.036 | 1.86 | 0.018 | | |
| 10–0.18–0.6 | | Restek | Post | 1.09 | 0.012 | 3.62 | 0.050 | 2.99 | 0.057 | 2.83 | 0.036 | 1.87 | 0.019 | | |
| | | | | Methane | | Hexane | | Ethanol | | Acetone | | Methyl acetate | | Acetonitrile | |
| MXT 50 | 30/50 | WCOT | Pre | 1.42 | 0.023 | 4.24 | 0.351 | 3.27 | 0.143 | 5.03 | 0.223 | 5.77 | 0.263 | 7.04 | 0.200 |
| 15–0.18–1.0 | | Restek | Post | 1.43 | 0.022 | 4.25 | 0.345 | 3.29 | 0.138 | 5.06 | 0.219 | 5.80 | 0.560 | 7.15 | 0.194 |
| MXT 1701 | 30/50 | WCOT | Pre | 1.45 | 0.022 | 5.64 | 0.117 | 4.66 | 0.093 | 5.42 | 0.105 | 5.78 | 0.129 | 7.34 | 0.134 |
| 15–0.18–1.0 | | Restek | Post | 1.44 | 0.021 | 5.62 | 0.116 | 4.66 | 0.090 | 5.42 | 0.105 | 5.79 | 0.126 | 7.33 | 0.129 |
| | | | | Ala | | Leu | | Asp | | Met | | Pip | | Hep | |
| Chirasil-Dex | | WCOT | Pre | 7.14 | 0.02 | 10.25 | 0.03 | 16.10 | 0.05 | 18.06 | 0.04 | 5.32 | 0.04 | 5.14 | 0.10 |
| 10–0.25–0.25 | | Varian | Post | 7.19 | 0.02 | 10.50 | 0.04 | 16.50 | 0.05 | 18.49 | 0.04 | 5.26 | 0.04 | 5.10 | 0.12 |
| Chirasil-L-Val | | WCOT | Pre | 1.10 | 0.03 | 1.70 | 0.04 | 3.29 | 0.06 | 4.78 | 0.08 | 2.30 | 0.05 | 3.86 | 0.06 |
| 25–0.25–0.125 | | Varian | Post | 1.12 | 0.03 | 1.74 | 0.04 | 3.39 | 0.07 | 4.94 | 0.09 | 2.33 | 0.05 | 3.95 | 0.07 |

Abbreviations: L=length, I.D.=internal diameter, $d_f$=film thickness, Δp=column pressure drop, Ala=alanine (TFA-ester), Leu=leucine (TFA-ester), Asp=aspartic acid (TFA-ester), Met=methionine (TFA-ester), Pip=2-methylpiperidine (N-TFA), Hep=2-aminoheptane (N-TFA).

Table 2
Chromatographic behavior of the selected columns before and after exposure to radiation

| Columns L (m)–I.D. (mm) –$d_f$ (μm) | Type and supplier | $T$ (°C)/ $\Delta p$ (kPa) | Test | Compounds and retention time (min)/peak width at half height (min) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Methane | | Pentane | | Propanol | | Acrylonitrile | | Propanone | | Ethyl acetate | |
| MXT 1701 | WCOT | 60/40 | Pre | 1.25 | 0.020 | 1.59 | 0.030 | 2.10 | 0.050 | 2.73 | 0.053 | 2.12 | 0.044 | 3.10 | 0.100 |
| 10–0.18–0.6 | Restek | | Post | 1.26 | 0.020 | 1.68 | 0.032 | 2.25 | 0.047 | 2.87 | 0.058 | 2.18 | 0.043 | 3.35 | 0.108 |
| MXT 65 | WCOT | 30/50 | Pre | 0.79 | 0.014 | 0.97 | 0.058 | 1.37 | 0.097 | 2.16 | 0.085 | 1.54 | 0.081 | 2.81 | 0.196 |
| 10–0.18–0.4 | Restek | | Post | 0.79 | 0.014 | 0.96 | 0.058 | 1.34 | 0.092 | 2.24 | 0.082 | 1.52 | 0.083 | 2.73 | 0.185 |
| MXT 1 | WCOT | 50/40 | Pre | 1.37 | 0.013 | 2.00 | 0.013 | 1.90 | 0.014 | 1.99 | 0.014 | 1.86 | 0.022 | 2.97 | 0.016 |
| 10–0.18–0.6 | Restek | | Post | 1.38 | 0.013 | 2.06 | 0.013 | 1.96 | 0.014 | 2.07 | 0.014 | 1.92 | 0.022 | 3.08 | 0.016 |
| MXT 50 | WCOT | 30/50 | Pre | 1.52 | 0.03 | 2.90 | 0.30 | 4.95 | 0.52 | 10.25 | 0.48 | 6.39 | 0.56 | 14.35 | 0.90 |
| 15–0.18–1.2 | Restek | | Post | 1.52 | 0.03 | 2.87 | 0.31 | 4.98 | 0.53 | 10.19 | 0.49 | 6.36 | 0.56 | 14.25 | 0.91 |
| MXT U | PLOT | 120/50 | Pre | 0.83 | 0.053 | 1.90 | 0.028 | 3.00 | 0.034 | 3.30 | 0.039 | 2.42 | 0.028 | 5.65 | 0.068 |
| 10–0.18–3 | Restek | | Post | 0.85 | 0.053 | 1.95 | 0.029 | 3.06 | 0.035 | 3.35 | 0.041 | 2.53 | 0.030 | 5.80 | 0.073 |
| | | | | Methane | | Neon | | Argon | | Krypton | | Ethene | | $CO_2$ | |
| Carbobond | PLOT | 30/50 | Pre | 0.92 | 0.029 | 0.53 | 0.020 | 0.67 | 0.022 | 1.08 | 0.037 | 4.05 | 0.074 | 1.36 | 0.053 |
| 10–0.25–10 | Varian | | Post | 0.89 | 0.028 | 0.55 | 0.020 | 0.68 | 0.021 | 1.10 | 0.035 | 4.01 | 0.080 | 1.38 | 0.050 |
| | | | | Ala | | Leu | | Asp | | Met | | Pip | | Hep | |
| Chiraldex G-TA | WCOT | | Pre | 1.47 | 0.10 | 7.45 | 0.30 | 11.21 | 0.10 | 11.95 | 0.06 | 3.76 | 1.40 | 6.38 | 1.80 |
| 5–0.25–0.125 | Astec | | Post | 1.35 | 0.12 | 7.50 | 0.35 | 11.14 | 0.10 | 11.92 | 0.10 | 3.75 | 1.40 | 6.35 | 1.80 |
| Chiraldex B-DA | WCOT | | Pre | 7.50 | 0.05 | 10.27 | 0.04 | 16.26 | 0.05 | 20.54 | 0.10 | 2.51 | 0.08 | 2.89 | 0.10 |
| 10–0.25–0.125 | Astec | | Post | 7.54 | 0.10 | 10.28 | 0.08 | 16.28 | 0.08 | 20.61 | 0.15 | 2.57 | 0.14 | 2.93 | 0.10 |
| Chiraldex B-PH | WCOT | | Pre | 5.93 | 0.20 | 8.61 | 0.10 | 12.95 | 0.15 | 15.75 | 0.28 | 4.98 | 0.18 | 11.83 | 0.18 |
| 10–0.25–0.125 | Astec | | Post | 5.78 | 0.18 | 8.56 | 0.10 | 12.93 | 0.15 | 15.67 | 0.25 | 4.93 | 0.15 | 11.67 | 0.25 |
| Chirasil-D-Val | WCOT | | Pre | 1.10 | 0.02 | 1.71 | 0.03 | 3.30 | 0.04 | 4.78 | 0.05 | 2.26 | 0.06 | 3.83 | 0.05 |
| 25–0.25–0.08 | Varian | | Post | 1.10 | 0.02 | 1.70 | 0.03 | 3.29 | 0.04 | 4.78 | 0.05 | 2.30 | 0.04 | 3.86 | 0.05 |

Abbreviations: same as in Table 1.

**Table 3**
Chromatographic behavior of the selected columns before and after exposure to thermal vacuum cycles

| Columns L (m)–I.D. (mm) –$d_f$ (µm) | Type and supplier | $T$ (°C)/ $\Delta p$ (kPa) | Test | Compounds and retention time (min)/peak width at half height (min) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Methane | | Heptane | | Ethanol | | Propanone | | Methyl acetate | | Ethanenitrile | |
| MXT 1 | WCOT | 40/50 | Pre | 0.88 | 0.012 | 5.54 | 0.029 | 1.28 | 0.018 | 1.42 | 0.016 | 1.69 | 0.014 | 1.35 | 0.018 |
| 10–0.18–0.6 | Restek | | Post | 0.88 | 0.012 | 5.46 | 0.027 | 1.27 | 0.018 | 1.42 | 0.015 | 1.71 | 0.016 | 1.36 | 0.019 |
| MXT 65 | WCOT | 40/50 | Pre | 0.73 | 0.014 | 1.56 | 0.209 | 0.99 | 0.054 | 1.20 | 0.081 | 1.30 | 0.098 | 1.48 | 0.066 |
| 10–0.18–0.4 | Restek | | Post | 0.72 | 0.014 | 1.54 | 0.195 | 0.97 | 0.053 | 1.21 | 0.079 | 1.27 | 0.097 | 1.45 | 0.070 |
| MXT 1701 | WCOT | 40/50 | Pre | 1.03 | 0.017 | 4.12 | 0.163 | 1.94 | 0.064 | 2.14 | 0.074 | 2.25 | 0.082 | 2.74 | 0.086 |
| 10–0.18–0.6 | Restek | | Post | 1.04 | 0.017 | 4.17 | 0.160 | 1.95 | 0.066 | 2.2 | 0.080 | 2.29 | 0.079 | 2.74 | 0.085 |
| MXT U | PLOT | 120/50 | Pre | 1.55 | 0.039 | – | – | 6.11 | 0.124 | 8.78 | 0.219 | 10.40 | 0.318 | 8.16 | 0.286 |
| 15–0.28–10 | Restek | | Post | 1.52 | 0.038 | – | – | 6.30 | 0.120 | 8.84 | 0.235 | 10.30 | 0.302 | 8.33 | 0.292 |
| | | | | Neon | | Nitrogen | | CO | | Krypton | | Methane | | | |
| Carbobond | PLOT | 30/20 | Pre | 1.90 | 0.038 | 2.03 | 0.043 | 2.14 | 0.049 | 2.76 | 0.079 | 2.66 | 0.073 | | |
| 15–0.25–6 | Varian | | Post | 1.95 | 0.037 | 2.07 | 0.042 | 2.14 | 0.052 | 2.73 | 0.077 | 2.67 | 0.069 | | |
| | | | | Ala | | Leu | | Asp | | Met | | Pip | | Hep | |
| Chiraldex G-TA | WCOT | | Pre | 2.28 | 0.15 | 7.99 | 0.30 | 11.92 | 0.12 | 13.25 | 0.22 | 1.16 | 0.10 | 1.10 | 0.10 |
| 5–0.25–0.125 | Astec | | Post | 2.18 | 0.20 | 7.87 | 0.30 | 11.84 | 0.15 | 13.16 | 0.25 | 1.29 | 0.15 | 1.18 | 0.15 |
| Chiraldex B-DA | WCOT | | Pre | 7.58 | 0.20 | 10.28 | 0.10 | 16.24 | 0.20 | 20.44 | 0.32 | 2.55 | 0.20 | 2.88 | 0.10 |
| 10–0.25–0.125 | Astec | | Post | 7.50 | 0.20 | 10.27 | 0.10 | 16.26 | 0.20 | 20.54 | 0.40 | 2.51 | 0.25 | 2.89 | 0.18 |
| Chiraldex B-PH | WCOT | | Pre | 5.94 | 0.22 | 8.59 | 0.10 | 12.89 | 0.10 | 15.56 | 0.20 | 5.06 | 0.20 | 12.03 | 0.40 |
| 10–0.25–0.125 | Astec | | Post | 5.93 | 0.20 | 8.61 | 0.10 | 12.95 | 0.15 | 15.75 | 0.20 | 4.98 | 0.25 | 12.04 | 0.40 |
| Chirasil-D-Val | WCOT | | Pre | 1.14 | 0.04 | 1.74 | 0.05 | 3.35 | 0.07 | 4.85 | 0.09 | 2.38 | 0.07 | 3.94 | 0.09 |
| 25–0.25–0.08 | Varian | | Post | 1.14 | 0.04 | 1.75 | 0.05 | 3.37 | 0.06 | 4.85 | 0.09 | 2.33 | 0.05 | 3.90 | 0.09 |

Abbreviations: same as in Table 1.

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stationary phases, gas chromatographic measurements were carried out on a Varian CP-3800 gas chromatograph having a split/splitless syringe injector, a flame ionization detection (FID) system and a thermal conductivity detection (TCD) system. An electro-pneumatic sampling valve (Valco), with a 2-$\mu$l sample loop, permits injection of gaseous samples. During the measurements, the TCD system was heated at 110 °C and the FID system at 250 °C. Their signal was, respectively, connected to a PE-Nelson Turbochrom IV and a Varian Star data acquisition system. The sampling with the valve injection was performed in the splitless mode whereas a split ratio of about 1:150 was used for syringe injections. The carrier gas was helium (purity >99.9995%), as it will be used for the COSAC experiment. A series of three filters removing moisture, hydrocarbons and oxygen traces was used in laboratory to improve the carrier gas purity. The GC columns were operated isothermally at temperatures in the range 20–80 °C (Table 1).

For the columns with chiral phases [9,10], a Perkin-Elmer GC system (8500) connected to a Shimadzu Chromatopac C-R6A integrator was used to perform analyses. The compounds tested were trifluoroacetyl derivatives of amines and of amino acids. In this case, the carrier gas used for laboratory tests was hydrogen (purity=99.999%). Both syringe injector and FID system were heated at 200 °C. The split ratio was about 1:100.

### 2.3. Reagents

Liquid compounds were provided by Aldrich (Strasbourg, France), Acros (Noisy-le-Grand, France) and Merck (Nogent-sur-Marne, France), whereas gaseous ones were bought to Linde (Lyon, France) and Air Liquide (Moissy Cramayel, France). All these compounds are analytical grade ones. Racemic mixtures of the amino acid derivatives in methylenechloride (1 mg/ml) were purchased from Chrompack. The amine derivatives were received from Astec. They were solutions of 5 mg derivative per millilitre of ethanol.

Direct injections of pure compounds (gas or liquid) were performed through the injectors septum with Hamilton gas (1 ml) or liquid (1–10 $\mu$l) syringes equipped with a tight stopcock. Gas mix-

tures were made with the procedure previously described [11], and injected with the sampling valve of the Varian CP-3800 chromatograph.

### 2.4. Space environmental tests

Vibration tests were performed at the Max-Planck-Institut für Aeronomie of Lindau (Germany). The glued columns were fixed on a horizontal plate with three fixation points. Then, they were shaken by two ways: (1) horizontally (plane defined by the column) and normally to the plane with fixed frequencies; (2) randomly in all the directions with frequency variations. The frequencies are between 28 and 100 Hz. The lower limit correspond to the minimal vibration threshold at which the columns should be effectively exposed; the upper limit is the maximum threshold that the columns must tolerate (defined by ESA technical group).

Irradiation tests were performed by the Office National d'Etudes et de Recherches Aérospatiales (ONERA) at the Département de l'Environnement SPatial (DESP) in Toulouse (France). To simulate space like radiation in laboratory, the columns were exposed to gamma rays generated by a $^{60}$Co source (energy ≈1.2 MeV). For an instrument inside the Lander (derived from Rosetta Radiation Environment document), the test specification for the total cumulated dose is 14 krad, calculated as twice the effective exposition over the duration of the mission. As oxygen in air could produce degradation or recombination of the polymers in presence of the radiation, the columns were placed in a small chamber under primary vacuum ($10^{-2}$ Torr), at a temperature of 20 °C for the duration of the irradiation. The average dose rate was 0.42 Gy(Si) h$^{-1}$ (corresponding to the equivalent dose absorbed by silicon material in 1 h, silicon constituting the main part of the stationary phases composition). A low dose rate was needed to guaranty a good homogeneity of the dose on the columns, and the columns were also rotated by 180° during the irradiation in order to further improve this homogeneity. The total dose accumulated on the columns was 151 Gy(Si) or 15.1 krad(Si).

Thermal vacuum tests were performed at the Institut d'Astrophysique Spatiale (IAS) at Orsay (France). The columns were mounted together on a

cylinder which was placed on a ceramic plate, inside a thermal vacuum chamber. Temperature of the columns was measured by thermo-couples. Vacuum was then obtained ($4 \cdot 10^{-7}$ mbar) inside the chamber. Finally, temperature cycling was performed in three steps: (1) columns were heated at 200 °C for 96 h, (2) 13 cycles from −50 °C up to 200 °C with a stage of 1 h at 200 °C, and (3) 81 cycles from 20 °C to 200 °C with a stage of 1 h at 200 °C were performed. The temperature variation observed during a part of the thermal cycling sequences is presented in Fig. 1. Step 2 simulates the temperature behaviour of the experiment during its switch on and switch off whereas step 3 is close to the cycles of temperatures that should be used during the analysis of the samples. However, it must be underlined that these tests simulate much larger number of thermal cycles than what the COSAC experiment will endure.

## 3. Results and discussion

The chromatographic performances of the columns were characterised prior to and after each space environmental test by the injection of several key compounds representative [12,13] of the different chemical families potentially present in the cometary nuclei and targeted by each tested column (Table 1). They were evaluated with two chromatographic parameters: the retention time, to test the thermo-
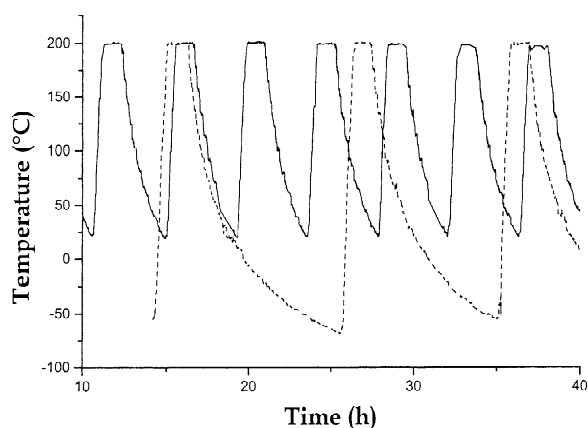


Fig. 1. Temperature cycles measured during the thermal vacuum test. Step 2 of the test is represented in dotted line and step 3 in solid line.

dynamic of the chromatographic process, and the peak width at half height, to estimate an eventual modification of the kinetic processes when combined with retention time. Methane was used as the non retained compound, except for the Carbobond columns. In this last case, neon was considered. Results obtained for each test are presented in Tables 1–3 and chromatograms representative of those obtained with all columns (both WCOT and PLOT ones) are shown on Fig. 2.

In a general way, results show that retention times measured before and after having performed the tests are nearly identical (Tables 1–3). Slight deviations are observed for some compounds but the measured retention times remain in the repeatability domain of the injection of the chromatographs used [14]. In the same way, Tables 1–3 show that peaks width at half height are not affected by the environmental tests as they remain quite constant prior to and after each test. The non enlargement of the peaks obtained on the chiral columns is all the more important as the resolution obtained with these columns between specific enantiomers is very low. As both the retention times and the peak width at half height are not altered, it also means that the columns efficiency is kept constant.

In a more particular point of view, these results demonstrate the robustness of the chiral columns which are generally thought to be fragile. Moreover, the new bonding technology used for the PLOT columns manufacturing allow to use such columns in space experiment whereas it was not possible so far with old technology ones, as they were demonstrated not to be resistant to mechanical constraints [15]. Concerning the liquid phases, their analytical properties are not changed by radiation (Table 2) in spite of the existence of a modification of the crosslinking between the chemical groups which is due to the homolytical cleavage of chemical bonds [16–19]. Beyond the stationary phases, it was also not observed any degradation of the polyimide external coating used for several columns, contrary to what was observed 20 years ago [18,20]. Therefore the materials used for the external capillary walls of silica coating are resistant to the radiation. Finally, neither the high temperatures nor the repeated transition of the liquid phases between a crystalline and a liquid state when passing across the crystallisation
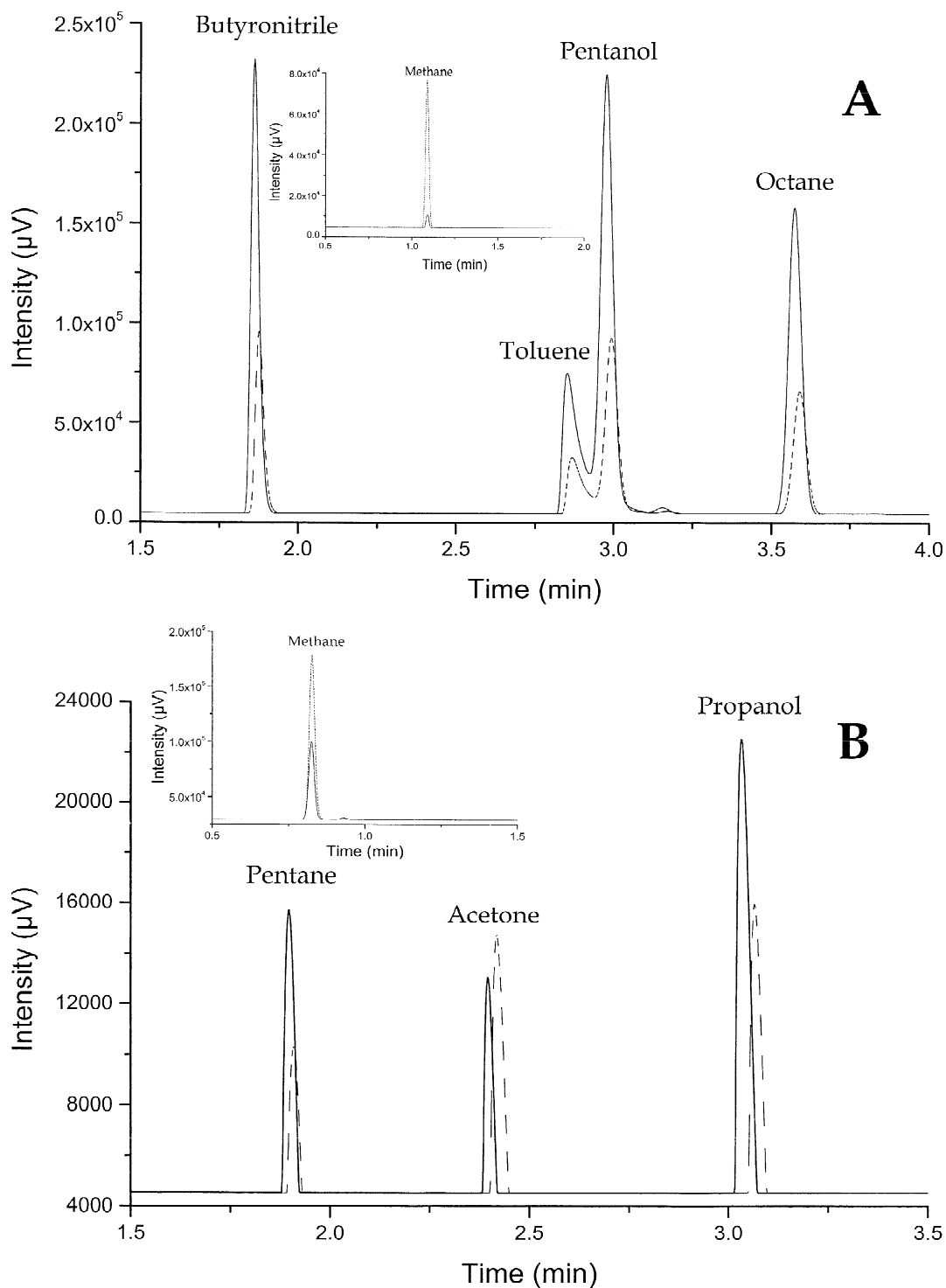
Fig. 2. Typical chromatograms obtained with different tested columns prior to (solid line) and after (dashed line) environmental tests: (A) MXT 1 WCOT column, vibration tests; (B) MXT U PLOT column, radiation tests; (C) Chiral GT-A column, radiation tests.
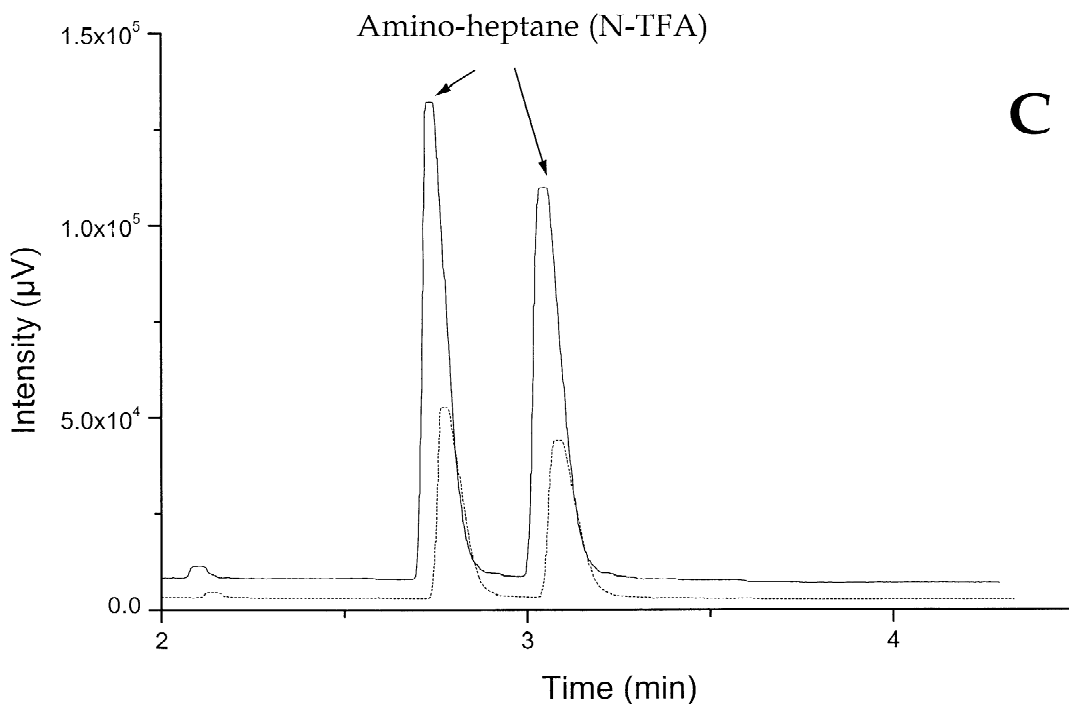
Fig. 2. (*continued*)

temperature [21] are shown to alter the stationary phases properties (Table 3).

As a consequence, the capillary columns selected in the COSAC experiment are shown to be resistant to each of the three tests performed separately. However, we have no information about the behaviour when the capillary columns are exposed to the three constraints simultaneously because it was not possible to perform such an experience for practical considerations. Nevertheless, one can reasonably expect that porous polymers should not be sensitive to the cumulative effect of the different space constraints because their structure does not change with the temperature and pressure conditions. On the contrary, the state of the liquid stationary phases change with the temperature, and therefore, their mechanical and absorption properties too. But one can reasonably assume that these phases will not be altered during the flight, whether because different constraints are not simultaneously applied to the GC in reality (e.g. vibration during the launch and radiation during the journey of the probe), or because the modification of the liquid phases state does not

significantly modify their mechanical and absorption properties.

One can therefore conclude that the capillary chromatographic columns selected to be mounted in the COSAC experiment are qualified to the space application as they will keep their analytical properties during the journey of the Rosetta probe in space.

## 4. Conclusion

Tests were performed to evaluate the effect of environmental constraints imposed by the space environment on the different types of capillary columns and stationary phases selected for the COSAC space experiment. Whereas other authors already reported results showing the good behaviour of chromatographic columns in space conditions [22,23], it is the first time that all the tests presented in this paper were performed. Results show that the chromatographic behaviour of all the columns tested, either classical or chiral ones, are not affected by the

environmental constraints. It is thus demonstrated that the current commercial columns have a satisfactory robustness. In conclusion, all the capillary columns and stationary phases evaluated in these tests were qualified for space application, and in the present case especially, for the COSAC experiment.

The only parameter which was not tested is the duration of the exposure to these constraints as the probe will be spending 11 years in space. At present, we are unable to estimate the ageing effect of the phases and the eventual impact on chromatographic performances. However, as the stationary phases robustness was demonstrated, we expect that the columns will resist to these space constraints and data collected with the GC–MS experiment of the Huygens probe (2005) will give interesting information regarding the long-term stability behaviour in space conditions.

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